MISHRA, SUMEET RAVISHANKAR. Selective Actuation of Polymer Nanocomposites by Controlling Properties of Magnetic and Plasmonic Nanoparticles for Soft Robotics Applications. (Under the direction of Dr. Joseph B. Tracy).

The field of soft robotics is associated with soft materials that are amenable to reshaping, which encompasses a broad range of material systems – in terms of both their composition and structural design. Commonly employed materials include elastomers, hydrogels, thermoplastics or their composites with other functional “hard” materials. These hard materials allow for actuation of their soft matrices using mechanical, chemical, magnetic, or electrical stimuli. Polymer nanocomposite (PNC) actuators for soft robotics combine the elastic properties of the matrix with the functional response of nanoparticles (NPs). The response of these actuators can be tuned by the functionality and physical properties of the nanoparticles as well as by their arrangement within. The focus of this dissertation is to devise such systems where selective actuation of a polymer nanocomposite is achieved by controlling one or more of the above factors.

The experiments establish the proof of concept for the various techniques to achieve actuation in selected polymers. Specifically, systems with two different sets of nanoparticles were studied: magnetic and plasmonic nanoparticles. One-dimensional (1D) arrangement of magnetic particles into chains imparts anisotropic magnetic properties to the resulting composite, which has been utilized to obtain an anisotropic mechanical response. This selectivity in actuation was shown to be present in uniform field as well as magnetic field gradients. A model was also designed to describe the actuation behavior for simple bending experiments.
In the second project, plasmonic nanoparticles were incorporated into shape memory polymers, which allowed shape recovery by photothermal heating. By using two different sets of plasmonic NPs and using the light source with the correct wavelength corresponding to one of the NPs, selective heating and therefore selective recovery was obtained. This is useful for designing sequential or selective actuators from the same composite.

An electrospinning setup was designed and fabricated to obtain nanoscale fibers of different materials. Collaborative projects were undertaken to incorporate interesting nanomaterials in electrospun fibers.

The overall goal of this research is to lay the groundwork towards development of more advanced soft robotic actuators based on functional polymer nanocomposites.
Selective Actuation of Polymer Nanocomposites by Controlling Properties of Magnetic and Plasmonic Nanoparticles for Soft Robotics Applications

by

Sumeet R. Mishra

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Materials Science and Engineering

Raleigh, North Carolina

2016

APPROVED BY:

Prof. Joseph Tracy
Committee Chair

Prof. Michael Dickey

Prof. Yaroslava Yingling

Prof. Richard Spontak
DEDICATION

To my parents Saroj and Ravishankar Mishra, and my brother Sanket Mishra, for their support in getting me here.
BIOGRAPHY

Sumeet Mishra was born on February 17, 1988 in the city of Nagpur, Maharashtra, India. He graduated with his Bachelors in Metallurgical & Materials Engineering from Visvesvaraya National Institute of Technology in 2009, and then his Masters in Materials Engineering from Indian Institute of Science, Bangalore in 2011. In fall 2011, he joined Prof. Joseph Tracy to work in the field of polymer nanocomposites towards his PhD.
ACKNOWLEDGMENTS

I thank Prof. Joseph Tracy for his mentoring and support during my PhD. I am grateful for his patience and understanding in working with me. I enjoyed the intellectual discussions I had with him over the years, which enabled us to come up with research ideas for our work in the field of polymer composites.

I also thank my friends and lab mates, at NCSU, and back in India for helping me have a great time during my stay here at NCSU. Thank you for those bouts of laughter and keeping me grounded.

I have had the pleasure of working with several professors, each an expert in his own field. I thank Prof. Michael Dickey, Prof. Richard Spontak, Prof. Yaroslava Yingling, Prof. Orlin Velev, Dr. Lew Reynolds, Prof. Jason Bochinski, Prof. Laura Clarke, Prof. Dick Guarneri, Prof. Amy Oldenburg, Prof. Russell Gorga, and Prof. Yong Zhu for all the knowledge and resources they provided to help me reach my goals.

I would also like to thank the graduate students from different groups, who took their precious time to train, help and guide me in experiments beyond my expertise: Dr. Sharvil Desai, Mohammed Mohammed, Duncan Davis, Ying Liu, Wyatt Shields, and Xu Zhang.
# TABLE OF CONTENTS

List of tables .............................................................................................................. vi
List of figures .............................................................................................................. vii
1. Soft robotics ............................................................................................................ 1
2. Nanoparticles (NPs): ............................................................................................ 9  
   Properties on the nanoscale .................................................................................. 9  
   Applications .......................................................................................................... 15  
   Synthesis of nanoparticles .................................................................................... 19  
   Assembly of nanoparticles .................................................................................... 22  
3. Polymer nanocomposites ...................................................................................... 32  
   Polymer nanocomposites on different scales ....................................................... 34  
4. Anisotropic actuation using magnetic chains ....................................................... 42  
   Manuscript reprint .................................................................................................. 47  
5. Plasmonic nanoparticles for photothermal heating of shape memory polymers .... 64  
   Photothermal heating ............................................................................................ 69  
   Applications .......................................................................................................... 71  
   GNRs synthesis and processing ............................................................................ 75  
   Polarization selective photothermal heating ....................................................... 86  
   Wavelength-selective photothermal heating ......................................................... 88  
   Additional experiments ......................................................................................... 96  
6. Electrospinning .................................................................................................... 105  
7. References ............................................................................................................. 119
List of tables

Table 2-1. Typical values of the single domain limit and the superparamagnetic limit for magnetic nanoparticles at 300 K\textsuperscript{23} .............................................................. 14

Table 5-1. Concentrations of various solutions for GNR synthesis ...................................... 77

Table 5-2. Anisotropy of stretch annealed Diaplex films ..................................................... 104
List of figures

Figure 1-1. Functional inspirations from nature\textsuperscript{3} ................................................................. 4

Figure 1-2. Biomimetic soft robots capable of unidirectional motion\textsuperscript{4,7} ........................................... 5

Figure 1-3. Soft robotic hands\textsuperscript{11,12} .......................................................................................... 6

Figure 1-4. Prototypes for wearable electronic devices\textsuperscript{13,14} ......................................................... 7

Figure 1-5. 3D printed soft robots\textsuperscript{15,16} .................................................................................... 8

Figure 2-1. Theories for melting point depression in nanoparticles\textsuperscript{18} .............................................. 10

Figure 2-2. Separation of the conduction and valence bands into discrete energy levels in a semiconductor quantum dot\textsuperscript{20} ................................................................. 12

Figure 2-3. a. Superparamagnetism as evident from $M$ vs $H$ data. b. Superparamagnetic size limit for Fe$_3$O$_4$ nanoparticles\textsuperscript{25} ....................................................................................... 14

Figure 2-4. Applications of nanoparticles (source: http://people.forestry.oregonstate.edu/john-simonsen/research-areas, John Simonsen, OSU) ......................................................................................... 15

Figure 2-5. Conceptual force sensor based on SPR shift with changes in interparticle distance\textsuperscript{28} ................................................................................................................................. 16

Figure 2-6. Multifunctional nanoparticle for imaging, targeting, and heat induced drug delivery\textsuperscript{43} ............................................................................................................................... 18

Figure 2-7. Role of the capping ligands in determining nanoparticle size\textsuperscript{69} ........................................ 20

Figure 2-8. Monodisperse Fe$_2$O$_3$ NPs\textsuperscript{71} ..................................................................................... 21
Figure 2-9. 2D self-assembly of NPs: cubic NPs into square lattice and hexagonal polyhedral NPs into hexagonal lattice\textsuperscript{94}........................................................................................................25

Figure 2-10. 2D self-assembly of GNRs into close packed arrays/tiles\textsuperscript{94}......................25

Figure 2-11. Segregation during 2D assembly of gold nanoparticles of different sizes and shapes\textsuperscript{94}........................................................................................................26

Figure 2-12. GNRs with very high aspect ratios forming directional ribbons/bundles\textsuperscript{95}......26

Figure 2-13. 3D superlattices self-assembled from CoPt\textsubscript{3} NPs\textsuperscript{96}.............................27

Figure 2-14. Chainlike assembly of end-end linked GNP\textsc{ps} with small molecules\textsuperscript{104}........30

Figure 3-1. Polymer nanocomposites on different scales. a. capsules b. fibers c. thin films d. bulk ..............................................................................................................................................35

Figure 3-2. Control over particle morphology by tuning interfacial interactions\textsuperscript{129}..........36

Figure 3-3. Assembly of a. GNSs and b. GNRs in fibers by electrospinning\textsuperscript{136,138}............38

Figure 4-1. Classification of magnetic materials based on spin ordering of moments ........43

Figure 4-2. Schematic for Stoner-Wohlfarth model ........................................................................45

Figure 4-3. Alternating lifting and bending of parallel arms of the rotating cross in uniform 3.1 kOe field with schematic overlays of the magnetization of chains within the composite. Twisting at $\frac{1}{4}$ rotation causes inward bending at $\frac{1}{2}$ total rotation .................................................63

Figure 4-4. Plot of the calculated dependence of the bending angle, $\theta$, on the moment angle, $\alpha$, measured with respect to the chain direction for the disordered chains .................................................63

Figure 5-1. Gold NPs by Michael Faraday. Source: Paul Wilkinson: www.rigb.org.................64

Figure 5-2. Surface plasmon resonance .........................................................................................65

Figure 5-3. Variation of SPR with NP size\textsuperscript{180}..................................................................66
Figure 5-4. Typical absorbance spectrum of GNRs (red: after second growth, black: after first growth). .......................................................... 67

Figure 5-5. Variation of SPR with aspect ratio (R)\textsuperscript{181} . .......................................................... 68

Figure 5-6. Variation of SPR with change in the relative ratio of Au to Ag in an alloy NP\textsuperscript{181} . .......................................................... 68

Figure 5-7. Mechanism of photothermal heating and their relative time scales\textsuperscript{184} . .................. 70

Figure 5-8. Typical steps in single stage one way shape memory effect (SME) . .................. 73

Figure 5-9. Schematic for large scale gold nanorod synthesis .......................................................... 76

Figure 5-10. Relative spectral emission of the LED. Source: Osram .................................................. 81

Figure 5-11. 3D map of the power output of the LED a. axial variation b. radial variation . 82

Figure 5-12. Photothermal heating of GNRs in water a. Temperature rise vs time b.
Absorbance spectra of the GNR before and after the heating experiment ........................................... 83

Figure 5-13. Chemical composition of the thermoplastic polyurethanes used\textsuperscript{203,204} . ........... 84

Figure 5-14. Selective heating using polarized light of a stretch annealed GNR/Diaplex sample a. parallel case: heating causes shape recovery b. perpendicular case: no heating occurs .................................................................................................................. 88

Figure 5-15. Normalized absorbances SPR for GNRs and GNSs .................................................. 89

Figure 5-16. Wavelength selective photothermal heating GNS/Diaplex. Samples do not heat under 860 nm (center column) light but heat and recover shape under 530 nm light (right column). ........................................................................................................................ 91
Figure 5-17. Wavelength selective photothermal heating GNS/Diaplex. Samples do not heat under 860 nm light (center column) but heat and recover shape under 530 nm light (right column).

Figure 5-18. Absorption spectra of Diaplex-GNR and Diaplex-GNS samples with 0.5 wt. % concentration.

Figure 5-19. Shape recovery for correct combination of light (860 nm: GNRs and 530 nm: GNSs) and no recovery for the other case.

Figure 5-20. Absorption spectra of 0.5 wt. % Diaplex-GNR and 3 wt. % Diaplex-GNS samples.

Figure 5-21. Selective heating and shape recovery.

Figure 5-22. Absorbance analysis of different seeds synthesized for GNRs.

Figure 5-23. GNRs synthesized by using 0.17x of standard seed volume.

Figure 5-24. Effect of AA addition rate on the LSPR.

Figure 5-25. GNRs with different AA addition rate during second growth.

Figure 5-26: Effect of PEGylation on LSPR of GNR.

Figure 5-27. Effect of annealing on the absorbance spectrum of the GNR/Diaplex films.

Figure 5-28. Absorbance measurements of Diaplex films with different strains and concentrations for parallel and perpendicular orientation of GNRs to polarized light.

Figure 6-1. Schematic of an electrospinning setup.

Figure 6-2. Formation of Taylor’s cone.

Figure 6-3. Electrospinning setup design and fabrication.

Figure 6-4. Electrospinning of different materials.
Figure 6-5. Incorporation of GNRs in electrospun fibers ........................................ 114

Figure 6-6. Electrospinning of Ag nanowires in PEO ............................................ 115

Figure 6-7. Electrospinning of Cu nanowires in PEO ............................................. 116

Figure 6-8. Electrospinning of ZrO$_2$ nanoplatelets ............................................. 117
1. Soft robotics

Soft robots, in their simplest form, are flexible actuators which can be manipulated using external triggers. While conventional hard robots are now omnipresent, more so in industries, they lack adaptability and therefore the safety required while working in conjunction with humans. Soft robotics can be seen as one step closer to the transition between humans and conventional hard robots. Soft robots bridge this gap by using structural materials that are more flexible, adaptable and therefore can be safely used in harmony with humans. While a soft robot encompasses a wide variety of material systems it typically has the following characteristics:

1. The main structural part is composed of a soft material, mostly polymers
2. They are more flexible, and therefore adaptable to their environments

Several material systems can fall into the soft materials category and classifying soft robots is thus an uphill task. It is important to note that not all soft robots are made entirely of flexible materials. As long as the main actuator body is soft enough to allow flexibility in motion, hard materials can be used to perform some of the other essential functions, like providing the actuation motion, the stimuli, or the power source. Also, entirely soft bodies do lead to less precision in control, which is usually counteracted by making the robot of these hybrid materials. These materials have distinct hard and soft components (major structural part), where the conventional metals provide the precision in movement and control, and the soft body performs the action. This is different from robots composed of several connected smaller hard pieces to provide greater range of motion. The fundamental building block in such cases are still rigid, and thus are not considered soft robots.1, 2
Because soft materials are extremely flexible, they do not need to be structurally predefined for motion control, i.e. hinges or joints. Moreover, they can be continuously deformed over their entire volume, both in shape and size, allowing for more complex and extended range motion, otherwise unachievable using conventional hard materials. Because of their adaptable nature, they provide less resistance while still maintaining support, which is the qualifying principle for rehabilitation devices. Hard robots made with much stronger materials are not as forgiving, so industrial practices have severe norms in place for operation of a machineries, but still need constant supervision to prevent injuries. Soft robots are inherently safer and therefore do not need a designed failsafe, as needed for most machines. This is especially critical in biomedical applications, where the tolerances are much lower. Often hard robots have to be preprogrammed or programmed in situ to handle materials and object with irregular topography. Sometime these objects themselves are soft, which causes them to deform under the applied force, and slip out. Soft robots are self-adapting in such cases: they flex according to the contours of the object and provide more stability. Also, most hard robots have appendages or attachments to handle different materials. By having lower elasticity, soft materials can accomplish this with a single arm and sometimes even without a need for programming.

An ideal, fully functional soft robot has the three following components, in the order of increasing functional complexity:

1. Actuation: range of motions available via programmed or adaptive stimuli
2. Adaptation: environmental feedback looped with motion control
3. Autonomy: onboard energy source
Soft robotics, as a field, evolved due to the efforts in biomimicry: emulating organisms from the natural world by understanding and replicating their structure, functional principles, and the governing mechanisms. Some of the best materials and most efficient systems are known to occur in nature. For example, human bone is the only known composite that has both the high strength for functioning and the flexibility to absorb impact without either function. An octopus, considered by many as the perfect example of an ideal soft robot, has enough crushing power enough to break an iron rod in half, but can easily pass its entire body through a hole no larger than a dessert plate. Starfish can regenerate entire organs, chameleons change to practically any skin color for camouflage. Human skin is the best known soft sensor: it is self-healing, can sense changes in temperature and humidity changes but can still handle the pressures of entire bodyweight. In fact, several current systems that work efficiently were inspired from such natural examples. Bhushan published an excellent review encompassing natural systems that have been the inspiration for the advancement of modern technology (figure 1-1).
Some of the simplest examples of soft robots are the ones capable of unidirectional translation. This peristaltic motion is observed in several organisms, and has distinct advantages when exploring confined spaces. In one study an inchworm type hybrid robot was developed that worked based on anchor and slide type movement, and in another study, jellyfish was used as a model to generate motion in “medusoids” by fast muscle contraction and slow elastic recoil, and rubber “manta” which moves by controlled pneumatic bending and stretching. An autonomous soft robot imitating snake-like motion was designed by Onal.
et al. It uses a pressure control to create undulating motion that leads to horizontal translation with “on-board actuation, power, computation and control capabilities.”

Figure 1-2. Biomimetic soft robots capable of unidirectional motion
In another biomimetic example, a soft robotic fish was designed that was capable of rapid maneuvers with response rates on par with an actual fish. A hybrid soft robotic “meshworm” crawler was designed by using a NiTi shape memory alloy fibers meshed with a soft body.

Soft materials are also finding applications in wearable technology. Soft wearable robots based are designed to aid/augment mobility and performance of the host while minimizing resistance to natural motions. Soft robotic sensors can move effectively with the human body and such have been explored for use in gait and posture determination. By using passive compliance in the design, Deimel et al. were able to design a dexterous soft robotic hand, which could mimic 31 of 33 grasp postures of a human hand. Design and testing of an inexpensive, modular, under actuated soft robot hand with pneumatically actuated fiber-reinforced elastomer digits. Several prototypes for assistive wearable devices have been developed to aid rehabilitation. Wearable technology is already here; the prototypes have

Figure 1-3. Soft robotic hands

6
already been made and designed. In one such prototype of a soft wearable keypad developed by Kramer and coworkers, microfluidic PDMS microchannels embedded with conductive liquid allow pressure sensitive change in resistance, serving as buttons.\textsuperscript{14}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Prototypes for wearable electronic devices\textsuperscript{13,14}}
\end{figure}

The current 3D printing revolution has opened up new frontiers in soft robotics. 3D printed robots incorporating self-healing material in the design also enables to receive excessive plastic deformation.\textsuperscript{15} Another example of 3D printed, bioinspired soft robot is the “GoQbot” which can crawl unidirectionally, and also increase its speed by rolling like a caterpillar. 3D printing also allows use of different materials for design, which can be combined to create multi-functional structures. One such example is a soft robot made with materials with incremental stiffness, which allows controlled, directional jumping via a chemical reaction.\textsuperscript{16}
Soft robots are already here, and their use is anticipated to greatly expand in the future. In one of the foremost examples, “a team of roboticists, engineers and surgeons at King’s College London have for the first time operated on a human body using a soft surgical robot as part of keyhole surgery, with the aim of dramatically improving future surgical practice.”

![Figure 1-5. 3D printed soft robots](image-url)
2. Nanoparticles (NPs):

Properties on the nanoscale

Nanoscale materials are defined as structures having at least one dimension less than 100 nm. Following this definition, the number of dimensions smaller than 100 nm are 3 for a nanoparticle, 2 for nanowires/nanofibers, and 1 for a nanofilm. Even so, there are widespread examples in the literature and in practical use, where the term “nano” has been ambiguously used for particles with larger dimensions. By virtue of their small size, nanoparticle have a huge surface area-to-volume ratio (which scales as 1/R); and a much larger proportion of surface atoms as compared to bulk. Due to the incomplete coordination of Surface atoms, they are have greater chemical reactivity and can impart novel properties that are distinct from bulk materials.

Melting point depression: In the nanoscale regime, the melting point becomes size dependent. More specifically, as the nanoparticle size becomes smaller, the melting point monotonically decreases, which is termed as “melting point depression.” Several theories have been put forth to explain this phenomenon. A few of them are depicted in the figure below. In the homogenous melting hypothesis (HMH), melting occurs at a single temperature, where the entire nanoparticle is liquefied. In the liquid nucleation and growth (LNG) model, a liquid skin forms at a lower temperature and continues to grow inwards until the entire nanoparticle is liquefied at the melting point. Liquid skin melting (LSM) is similar to HMH, but predicts formation of a liquid layer on the surface of nanoparticle initially, followed by complete liquefaction at a higher temperature.
Surface plasmon resonance (SPR): Since the size of the nanoparticles is smaller than the wavelength of the visible light, nanoparticles can interact differently with light than bulk materials. In noble metal nanoparticles, e.g. Au and Ag, this leads to increased absorption of a specific wavelength. This can lead to significant enhancement of Raman signals which is useful for imaging as in surface enhanced Raman scattering (SERS), or converted to heat in the surrounding medium (photothermal heating). Furthermore, the SPR characteristics of noble
metal nanoparticles can be tuned by designing different plasmonic structures based on their size, shape, composition, and environment.\textsuperscript{19} The SPR and ensuing photothermal heating are discussed in more detail in the Chapter 5.

**Quantum confinement:** Bulk materials have a fixed band gap between the conduction and valence bands, which dictates their characteristic electronic properties. When the excitation light pulse has higher energy than the band gap ($E_g$), it causes an electron to jump to the conduction band, leaving a hole in the valence band. This electron-hole pair is called an exciton. The minimum energy of an exciton is thus given by $E_g$, with a corresponding average separation distance known as the Bohr radius. In a semiconducting nanoparticle, where the size of the material is close to or below twice the Bohr radius, such that it is “quantum-confined,” the energy of the exciton increases, and the properties of the exciton now depend on the size of nanoparticle. In such a nanoparticle, also called a quantum dot (QD), confinement in 3D causes the conduction and valence bands to have discrete energy levels, as shown in figure 2-2.\textsuperscript{20} This quantum confinement is also present in nanowires or nanofilms, corresponding to 2 or 1 confined dimensions, respectively. For a semiconducting material (constant $E_g$), recombination in a bulk crystal can lead to photoemission, which is characteristic of that material. Since $E_g$ for QDs can be controlled by their size, it also allows control of their optical properties.\textsuperscript{20} Compared to their bulk counterparts, QDs can also have very high efficiency of
emission, which is the energy ratio of the emitted to absorbed light. Indeed, some core-shell structured semiconducting QDs have been shown to achieve close to 100% quantum yields.\textsuperscript{21}

**Figure 2-2.** Separation of the conduction and valence bands into discrete energy levels in a semiconductor quantum dot\textsuperscript{20}

**Magnetic properties:** Most bulk ferromagnetic materials are composed of multiple domains, which are separated by domain walls. Frenkel and Dorfman were the first to predict the existence of such individual domains, where each domain has its own magnetization vector and therefore a net magnetic moment.\textsuperscript{22} As the size of the material decreases, the energy needed to maintain a domain wall increases, to a point where it becomes energetically unfavorable and the system collapses to a single domain. This single-domain limit is given by:

\[ R_{SD} = 36kT_{ex} \]
where, \( l_{\text{ex}} = \sqrt{\frac{A}{\mu_0 M_s^2}} \)

and \( \kappa = \sqrt{\frac{K}{\mu_0 M_s^2}} \)

Where \( l_{\text{ex}} \) and \( \kappa \) represent the balance of dipolar interactions with exchange interactions \((A= \text{exchange stiffness constant})\) and anisotropy energy \((K= \text{crystallographic anisotropy constant})\) respectively. \( M_s \) is the saturation magnetization, characteristic for the material.\(^{23}\)

Within a crystal structure, magnetization is favored along certain directions, referred to as the easy axis (or axes), and unfavored along hard axes. These easy and hard axes dictate a preference for the orientation of the magnetic moment, which is expressed as an anisotropy energy, \( KV \), where \( K \) is the aforementioned anisotropy constant and \( V \) is the volume. The anisotropy constant \( K \) is characteristic for the material and dictates the single domain spontaneous magnetization direction of a magnetic nanoparticle under zero field. This is usually reflected by the large coercivity of these nanoparticles.

As the nanoparticle size (and therefore volume) is reduced further, thermal fluctuations within the material start to exhibit significant effects on the nanoparticle magnetization. At a size smaller than single domain limit \((R_{SD})\), thermal energy is high enough (or more precisely the volume anisotropy energy has decreased enough) to randomize the net magnetic dipole of the domain, such that there is no preferred direction. Such a nanoparticle exhibits magnetic behavior resembling a paramagnetic material with a large magnetic moment, where the coercivity is zero. Hence, the phenomenon is called as “superparamagnetism.” The superparamagnetic size limit \((R_{SP})\) for a nanoparticle is given by:
\[ R_{SP} = \sqrt{\frac{6kT}{K}} \]

**Table 2-1.** Typical values of the single domain limit and the superparamagnetic limit for magnetic nanoparticles at 300 K

<table>
<thead>
<tr>
<th>Material</th>
<th>( R_{SD} ) (nm)</th>
<th>( R_{SP} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_2)O(_3)</td>
<td>42.5</td>
<td>17.5</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>52.7</td>
<td>12.2</td>
</tr>
<tr>
<td>Fe</td>
<td>8.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Co</td>
<td>56.4</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Typical values of the single domain limit and the superparamagnetic limit for magnetic nanoparticles at 300 K are shown in table 2-1. Superparamagnetism is reflected in \( M \) vs \( H \) (moment vs applied magnetic field) measurements, as performed in magnetometry, with zero coercivity and no hysteresis, since any directional magnetization preference has been lost.

**Figure 2-3.** a. Superparamagnetism as evident from \( M \) vs \( H \) data. b. Superparamagnetic size limit for Fe\(_3\)O\(_4\) nanoparticles
Applications

As summarized in the figure 2-4 below, the applications of nanoparticles are many, ranging from cancer therapy to quantum computing to self-cleaning textiles. While each of these applications has detailed reviews of their own, a few relevant ones are discussed below:

Figure 2-4. Applications of nanoparticles (source: http://people.forestry.oregonstate.edu/john-simonsen/research-areas, John Simonsen, OSU)

Plasmon rulers: The SPRs of Plasmonic nanoparticles can couple when they are assembled with interparticle distances on the order of their size, resulting in shift in their absorption. This shift towards longer wavelength (or red shift) is due to ensemble acting as a longer particle. Alivisatos and coworkers have shown this by coupling Ag and Au
nanoparticles into pairs using single-stranded DNA.\textsuperscript{26} Moreover, the shift in the SPR peak increases as the interparticle separation decreases and the strength of the coupling increases. Jain et al. studied the shift in the SPR wavelengths between pair of Au nanodiscs with different separation distances and concluded that it follows an exponential decay of the form:

\[
\frac{\Delta \lambda}{\lambda_0} = Ae^{-(s/D)/\tau}
\]

where $\Delta \lambda/\lambda_0$ is the fractional plasmon shift, $s$ is the interparticle separation, $D$ is the particle diameter, and $\tau$ is the decay constant.\textsuperscript{27} Since absorbance measurements are highly sensitive, SPR shifts allow precise measurements of nanoscale distances using this system, and can be used as plasmon rulers and force/strain sensors.\textsuperscript{28–38} Figure 2-5 shows a conceptual image of one such force sensor.\textsuperscript{39}

\textbf{Figure 2-5.} Conceptual force sensor based on SPR shift with changes in interparticle distance\textsuperscript{28}
**Biological applications:** Because of the inherent property of nanoparticles to generate large local field enhancements, they are very useful as sensitive detection systems. Inorganic nanoparticles can also be functionalized with specific molecules that allows them to target certain kinds of cells or tissues. When designed with a porous outer shell, they can also be used to carry drugs and induce their controlled release. Plasmonic Au and Ag nanoparticles, and semiconducting QDs therefore provide excellent sensitivity for biological imaging.\textsuperscript{40} By suitably modifying the surface of the QDs, Ballou et al. were able to stabilize them in vivo for long-term detection and also improved the targeted tissue uptake.\textsuperscript{41} Magnetic nanoparticles have been used for ultra-sensitive magnetic resonance imaging (MRI) of cancer cells.\textsuperscript{42} Nanoparticles can further be engineered to have multiple functionalities. In a notable design, as shown in figure 2-6, Ling et al. synthesized iron oxide nanoparticles with mesoporous silica coating. Incorporation of a fluorescent dye allowed for fluorescence imaging in addition to the magnetic resonance imaging by the iron oxide core. By adding targeting molecules on the surface and including a drug within the pores, the nanoparticle was also made a targeting drug delivery agent, thus combining many functions into one.\textsuperscript{43} A similar approach was used by Gao et al. to synthesize multifunctional semiconducting QDs with imaging, targeting and drug delivery applications.\textsuperscript{44}
Moreover, plasmonic and magnetic nanoparticles have the capability of generating localized heat. Combining this property with the targeting capability of nanoparticles, makes them good candidates for hyperthermia, especially in cancer therapy. Plasmonic gold nanorods (GNRs) and hollow nanoshells, that have their SPR in the near infrared region, have been used to selectively bind to and destroy tumor cells. Magnetic nanoparticles can be heated with alternating magnetic fields and have been used in cancer therapy as well. In one such study, an antibiotic drug ciprofloxacin was released by means of swelling a composite of PVA/MMA-based polymer and Fe₃O₄ nanoparticles. In addition to composite particles, thin films or membranes can also be used as “drug delivery patches,” for external or subcutaneous onsite delivery. The polymers used for these applications are thermoresponsive. For example, PNIPAM (poly(N-isopropylacrylamide) shrinks or expands in response to temperature. This alternate swelling/deswelling can be used for controlled drug release. In one such study, subjecting Fe nanoparticles incorporated in a PNIPAM membrane subjected to an external oscillating magnetic field caused release of a drug. Furthermore, by controlling the pulse
duration and frequency, the release could be cyclically controlled. These membranes were also tested for biocompatibility and could perform release drugs 45 days after their injection.\textsuperscript{51} Since magnetic particles can be manipulated and heated with external magnetic fields, it has good potential for targeted delivery and atheroma. A chitosan Fe nanoparticle composite has been shown to work successfully for cancer therapy, where higher drug loading and efficient targeting can be achieved. Moreover this also allows a slower release profile allowing for more control.\textsuperscript{52}

**SERS:** Clusters of plasmonic nanoparticles generate high local enhancements (or hot spots) in electromagnetic fields. The Raman signal enhancement factors for these clusters of nanoparticles are very high, up to $10^{14}$ and can be used for detection of single molecules.\textsuperscript{53–55} These plasmonic nanoparticles could be also be electrospun into nanofibers to create large-scale, free standing SERS substrates.\textsuperscript{56,57}

**Catalysis:** Owing to their high surface area-to-volume ratio and correspondingly high fraction of high-energy surface atoms, nanoparticles make excellent catalysts. To access the surface however, the nanoparticles have to be homogenously separate well enough, typically in a solution. The caveat is that stabilizing a nanoparticle in a solution requires a capping ligand which reduces the actual surface area available for catalysis. Nevertheless, nanoparticles have been used as catalysts for a number of reactions: oxygen reduction, alkene-reduction, CO oxidation, hydrogenation, and coupling reactions among others.\textsuperscript{58–68}

**Synthesis of nanoparticles**

**Chemical synthesis of nanoparticles:** Faraday used a bottom-up approach to make Au NPs, and bottom-up approaches continue to be commonly used for reproducibly obtaining
inorganic nanoparticles with precisely controlled structures and properties. Organic ligands are also often employed, where both the functional group and side chain have important roles in mediating nucleation and growth and in determining the interaction of the nanoparticles with the solvent and with each other. Sometimes, additional ligands or surfactants are added to either catalyze or direct the growth of nanoparticle to a certain shape. The precursor chemicals are usually metal compounds, such as H Au Cl\textsubscript{4} for gold and Fe(acetylacetonate)\textsubscript{3} for iron/iron oxide nanoparticles. Upon reduction or thermolysis of the precursors, the inorganic atoms begin to undergo nucleation and growth. Ligands can mediate nucleation and growth by dynamically attaching to the surfaces of the growing clusters and of the precursor metal atoms. Steric effects can also have an important role in directing nanoparticle growth. Usually, nanoparticles can be capped to a certain size by controlling the amounts and concentrations of the precursors and the temperature and reaction time. Ligand stabilization can be electrostatic, where like charges on the ligands repel other nanoparticles and keep them stable in a solution. Ligands can also provide steric stabilization, where steric interactions between nanoparticles prevents their cores from coming into contact and coalescing. It has been shown that changing the shape of the ligands can be used to control the nanoparticle size, as shown in figure 2-7.69

Figure 2-7. Role of the capping ligands in determining nanoparticle size
While solvothermal methods are reproducible and provide good control over the resultant nanoparticle size, obtaining monodisperse nanoparticles can be more challenging. Size control during solvothermal synthesis can be achieved by tuning several factors. Concentration of precursor affects both nucleation and growth rate. Using higher concentrations of the precursor is desirable to obtain monodisperse sizes with higher yields. Careful control of the process temperature can also give monodisperse nanoparticles. Hyeon et al. were able to obtain excellent monodispersity of maghemite (γ-Fe₂O₃) nanoparticles (figure 2-8) by thermal decomposition of Fe with excess oleic acid followed by ageing at much higher temperature. While most synthesis routes require high temperatures, nanoparticles can also be synthesized at room temperature (RT).

Several systems comprising different solvents, ligands or capping agents, reducing agents, and precursors have been explored. A variety of stabilizing or capping agents are used for nanoparticle synthesis. Brust et al. synthesized thiol-capped Au nanoparticles from biphasic
toluene-water systems containing HAuCl₄. Thiols are commonly used as capping agents for Au, Ag, and Pd nanoparticles. Amines, alcohols, and polymers like polystyrene and PVP (polyvinylpyrrolidone) are also routinely used as stabilizers for various kinds of nanoparticles. NaBH₄ is a commonly used strong reducing agent for synthesizing Au, Ag, Pt, and Pd nanoparticles. Reduction by citrate or tartarate salts can also produce stable aqueous dispersions of nanoparticles. Since these reducing agents are relatively weak, they can offer improved control over particle size and the morphology. For organic dispersions, formamide can serve as both reducing agent and a solvent with PVP as the capping molecule. By using o-anisidine as the reducing agent, which is soluble in both water and organic solvents, the same synthetic method could be used to selectively stabilize Au nanoparticles in either aqueous or organic solvents.

**Ligand exchange:** Typically, polar ligands make nanoparticles dispersible in polar solvents, and non-polar ligands render them dispersible in non-polar solvents. For further use, sometimes it is necessary to transfer the nanoparticles from polar to non-polar solvents or vice versa, which is achieved by ligand exchange. Typically, an excess of new ligands are added to the solution containing the nanoparticles and allowed to mix for extended duration. Ligands that are partially soluble in both polar and non-polar solvents are ideal candidates for ligand exchange.

**Assembly of nanoparticles**

To make the best use of nanoparticle functionalities and ensure the translation of their properties on the macroscale, assembly is desired. Several studies have therefore been focused on assembling these nanoparticles in 1D, 2D and 3D. Since it is not practically possible to
manipulate and control the position of each nanoparticle, assembly of nanoparticles relies exclusively on their interactions with each other and with a matrix phase, when present. Such self-assembly is especially important for assembly over length scales much larger than the nanoparticles themselves (microns or mm). An ensemble of such nanoparticles can be arranged into higher ordered structures by engineering their interactions with each other and with the matrix or substrate. Several methods of assembly of nanoparticles within polymers have been explored in literature. Many self-assembly processes involve functionalization of the nanoparticle surface. External stimuli can also be used to manipulate nanoparticles and assemble them in a controlled manner.\(^8\) Chains of nanoparticles have also been assembled at oil-water interface and then fixed via photo-polymerization.\(^9\)

**Self-assembly**

Self-assembly of nanoparticles occurs via particle interactions. As a simple approximation, the interaction between two atoms is given by the Lennard-Jones potential:\(^9\)

\[
U = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

Where, \(r\) is the distance between atom centers, \(\varepsilon\) is the depth of the potential well, and \(\sigma\) is the characteristic atomic diameter. Henderson et al. derived an extension of this equation for colloidal particles, with radii \(a_1\) and \(a_2\) as:\(^9\)

\[
U = \frac{2\pi \alpha_1 \alpha_2}{a_1 + a_2} \left[ \frac{\pi \varepsilon (\sigma^6 - 210L^5)}{630L^7} \right] \text{ for } L \ll \frac{a_1a_2}{a_1 + a_2} \quad \text{where } L = r - (a_1 + a_2)
\]

An excellent review of these different forces has been presented by Bishop et al.\(^9\) Just as in formation of chemical bonds, assembly of nanoparticles usually causes them to lose at
least one degree of freedom in their motion, thus reducing the entropy. The interactions between the nanoparticles, therefore, have to be strong enough to overcome this energy barrier. Typically, these interactions need to have a magnitude of few \( k_B T \) to assemble nanoparticles from solutions. The strength and range of the interactions thus have a critical role in self-assembly processes. For effective assembly, short-range interactions (few Å) must be strong (10-100 \( k_B T \)), and weak interactions should be long-range (10-100 nm). This becomes particularly important for dilute solutions. Relative to the nanoparticle sizes, short and strong interactions have been found to be more susceptible to formation of non-equilibrium aggregated phases, and therefore, long-range interactions are more preferable.\(^{93}\)

Van der Waals (VdW) forces are often important for guiding self-assembly. VdW forces are typically strong-short range and become largely irrelevant, in terms of assembly, when the surface separation exceeds \( \sim 10 \) nm. They can cause agglomeration or clustering for large nanoparticles (> few tens of nm diameter) and may also cause precipitation for higher concentration of nanoparticles in solutions. VdW attractions are typically balanced by using ligands that sterically or chemically repel each other, thereby stabilizing the dispersion. Nevertheless, VdW forces can be harnessed to provide a wide range of assembled structures dictated by particle geometry, i.e., particle shape, aspect ratio, and polydispersity.\(^{94,95}\)
Figure 2-9. 2D self-assembly of NPs: cubic NPs into square lattice and hexagonal polyhedral NPs into hexagonal lattice$^{94}$

Figure 2-10. 2D self-assembly of GNRs into close packed arrays/tiles$^{94}$
Figure 2-11. Segregation during 2D assembly of gold nanoparticles of different sizes and shapes.

Figure 2-12. GNRs with very high aspect ratios forming directional ribbons/bundles.
As shown in figures 2-8 to 2-12, monodisperse spherical nanoparticles assemble into hexagonal lattices or square lattices, and monodisperse anisotropic rods assemble into tile-like smectic structures, while longer rods assemble into ribbons via side-side interactions.

Similar 3D structures can also formed in 3D through VdW interactions. By controlling the nanoparticle size and evaporation conditions of a dispersion containing CoPt$_3$ nanoparticles (figure 2-13), they could be assembled in cubic closed-packed (CCP) structures for monodisperse nanoparticles or into a complex AB$_3$ type superlattice form binary mixtures.$^{96}$

![Figure 2-13. 3D superlattices self-assembled from CoPt$_3$ NPs$^{96}$](image_url)
More complex shapes can also be formed via self-assembly: flower-like, rhombic dodecahedron, and bipyramids shapes can be obtained from ZrO$_2$ nanoparticles,$^9$ or large micron scale cubic structures from cubic Fe$_2$O$_3$ nanoparticles.$^9$

**Magnetic assembly**

An iconic example of magnetic assembly and its application is that of magnetotactic bacteria, which have chains of magnetic nanoparticles within their flagella. These chains act as compasses for the bacteria and allow them to migrate using the earth’s magnetic field toward their intended habitat.$^9$ Magnetic nanoparticles are typically single crystalline and can be treated as individual magnetic dipoles, which can assemble when interparticle interactions between them are sufficiently strong. The magnetic dipolar interaction energy, $E_{12}$, between two neighboring spherical Magnetic nanoparticles is given by:

$$E_{12} = \frac{\mu_0}{4\pi} \left( \frac{m_1 m_2}{d^3} \right) (m_1 \cdot m_2 - 3(m_1 \cdot \hat{d})(m_2 \cdot \hat{d})),$$

where $m_1$ and $m_2$ are the moments of the magnetic nanoparticles, whose unit vectors denote their orientations, and $d$ is the center-to-center interparticle separation, for which the unit vector denotes the axis of their separation.

When present in proximity, these dipoles interact and then assemble together. The magnetic interactions are 3D, long range, both attractive and repulsive in nature, and have directional dependence. There is also a volume effect; below a critical size, the nanoparticles do not spontaneously self-assemble in zero field, though external fields can still drive assembly under certain conditions. Growing clusters of these dipoles create local fields and field gradients, which further affect the assembly process. In the absence of an external magnetic
field, ferromagnetic dipoles have a tendency to form a flux closure loops, so as to minimize the magnetic energy, as evident in rings formed by Co nanoparticles. Applied fields can overcome these local magnetic forces and cause the dipoles to orient along the field direction. In this case, while the loops are no longer closed, chains of magnetic nanoparticles instead form parallel to the applied field direction. These chains can then attract each other and come together to form clusters, resembling stretched loops. A similar effect can also be present in magnetic nanowires.

**Small molecule-assisted assembly**

Nanoparticle surface functionalization can also be used to direct assembly. The nature of interactions in this case is chemical, where the strength, spacing, and arrangement of the assembled structure is dictated by the interacting species. These linking molecules can be functionalized on the entire nanoparticle surface or specific to certain facets (crystallographic or geometric), which then further allows for directed assembly. For example, Glutathione can be selectively attach to the ends of GNRs, facilitating their end-to-end assembly. Mixtures of functionalized gold nanoparticles and GNRs can forms long composite chains of these nanoparticles (figure 2-14). Hydrogen bonding is an interesting force for driving assembly, since it is strong enough to withstand the entropic effects present in solution but can be reversed by heating. In one such example, Ag nanoparticles, capped with cysteine, could be reversibly assembled and disassembled with changes in temperature.
Figure 2-14. Chainlike assembly of end-end linked GNPs with small molecules\textsuperscript{104}
Block copolymers have also shown promise for assembling of anisotropic nanoparticles by means of confinement in specific domains. Using this method, GNRs can be assembled over long distances, limited only by the assembly of the polymer.\textsuperscript{106,107} Electric fields have also been used to reorient GNRs in melts or solutions.\textsuperscript{108} Other techniques for chemically crosslinking GNRs include using AgNO\textsubscript{3} as a crosslinker under UV light\textsuperscript{109} and use of cucurbituril\textsuperscript{110–112} or dendrons for 2D assembly.\textsuperscript{113}
3. Polymer nanocomposites

The field of polymer nanocomposites (PNCs) is quite young. The first documented synthesis of polymer nanocomposites, Nylon-6 mixed with clay, was in 1993, when Toyota developed it for use in their timing belt covers. This material class was invented exclusively for applications and has been in continual use by almost the entire automobile industry since then. Polymer nanocomposites are similar to bulk composites, only in this case the matrix (the larger phase) is polymer and the dispersant is a nanomaterial. Nanomaterials, specifically nanoparticles, have properties drastically different from the bulk. Some of these properties have already been discussed in Chapter 2. Analogously, their effects in blends can also be counterintuitive to those of larger particles. Properties of PNCs are therefore a combination of three factors: the polymer, nanoparticle, and the interfacial interactions. Perhaps the most important factor governing the degree of property changes on addition of colloids to polymers, whether required, expected or detrimental, is the dispersibility of nanoparticles in the matrix. By their nature, polymers and nanoparticles are chemically dissimilar and therefore incompatible. For many applications and for controlled properties, it is crucial to ensure a uniform distribution of nanoparticles in the matrix and to avoid clustering or agglomeration, so that the properties of the composite are consistent and predictable over different areas, batches or sections. Nanoparticles have a high surface area to volume ratio, and thus have a large surface area for exposed for interactions with the matrix. Therefore, the size, shape, and functionalization of the nanoparticles are key factors in designing the final properties of the PNC.

Size of the NPs is comparable to the free-volume of an individual polymer chain, represented by its radius of gyration, \( R_G \). Therefore, polymers and NPs interact on a physically
fundamental scale. For example, instead of increasing the dynamic viscosity as in larger particles, researchers found that smaller nanoparticles can potentially cause a decrease in viscosity. This was attributed to nanoparticles affecting the polymer on individual chain-scale, i.e., on their conformation and free volume. Specifically, the interaction of polymers and nanoparticle can be expressed in terms of $d/R_G$, where $d$ is the nanoparticle diameter. Nanoparticles tend to be miscible in the matrix when the diameter is smaller than $R_G$ of the polymer. Typically, when $d > R_G$, there is significant effect on the configurational entropy of the polymers, and if the nanoparticle size is much larger than the $R_G$, it causes phase separation. Furthermore, if the polymer under consideration is a diblock copolymer and the nanoparticle is compatible with one of the polymer chains, it would undergo phase separation into one of the blocks. In general, attractive interactions between the nanoparticle surface ligands and the polymer chains favor uniform distribution with negligible phase separation.

For the purpose of understanding and predicting these interactions, experimentalists and theorists alike have considered addition of nanoparticles as analogous to mixing of two polymers. As such, addition of a nanoparticle within the polymer matrix has both enthalpic and entropic contributions. In the case of polymer mixtures, the Flory mixing parameter $\chi$, which is the interaction parameter between the two polymers, dictates the formation of a homogenous or phase-separated blend. Similarly, for a spherical nanoparticle of diameter $d$, the insertion enthalpy, proportional to the surface area (extra area inserted) is given by $(4\pi d^2)$. The Enthalpy of mixing can be modified to improve the dispersion and stability of nanoparticles within the matrix, by modifying the surface of nanoparticles such that the ligand is compatible with the polymer chains. This can be manifested by use of appropriate ligands while synthesizing these nanoparticles or through ligand exchange. Another technique is to
graft chemically similar, or in some cases identical, polymer chains or “brushes” on the nanoparticles post-synthesis. Monomer brushes attached to NP surface can be further polymerized. There is however an optimum density of these brushes to induce miscibility in polymeric matrices.\textsuperscript{120} Theoretical studies have shown that by increasing the length of the grafted polymer chain, the resultant assembly of the nanoparticles can be controlled - from aggregated clusters of nanoparticles with no grafting to isolated ones with long chains.\textsuperscript{121}

**Polymer nanocomposites on different scales**

Polymer nanocomposites can occur on different scales, mostly depending on the size of the polymer matrix (figure 3-1). Core-shell PNCs have a much higher inorganic content, where the core is usually of thickness of the order of nanometers or microns. Polymeric fibers containing nanoparticles have higher polymer content, which utilizes the porous nature of the fibers/fiber mat to improve accessibility to the functional properties of the embedded nanoparticles. Bulk polymer nanocomposites encompass everything on the macroscale: thin films to large volume materials. In general, the complexity of synthesis and importance of the interfacial properties increases with the decreasing ratio of the polymer content. Therefore, some of the earliest PNCs were bulk materials designed for robust applications, with further developments in the core shell PNCs for sophisticated biomedical applications.
**Figure 3-1.** Polymer nanocomposites on different scales. a. capsules b. fibers c. thin films d. bulk

**Core-shell:** Typically, synthesis of core-shell particles is done by surface functionalization of inorganic nanoparticles with monomers/long chains followed by polymerization to create the polymer shell. For example, Fe$_3$O$_4$ nanoparticles can be functionalized with hydroxyl groups that initiate ring opening polymerization to create a PCL shell. The thermo-responsive PCL shell could then be heated by using AC magnetic fields. Gold nanoparticles were coated with polymer shells based on NIPA (poly (N-isopropylacrylamide)) by surface-initiated radical polymerization on the nanoparticle surface. Xu et al. grafted gold nanoparticles on the surface of a thermo-responsive polymer in a satellite fashion, which then could be brought closer or further apart by heat and pH. Composite structures can also be prepared by in situ precipitation of nanoparticles from their precursors after forming the polymeric shell. In an apparent reverse process, Kim et al. synthesized spherical polymer nanoparticles based on NIPAM, and used them as templates for
growth of gold nanoparticles within.\textsuperscript{127} Generally, this limits the size of the nanoparticles formed, which are not as monodisperse.\textsuperscript{128} Similarly to the synthesis of nanoparticles, control over the composite particle size and shape can also be obtained by tuning the interfacial interactions between the organic and inorganic constituents. By manipulating the interfacial tension between the polystyrene and silica coating, Yin and coworkers were able to obtain concentric, eccentric and anisotropic nanoparticles.\textsuperscript{129}

![Diagram showing particle morphology control](image)

**Figure 3-2.** Control over particle morphology by tuning interfacial interactions\textsuperscript{129}

Perhaps the most important application of a core-shell PNC is in controlled drug release. Typically, a functional nanoparticle is coated with a layer of stimulus-responsive polymer that undergoes reversible shape and volume changes with temperature or pH. The polymer coating further allows for loading of drugs, and its release is stimulated via the functional properties of the nanoparticle core. Several studies have been conducted using this approach.\textsuperscript{130–133} The polymer shell may encapsulate more than one set of nanoparticles to make them multifunctional. For example, adding fluorescent CdTe nanoparticles along with Fe\textsubscript{3}O\textsubscript{4} within a PNIPAM shell provides enhanced imaging with the capability of inductive heating.\textsuperscript{134} If the polymer shell is crosslinked, heating can cause irreversible cracking of the shell,
releasing a larger amount of loaded drug. In another example, an anti-cancer drug, doxorubicin, was loaded in a PNC nanoparticle with a magnetic core and porous thermoresponsive shell, and a high stimulated release rate was obtained by heating the particles with high frequency magnetic fields. Since heat induces volume changes, such a release can be controlled by switching on/off the field pulse. Such multifunctional nanoparticles, with capabilities of targeting, drug delivery, and even controlled in situ heating have found tremendous applications in the field of drug delivery.

**Fibers:** Electrospinning is the most popular technique to prepare polymer nanocomposite fibers with dispersed NPs. Electrospinning, or more precisely, electrohydrodynamic spinning, generates nanofibers by electrostatic extension and deposition of the polymer, via high voltages maintained between the polymer solution and a metallic collector. The process is described in greater detail in chapter 6. Large shear stresses are generated during electrospinning, which can be used for controlled assembly of nanoparticles. If the particles are anisotropic, this also cause them to align along the fiber direction, resulting in more interesting anisotropic properties. One-dimensional assemblies of spherical Au nanoparticles have been obtained within fibers by electrospinning. Electrospinning has also been used to assemble high concentrations of GNRs in PVA fibers, leading to plasmonic coupling, in both side-side and end-end directions for GNRs. By using special collectors, further alignment of the fibers on the macroscale is also possible giving gives anisotropic optical properties to these fiber mats.
Generally, the nanoparticles are pre-synthesized and dispersed in the polymer solution after suitable surface functionalization. In some instances, the only contribution of the polymer is its function as the carrier material. Another interesting technique to make PNC fibers is to incorporate the inorganic precursor within the polymer itself and then use UV irradiation to transform them into nanoparticles. This method does not require a ligand or a reducing agent, since the polymer matrix serves as both but tends to give very polydisperse sizes.

As expected, incorporation of functional nanoparticles into fibers translates those properties to the polymer composite itself. For example, embedding Magnetic particles in fibers can make them magnetically responsive. Iron oxide nanoparticles incorporated within the nanofibers have been shown to have larger coercivities as compared to dry nanoparticles. These fibers could then be used for filters applications. Due to their high surface area, nanofibers serve as excellent hosts for catalysis and highly sensitive detection systems. Incorporated ZnCl$_2$ salt in PAN fibers has been converted into distinguishable ZnS surface
crystals when exposed to H\textsubscript{2}S, which can be used for sensing.\textsuperscript{144} In another example, TiO\textsubscript{2}-loaded nanofibers were used as catalysts for water-gas shift reactions.\textsuperscript{145} Incorporation of nanoparticles can also increase the modulus of the fibers by up to 400\% of the value for the unloaded fibers.\textsuperscript{146} Chromatic materials, when put in nanofibers, could render them reversibly color responsive to stress and applied current.\textsuperscript{147} The Ability to make these fibers on a large enough scale for membranes, filters, and mats combined with the accessibility offered by the high surface area of the polymer fibers, makes these materials very appealing for filtration and wound dressing applications.

**Thin films and bulk:** Early developments in the PNCs shared a common theme: clay particles were used as fillers, the polymers selected were of commercial importance, and primarily physical properties were explored. With increasing appreciation of the polymer composites as candidates for specialized applications, research became more focused on chemical compatibility and novel functionalities. In one of the first studies back in 1998, for example, Wang et al. mixed montmorillonite with elastomeric polyurethanes and showed simultaneous increase the strength and the elasticity of the composite.\textsuperscript{148} In a recent paper from 2015, Cellini et al. designed a mechanochromic PNC, which can change color reversibly upon deformation of the polymer, providing a visual indicator of the applied strain.\textsuperscript{149} This was achieved by incorporating a fluorescent dye, capable of changing its emission from the excimer band to the monomer band, in an elastomer.\textsuperscript{150} Addition of conductive particles like carbon nanotubes or silver nanoparticles could increase the conductivity of polymers to the order of 1–10 S/cm.\textsuperscript{151–152} Presence of certain gas species causes chemical changes with ensuing changes in the electrical conductivity of these composites, and thus can be used for detection of pH changes and for sensing various gases.\textsuperscript{153–158} Use of nanoparticles in polymers can also
cause a shift in the refractive index, to both higher and lower values, for tunable optical applications. Nanomaterials, like carbon nanotubes, have also been shown to increase the flame resistance of certain polymers to a much greater extent. Even before the mechanism was understood, metal particles like Au, Ag and Cu have been known to have antimicrobial properties. Recent research has shown that the nanoparticles indeed can act as antimicrobial agents for several common bacteria and fungi that cause biofouling. These NPs could be incorporated within the select polymers, which can then undergo controlled degradation for tunable release of metal ions. This technique allows the use of antimicrobial properties of the metals for various applications. Polymers can be spin coated onto flat substrates, and thus can be used for making antimicrobial coatings. Films and membranes of these materials could be used for food packaging as well as antibacterial textiles for clothing. Uniform dispersions of nanofillers in polymers can also act as effective barriers for permeation. nanoparticles can decrease the gas permeability of the composites by providing a tortuous pathway for the penetrating gas molecules, and decelerate any ensuing degradation. nanoparticles can also acts as local heat sinks, preventing thermal damage to the surrounding polymer matrix, and thus allowing an electrically induced cyclic reversible polymer breakdown, which can be used for switches or sensor applications.

**Soft robotics potential:** For several soft robotic applications, remote actuation of the polymer is highly desirable. Typical stimuli used for these actuations are pneumatic, electrical, electrochemical, or magnetic. While most polymers themselves do not have the functionalities to respond to and therefore be actuated by these stimuli, addition of nanoparticles makes it possible. Polymer nanocomposites are thus great candidates for soft robots, as they allow the functional properties of the nanoparticles to be manipulated independently. This allows remote
programming of PNCs with independent control over the stiffness, for soft robots with better compliance for actuation.
4. Anisotropic actuation using magnetic chains

The Earliest known magnets were used as compasses for navigation or leading stones, hence named as lodestones. Lodestones are primarily iron (III) oxide (Fe₃O₄) occurring as deposits in Magnesia in ancient Greece (or the mythical Magnes, the shepherd, whose iron-soled shoes got stuck to the rocks), which spawned the name ‘magnet’ for the material and later Magnetite for Fe₃O₄. Since then, magnets and magnetism have been studied and understood by several scholars: Gilbert, Coulomb, Gauss, Faraday, Ampere, Maxwell, and Oersted, to name a few. Magnetic materials always have a dipole associated with them, such that the net magnetic charge is zero. For a magnet with pole strength \( p \) and distance \( l \) between the poles, the dipole moment is given by \( \mu = pl \). The Field generated by a dipole is additive; two identical dipoles combined together edgewise or lengthwise yield a dipole moment of \( \mu = 2pl \) and conversely every dipole can be subdivided into its constituent dipoles (or moments). An applied magnetic field generates a moment within the material. The relationship is given by \( B = \mu H \).

Depending on how these moments are arranged within the material, they can be classified as diamagnets, paramagnets, ferromagnets, antiferromagnets, and ferrimagnets. A simple visual comparison of different magnetic materials is shown in figure (4-1).
Magnetic Anisotropy

For most magnetic materials, the magnetic properties are different in different directions. Depending on their origin, they can be classified according to the following:

1. **Crystal Anisotropy**: For every crystal lattice, whether dimensionally isotropic or not, the atomic density depends on the crystallographic directions, which gives rise to an anisotropy in electronic conductivity. While the association is not as straightforward, magnetic properties are also anisotropic with respect to crystal directions. For magnetization along Easy directions, saturation is achieved at low fields; in comparison, higher fields are required for magnetization and saturation in hard directions. Every electron in an atom has four associated quantum numbers: principal (energy), azimuthal (angular), magnetic (orbital) and spin quantum number. Crystalline anisotropy arises when the spin of one electron interacts with the
orbital moment of another, resulting in coupling which varies for different directions along a crystal lattice. This directionality gives rise to the anisotropy energy, which is lowest along the easy axis. Hence, a single crystal will have non-zero magnetic moment, even when no field is applied, and an additional field is needed for reorienting the moments in any other direction. With increasing temperature, the thermal energy increasingly randomizes the magnetic dipoles, and the Curie temperature, ferromagnetic moments decouple from each other and from the crystal lattice.

The same is true for polycrystalline materials, except that the easy axis may point in different directions within each domain, so that the net moment will have smaller value than the sum of moment of each domain. A volume of atoms having net single dipole is called a magnetic domain. Domains can be smaller than the crystal size or as large as the sample itself. Domains magnetized along easy axes will be larger than domains magnetized along hard axes. With application of increasing magnetic field, the dipoles are aligned forcibly along the field direction, increasing the size of those domains. Domains pointing along different direction are separated by domain walls. As the field increases, the domain boundaries expand until the entire sample is a single domain with only one dipole, when it is said to be saturated. Regardless, saturation in this case requires rotation of the magnetic moment of each domain, referred to as domain rotation, parallel to the field until the domains coalesce into a single domain. The Direction of easy magnetization is effectively the spontaneous domain magnetization direction as well.

**2. Shape anisotropy:** For a single-dimension (spherical) polycrystalline material with randomly oriented grains, the net dipole moment is usually small. But externally applied magnetic fields induce secondary magnetic fields within the sample, which depends on the
dimension of the sample. For a non-spherical shape, the induced field will have different values along different directions, specifically weaker along shorter dimension, which therefore becomes the hard axis for the bulk sample. Therefore, in absence of other effects, a material can be magnetize most easiler along its longest dimension. the extent to which the shape plays a role in the anisotropy also depends on the ratio of the unequal dimensions and the magnetic properties of the material. The interaction of shape and crystalline anisotropies typically determines the equilibrium direction of the net magnetic moment, as shown in figure 4-2.

Consider a crystalline ferromagnetic material with a uniaxial magnetic anisotropy, subjected to applied field $H$. The Anisotropy energy of the crystalline material is given by

$$ E = K \sin^2 \theta, \text{ where } \theta \text{ is the angle between the easy axis (shape or crystalline) and the saturation magnetization } M_s. $$

The Magnetic potential energy is given by:

$$ E = -HM \cos(\alpha - \theta) $$

and the Net energy density is $E = K \sin^2 \theta - HM \cos(\alpha - \theta)$

The equilibrium position is calculated from $E' = 0$, which gives

$$ K \sin 2\theta = HM_s \sin \alpha - \theta. $$

3. **Stress-Induced Anisotropy:** When a magnetic material is subjected to external magnetic field, it undergoes physical dimensional changes. This effect was first observed by
Joule in 1842, and this phenomenon is known as magnetostriction. Conversely, a physically strained material will correspondingly exhibit changes in its magnetic properties. Thermodynamically it can be represented as:

\[ \frac{1}{V} \left( \frac{\partial V}{\partial H} \right)_{p,T} = -\left( \frac{\partial M}{\partial P} \right)_{H,T} \]

where \( M \) is the magnetization, \( P \) the pressure, \( H \) the external magnetic field, \( T \) the temperature, and \( V \) the volume. While it occurs in all materials, usually the effect is small, of the order of \( 10^{-5} \).
Remote actuation of polymers is of special interest for soft robotics and biomedical applications. One approach for actuating polymers is to embed them with optical, magnetic, or electrically responsive particles. Embedding magnetic particles in soft matrices like elastomers and gels allows actuation with external magnetic fields. Consequentially, magnetic polymer nanocomposites (MPNCs) have been used as remotely-actuated soft robots, including cilia, microtransporters and microbots. Magnetic nanoparticles, when suitably functionalized, can be directly incorporated into polymer matrices through solvent casting or bulk polymerization. Under application of an external magnetic field, magnetic nanoparticles can assemble into chains along the field direction. During chaining, the moments of the magnetic nanoparticles align in the field direction, and attractive dipolar interactions pull the magnetic nanoparticles together (head-to-tail) to form chains. Once the solvent evaporates or polymerization is complete, the chains remain embedded in the composite after removing the field. The length and thickness of the chains and spacing between them depend on the strength and frequency of the field, concentration of the magnetic nanoparticles, their surface functionalization, and conditions for drying or polymerization.

One-dimensional arrangement of magnetic nanoparticles in chains imparts anisotropic magnetic properties to the composite, which has been utilized here to obtain an anisotropic mechanical response. The chains of magnetic nanoparticles magnetize much more strongly when aligned parallel, rather than orthogonal, to the magnetic field direction. Consequently, alignment of the chains along the direction of an externally applied magnetic field is energetically favorable. This magnetic anisotropy of the chains allows for selective, controlled, and directional actuation in three dimensions (3D).
In a previous study, segments of µm-scale polymer films connected by flexible linkers were fabricated with embedded chains of magnetic nanoparticles oriented in different directions in each segment. Applying magnetic fields while these samples floated on water caused bending, curling, and other complex in-plane motions. A similar result can be achieved by employing anisotropy in the shape of the composite rather than of the arrangement of the magnetic nanoparticles within, as demonstrated in a microgripper composed of elongated magnetic films arranged in a zigzag manner. Magnetic nanoparticles can also generate heat in response to ac magnetic fields, which in turn can be used for triggering shape transitions in shape memory polymers, for magnetothermal repair of composites, as an actuation mechanism, and for hyperthermia. While actuation in these composites occurs on the µm scale, we are not aware of previous reports of macroscale actuation of MPNCs containing chains of magnetic nanoparticles.

Here, magnetic nanoparticles assembled as chains within elastomeric films enable direction-controlled actuation of MPNCs. A composite sample containing chains of magnetic nanoparticles, referred to as a “chained MPNC,” was prepared by solvent casting a dispersion of 29-nm Fe₃O₄ magnetic nanoparticles and thermoplastic polyurethane (TPU) in an external magnetic field (Figure 1). Magnetometry measurements were conducted to evaluate the anisotropic magnetic properties of MPNC. Higher magnetization was obtained parallel rather than perpendicular to the magnetic nanoparticle chains. The magnetization directions of the magnetic nanoparticles are determined by minimizing the magnetostatic energy, for which the dipolar interaction energy among the magnetic nanoparticles and the Zeeman energy generated by the applied field are the prevailing terms. Assembly of the magnetic nanoparticles into chains causes a directional dependence in the magnetostatic energy, allowing for anisotropic
actuation of the composite in 3D. Actuation experiments were conducted on a thin film composite sample cut into the shape of a cross, where the arms facilitate bending and the chains of magnetic nanoparticles point along two of the arms. The terms, “parallel arms” and “perpendicular arms” refer to orientations of the arms parallel and perpendicular to the chains, respectively. Actuation was investigated in both spatially uniform fields and field gradients.

In the spatially uniform, horizontal field of the electromagnet, the sample was supported in the center, while gravity caused the arms of the thin elastomer film to hang down, nearly vertically. Two orientations of the sample were studied (Figure 2a), parallel arms hanging to the left and right sides (LR) and parallel arms hanging to the front and back (FB). In orientation LR, as the field is increased, the parallel arms lift up toward horizontal, bringing the arms and magnetic nanoparticle chains closer to alignment with the field. The perpendicular arms are unaffected, since the chains are already aligned with the field. In orientation FB, the chains in all of the arms are oriented perpendicular to the field. Therefore, the field causes a twisting torque in each arm to bring the chains closer to alignment. Rotating the sample within the gap of an electromagnet also shows a marked dependence on orientation. Periodicity in the lifting behavior of 360° was observed for the parallel arms (Supporting Information, Video S1 and Figure S1). At certain angles of rotation, the perpendicular arms snapped to obtain a new, more stable configuration. Snapping is caused by the release of elastic energy that accumulates as the arm twists.\cite{41}

For experiments in a magnetic field gradient, the sample was mounted in the center of a flat rotating stage, and a permanent magnet was held at a fixed height above the edge of the sample, such that the ends of the arms would pass beneath it (Figure 2b and Supporting Information, Video S2). Only the parallel arms lift toward the magnet as they are rotated below.
If the magnetic nanoparticles had been dispersed in the elastomer without chaining, the same result would be expected for all four arms, either lifting if the magnetic force overcomes gravity, or not lifting if gravity prevails. Selective lifting of the parallel arms can be understood from the magnetic force, which is the negative gradient of the magnetostatic energy. The magnetic force is strongest when the moments point in the direction of the field gradient. For both perpendicular and parallel configurations, the field causes (via the Zeeman energy) magnetic moments of the magnetic nanoparticles to tilt toward the field direction, and the field gradient generates an attractive lifting force toward the permanent magnet. The magnetization of the chained magnetic nanoparticles in the direction of the field gradient is expected to be higher for the parallel arms than for the perpendicular arms, which is consistent with the higher magnetization of parallel than perpendicular chains at a given field, observed in magnetometry measurements (Figure 1c). Furthermore, magnetizing the parallel arm causes increasingly favorable dipolar coupling as the arm lifts up, generating a sufficient force to overcome gravity. Dipolar coupling in the perpendicular arm under the permanent magnet reduces the magnetization in the direction of the field gradient; the resulting force is too weak to lift the perpendicular arm. As the sample rotates, aligning the field lines with the perpendicular arms is expected to generate twisting rather than lifting, which is observed as a minor deflection in their ends as they pass beneath the permanent magnet. The selectivity of lifting depends on the distance between the sample and the magnet. At significantly shorter separations, both parallel and perpendicular arms lift, while neither arm lifts at longer distances.

It is also important to consider potential non-magnetic effects caused by assembling the magnetic nanoparticles on the bending modulus of the composite, for example due to particle jamming. Mechanical deformation tests on chained MPNCs have shown that chaining
increases the modulus along the direction of the magnetic nanoparticle chains.\cite{42, 43} Therefore, the modulus for bending the parallel arms is expected to be higher than for the perpendicular arms, if the magnetic nanoparticles would have a structural effect. Consequently, the magnetic rather than structural anisotropy of the MPNC is the dominant effect in these experiments.

To better understand the actuation mechanism, the bending angle of the parallel arms aligned with the field of an electromagnet (orientation LR in Figure 2a) was measured as a function of the horizontal magnetic field strength, $H$. As $H$ increases, the arms lift higher toward horizontal, decreasing the bending angle, $\theta$. A simple model (see Supporting Information for details) was constructed for interpreting this experiment. The equilibrium positions of the arm and of the magnetic moments within the arm are obtained by balancing the mechanical torques on the arm and the magnetic torques on the magnetic nanoparticle moments. Linear, continuous chains of touching spherical magnetic nanoparticles with negligible interchain interactions are used to model the MPNC. Two magnetic forces generate torques on the moments: dipolar interactions between magnetic nanoparticles, which favor alignment with the chain direction, and the Zeeman energy, which favors alignment with the direction of the applied field. The model of the torques on the moments mimics the Stoner-Wohlfarth model for the magnetization of single-domain, single-crystal magnetic particles, where the Zeeman energy is balanced by crystal anisotropy.\cite{44} Two forces generate mechanical torques on the arm: gravity and dipolar interactions between magnetic nanoparticles, which favors alignment of the arm with the moments in the chains, thereby generating more favorable head-to-tail interactions and fewer side-by-side interactions. Dipolar interactions between magnetic nanoparticles therefore affect equilibrium of both the moments and the arm. The process of lifting the arm up toward the field direction can be
understood as follows: The applied magnetic field rotates the moments slightly out of the chain direction (at a “moment angle,” $\alpha$) and toward the applied field direction, causing less favorable dipolar interactions among the moments. Lifting the arm toward the field direction gives more favorable dipolar interactions while also allowing the moments to point toward the field direction and reducing $\alpha$.

In the experimental sample, the chains are multiple magnetic nanoparticles wide (Figure 1b), as also noted elsewhere;$^{[19, 32]}$ which has not been accounted for in this model of chains of a single magnetic nanoparticle in width. A disorder parameter ($\gamma$) is introduced to account for structural and accompanying magnetic disorder within the chains. In disordered chains, saturation of the moments along the chain axis causes side-by-side interactions along with favorable head-to-tail interactions. We compensate for the side-by-side interactions by multiplying the moment of the magnetic nanoparticle by $\gamma$, where $0 \leq \gamma \leq 1$. The limit $\gamma = 1$ corresponds to the perfect chains described by the model without correction, and $\gamma = 0$ would describe an isotropic arrangement of moments without a chaining direction. The value of $\gamma$ has been approximated as the remanent magnetization divided by the saturation magnetization ($M_R/M_S$) for measurements parallel to the chain direction. This is a reasonable approximation,$^{[45]}$ because a perfect chain would theoretically have $M_R = M_S$.

According to the model, at equilibrium, $H = 0.598 \frac{\cos \theta}{\sin(\theta - \alpha)}$ kOe, where $\sin 2\alpha = 0.742 \cos \theta$. When this expression for $\theta$ vs. $H$ is plotted along with the experimental data, $\gamma = 0.445$ from magnetometry gives an excellent fit (Figure 3), which is remarkable for a simple model with a single, experimentally determined parameter. The maximum value of $\alpha$ is less than 0.4° (Supporting Information, Figure S2), which suggests the moments remain
nearly aligned with the chain direction. Several simplifying assumptions, described in the Supporting Information, have been made about the magnetic properties of the magnetic nanoparticles. It should further be noted that the mechanical properties of the polymer have been neglected in this model; the mechanical response of the MPNC is determined solely by the magnetic behavior of the chains rather than the mechanical properties of the polymer. The good agreement between the model and the experimental system, however, indicates that the properties of such anisotropically responsive materials can be predicted and controlled by corresponding adjustments in the magnetic characteristics of the magnetic nanoparticles and their arrangement within the polymer.

In conclusion, we have demonstrated and modeled the anisotropic response of a chained MPNC via selective bending and actuation of the arms of the elastomer film. The interaction of the magnetic anisotropy of the chains with the direction of the applied field allows for controlled, directional actuation of these macroscale samples in 3D. Flexible thin films with magnetically driven, directional mechanical responses are an example of a new class of materials that can be employed for remote directional manipulation of soft actuators, valves, motors, and other soft robotics applications.
Figure 1. (a) schematic for the process of preparing a chained magnetic particle nanocomposite (MPNC) cross sample, (b) left to right: TEM image of magnetic nanoparticles (magnetic nanoparticles), optical micrograph of chained MPNC, photograph of cross sample, and (c) magnetometry of a chained MPNC at 300 K measured parallel and perpendicular to the chains.
Figure 2. Photos showing anisotropic actuation under (a) uniform magnetic field for the cross mounted by its center, where the chains for the flattened cross would be aligned (left) parallel (LR) to the field and (right) perpendicular (FB) to the field, and (b) field gradients from a permanent magnet that selectively lifts parallel but not perpendicular arms as the sample is rotated. (c) schematic showing relative orientation of magnetic nanoparticle dipoles with respect to the chain direction in presence and absence of field lines generated by permanent magnet, which causes selective lifting in (b). See Supporting Information, Videos S1-2 for movies of these lifting processes.

Figure 3. Plot of the bending angle, $\theta$, as a function of the applied uniform magnetic field for experimental data and the model.
References
Experimental Details (Supporting Info)

Magnetite (Fe₃O₄) magnetic nanoparticles functionalized with oleic acid of an average size of 29 nm were synthesized according to an established method. Complete details for the synthesis and purification are provided in the Supporting Information. Magnetometry measurements were performed at 300 K using a Quantum Design MPMS 3 SQUID VSM.

Alignment and Bending Studies:

To study the response in uniform magnetic fields, a cross-shaped sample with average arm length of 20 mm, width of 4 mm, and thickness of 121 µm was mounted by its center on
a stage. The entire assembly was placed between the poles of a GMW 3472-70 electromagnet with a pole cap separation of 60 mm. The position of a parallel arm at different applied fields was monitored to give the dependence of the bending angle, \( \theta \), on the applied magnetic field strength, \( H \). \( \theta \) was measured at the middle of the arm. In another experiment, the sample was rotated at a rate of 3.66 rpm under a static applied field of 7.2 kOe. For studying actuation in a magnetic field gradient, the sample was pinned flat on a rotating stage (1.2 rpm), and a FeNdB permanent magnet was positioned above the edge of the sample. The bending behavior of each arm was observed as it passed under the magnet.

**Modelling Actuation Behavior in Uniform Magnetic Fields:**

Magnetic nanoparticles are treated as single-domain, spherical nanoparticles assembled into parallel, non-interacting chains of one nanoparticle width. Magnetocrystalline anisotropy and thermal energy are neglected, giving these magnetic nanoparticles zero coercivity and eliminating the effect of superparamagnetism randomizing the magnetic nanoparticle magnetization directions. The magnetization behavior of magnetic nanoparticles described in this model is a step function, matching a Langevin function describing a superparamagnet at 0 K temperature. In this model and the associated experiments, dipolar interactions among magnetic nanoparticles, alignment of the magnetic moments within the magnetic field, and gravity determine the behavior.

When the sample arm (and hence the chains) is at a given bending angle, \( \theta \), with respect to the horizontal external field, \( H \), the individual magnetic nanoparticle dipoles are rotated by a moment angle, \( \alpha \), where \( \alpha < \theta \), as depicted below:
The magnetic dipolar interaction energy, $E_{12}$, between two neighboring magnetic nanoparticles is given by: \[ E_{12} = \frac{\mu_0}{4\pi} \left( \frac{m_1 m_2}{d^3} \right) \left( m_1 \cdot m_2 - 3 (m_1 \cdot \hat{d}) (m_2 \cdot \hat{d}) \right), \]

where $m_1$ and $m_2$ are the moments of the magnetic nanoparticles, whose unit vectors denote their orientations, and $d$ is the center-to-center interparticle separation, for which the unit vector denotes the axis of their separation. For a chain of identical magnetic nanoparticles, depicted above,

$$\bar{m}_1 = \bar{m}_2 = \bar{m} \ldots \text{ and } m_1 \cdot \hat{d} = \cos \alpha \text{ gives}$$

$$E_{12} = \frac{\mu_0}{4\pi} \left( \frac{m^2}{d^3} \right) (1 - 3 \cos^2 \alpha).$$

Therefore the net energy for the interaction of each magnetic nanoparticle with its two nearest neighbors is $2E_{12}$. For infinitely long chains (i.e., more neighbors at distances of $2d, 3d, 4d, \ldots$):
\[ E_{\text{int}} = 2RE_{12}, \text{ where } R = \sum_{i=1}^{\infty} \frac{1}{n^3} = 1.20. \]

The total magnetic dipolar interaction energy, \( E \), for \( N \) magnetic nanoparticles within parallel, non-interacting chains is thus given by:

\[ E = \frac{0.6 \mu_0 N}{\pi} \left( \frac{m^2}{d^3} \right) (1 - 3 \cos^2 \alpha). \]

The (clockwise) torque on the moments caused by chaining is denoted by:

\[ T_m = -\frac{dE}{d\alpha} = -\frac{1.8 \mu_0 N}{\pi} \left( \frac{m^2}{d^3} \right) (\sin 2\alpha). \]

This is physically equivalent to generating an opposite torque by the moments on the chains,

\[ T_c = \frac{1.8 \mu_0 N}{\pi} \left( \frac{m^2}{d^3} \right) (\sin 2\alpha). \]

\( T_c \) acts to rotate the chains and hence the sample arm toward horizontal (counterclockwise). The gravitational torque (clockwise) acting on sample length \( L \) and mass \( w \) is given by:

\[ T_g = -\frac{gwL}{2} \sin (90^\circ - \theta). \]

\( T_g \) opposes \( T_c \) to rotate the sample arm (and the chains) downward (clockwise). Mechanical equilibrium gives a relationship between \( \theta \) and \( \alpha \):

\[ T_g + T_c = 0 \]

\[ -\frac{gwL}{2} \sin (90^\circ - \theta) + \frac{1.8 \mu_0 N}{\pi} \left( \frac{m^2}{d^3} \right) (\sin 2\alpha) = 0 \]

\[ \sin 2\alpha = \frac{gwL\pi d^3}{3.6 \mu_0 Nm^2} \cos \theta. \]
The Zeeman energy for $N$ magnetic nanoparticles in the configuration shown above is given by:

$$E_z = -Nm\mu_o H \cos(\theta - \alpha).$$

The magnetic torque ($T_H$) acting on the moments due to the external magnetic field, $H$, is obtained as the derivative of the Zeeman energy:

$$T_H = -\frac{dE_z}{d\alpha} = Nm\mu_o H \sin(\theta - \alpha).$$

$T_H$ acts to rotate the moments (counterclockwise) toward the field direction, and the torque on the moments caused by chaining ($T_m$) works to align them (clockwise) with chain axis. For equilibrium of the magnetic moments,

$$T_H + T_m = 0$$

$$Nm\mu_o H \sin(\theta - \alpha) - \frac{1.8\mu_o N}{\pi} \left(\frac{m^2}{d^3}\right)(\sin 2\alpha) = 0$$

$$H = \frac{1.8m}{\pi d^3} \frac{\sin 2\alpha}{\sin(\theta - \alpha)}.$$

In experiments, the chains are multiple magnetic nanoparticles wide, giving a significant number of side-by-side interactions along with head-to-tail interactions. The effect of side-by-side interactions is to make the total dipolar interaction energy, $E$, more positive (less favorable). Decreasing the effective moment of the magnetic nanoparticles would give a similar effect. We have thus defined an effective moment,

$$m' = \gamma m = \gamma M_{s}V,$$
where the disorder parameter, $\gamma < 1$. $M_s$ is the saturation magnetization and $V$ is the magnetic nanoparticle volume, $V = \pi d^3/6$. Therefore, $NV$ is the total volume of magnetic nanoparticle core material, which is equal to the weight fraction of Magnetic nanoparticles ($f$) multiplied by the weight of sample ($w$) and divided by the density ($\rho$) of Fe$_3$O$_4$:

$$NV = fw/\rho$$

$$w = \rho NV/f.$$

The equations describing magnetic and mechanical equilibrium for disordered chains can thus be rewritten,

$$H = 0.3\gamma M_s \frac{\sin 2\alpha}{\sin(\theta - \alpha)}, \text{ where } \sin 2\alpha = \frac{g\rho L}{0.6\mu_0 f \gamma^2 M_s^2} \cos \theta.$$

Since the effects of coercivity and thermal energy are neglected, there is no dependence on the Magnetic nanoparticle size. From magnetometry measurements of the parallel configuration at 300 K (Figure 1c), the saturation moment is $2.956 \times 10^{-3}$ emu, and the remanent moment is $1.315 \times 10^{-3}$ emu. The disorder parameter is thus calculated as $\gamma = 1.315 \times 10^{-3} / 2.956 \times 10^{-3} = 0.445$. Inserting the following values for physical constants and fixed experimental parameters, $g = 9.8 \text{ m s}^{-2}$, $\rho = 5240 \text{ kg m}^{-3}$, $L = 0.02 \text{ m}$, $f = 0.0402$, $M_s (\text{at 20 °C}) = 480,000 \text{ A m}^{-1}$, $\mu_0 = 4\pi \times 10^{-7} \text{ kg m s}^{-2} \text{ A}^{-2}$, and $1 \text{ Oe} = 1000/4\pi \text{ A m}^{-1}$ gives:

$$H = 0.598 \frac{\cos \theta}{\sin(\theta - \alpha)} \text{ kOe}, \text{ where } \sin 2\alpha = 0.742 \cos \theta.$$
Photos and Schematics Depicting Inward Bending of Parallel Arms Alternating with Lifting:

Figure 4-3. Alternating lifting and bending of parallel arms of the rotating cross in uniform 3.1 kOe field with schematic overlays of the magnetization of chains within the composite. Twisting at ¼ rotation causes inward bending at ½ total rotation

Modelling Dependence of the Mechanical Bending on the Orientation of the Magnetic Moments:

Figure 4-4. Plot of the calculated dependence of the bending angle, $\theta$, on the moment angle, $\alpha$, measured with respect to the chain direction for the disordered chains
5. Plasmonic nanoparticles for photothermal heating of shape memory polymers

Surface Plasmon Resonance and Photothermal Heating

The first metallic gold colloids or “gold sol” as he called it, were discovered by Faraday, and gave rise to the field now we know as nanoscience. In Faraday’s own words “This ruby fluid is well obtained by pouring a weak solution of gold over the phosphorus which has been employed to produce films and allowing it to stand for twenty-four or forty-eight hours.”

Interestingly, the particles he prepared are still stable after over 150 years since their making. But it was not until 1908, that Mie came up with the theory to describe the absorption and scattering (extinction) by metal particles. Building on Mie’s theory, this phenomena, called surface plasmon resonance, is now well understood for particles of different shapes, sizes and composition.

Figure 5-1. Gold NPs by Michael Faraday. Source: Paul Wilkinson: www.rigb.org
Light, as an electromagnetic wave, has orthogonal electrical and magnetic fields. Optical properties of any material are the result of interaction of these wave components with the material atoms, or specifically electrons. Metallic bonds are understood as metals ions in a sea of delocalized electrons where their mutual, collective electrostatic attraction gives the strong metallic bonding, while still allowing the electrons to move around, leading to high electronic and thermal conductivities. The characteristic color of the metal depends on the interaction of these large numbers of free electrons with light. On the nanoscale, however, properties of metals are remarkably different. A typical nanoparticle (nanoparticle) has very small number of atoms (of the order 10-100), such that the ratio of surface to bulk atoms increases dramatically. For a particle smaller than wavelength of the light, the individual phase of the light waves can interact with the surface electrons of the metal nanoparticle atoms. As the wave passes through, it creates alternating attraction and repulsion for the electrons, leading to periodic oscillations of the electron cloud. This leads to increased absorbance at and near that specific wavelength and is called surface plasmon resonance (SPR). Typically SPR wavelengths of noble metal particles lie within the visible light range (400-800 nm). The effect is that these nanoparticles appear of a different color than the bulk material. Gold appears red,
silver appears green/brown and so on. Moreover, by changing the size and shape of these nanoparticles, the color can be tuned. Several factors contribute to absorbance spectrum of a nanoparticle and hence the SPR wavelength(s) of the particular nanoparticle.\(^{180}\)

**Size.** Typically, for a spherical particle, within a certain range of sizes, as the nanoparticle diameter increases, the SPR wavelength that interacts with the particle also increases, leading to a red shift towards higher wavelength. The plasmonic bandwidth, characterized by FWHM, also increases, but only for nanoparticle larger than a threshold size.\(^{180}\)

![Figure 5-3. Variation of SPR with NP size\(^{180}\)](image)

**Aspect ratio:** For anisotropic particles, there is absorption associated with each dimension. A typical SPR for a gold nanorods (GNR) is shown in figure 5-4. Since, GNRs have two significantly different dimensions, the SPR that interacts with each one of them occurs at different wavelengths. As seen in the figure 5-4, the peak close to 800 nm is for the longer dimension called the longitudinal SPR (LSPR), and the one at 530 nm is the transverse SPR (TSPR).
The LSPR shows remarkable dependence on the aspect ratio of the GNRs. Several studies have been devoted to determine this relationship. In one particular study, it was estimated to be:

$$SPR = (33.34R - 46.31)e_m + 472.31 \text{ nm},$$

where $e_m$ is the dielectric constant of the medium, $R$ is the aspect ratio of the GNR. However, these equations are not universally applicable and are only accurate within a certain range of nanoparticle sizes. Typically, the LSPR red shifts to higher wavelengths, with increasing aspect ratio and vice versa. There have been reports of red-shift in the TSPR as well, but it is small compared to the LSPR.\textsuperscript{181}
Composition: Since the dielectric constant of the material is the underlying property for SPR, for two different materials with same spherical nanoparticle diameter, the SPR will be different. As shown in figure 5-6, for different weight fraction of gold in a gold-silver alloy particle, the SPR shifts to lower wavelengths as the gold content increases.
Medium: Increasing $e_m$ leads to an increase in the plasmon band bandwidth and a red shift of the plasmon band maximum. But this dependence of the SPR on the effective medium dielectric constant is complicated by the fact that it can itself change with the size of the particles.$^{181}$

Assembly: When two or more nanoparticles come close enough (within few nanoparticle diameter length), their SPRs starts to interact because of the near field effects. This gives rise to a red-shift in SPR of the sample which directly correlates with the nanoparticle spacing. In fact, this concept has been used for several applications. By accurately measuring the shift in SPR, a plasmon ruler can be used to measure the distance between the nanoparticles,$^{14,18,20,21}$ as well as to enhance the signals from SERS.$^{182}$ For anisotropic particles like GNRs, plasmon coupling can also differ based on the relative orientations of the nanoparticles.

Photothermal heating

Due to the high absorption at the SPR, in the visible light range, GNRs can harvest energy from an optical source and convert it into other energy forms, mostly heat. This heat generated is transferred then to the surrounding medium via photothermal heating. Femtosecond laser pulses have been used to investigate the mechanism of photothermal heating, especially for gold nanoparticles.$^{183,184}$ The absorption of the laser pulses increases the energy of the electrons to a broad non-Fermi level in the conduction band. This non-thermalized distribution (nTD) leads to formation of hot electrons, which then redistribute their energy via electron-electron coupling to an internally thermalized distribution (iTD). Furthermore, the electrons then thermalize (thermally equilibriate) with the lattice via electron-phonon interactions, leading to lattice heating. This last step, being the slowest, occurs over a
time scale of few picoseconds. As the energy is further propagated via phonons, it leads to heating of the surrounding matrix of the gold nanoparticles. Figure 5-7 shows the relative time scales of the processes.

\[\text{Figure 5-7. Mechanism of photothermal heating and their relative time scales}\]

Several attempts have been made to calculate the photothermal efficiency of GNRs. Infrared cameras have been used to monitor the temperature changes local to the GNR surface, when embedded in polymers. Another method involved embedding gold nanoparticles in ice, and monitoring the melting by recording the Raman signals over time. One other technique is using fluorescence polarization anisotropy (FPA) where fluorescein is a xanthene-type chromophore characterized by a high photostability and a fluorescence quantum yield close to 100%, which enables mapping the local temperature near nanoparticles with 300 nm spatial resolution and a typical accuracy of 0.1 °C. One of the easier methods uses calorimetry: gold nanoparticles are dispersed in water, and the temp carefully monitored to calculate the photothermal efficiency.
As with SPR, photothermal heating depends on several factors: SPR wavelength, nanoparticle volume, shell coating, and assembly state. Larger particles with essentially same shape are less efficient since they do not scatter as well. Use of a chemically different shell, can actually increase the photothermal efficiency by absorbing more light, and changing the dielectric constant of the medium.\textsuperscript{186}

It is also interesting to note that since the gold nanoparticles are usually stabilized by organic ligands, due to generation of high temperatures strip/destroy these surface ligands, and the gold atoms start to redisperse in the medium, leading to reshaping of the gold nanoparticle. Since for GNRs, heating efficiency is much higher at the ends, they dissolve/melt faster, leading to more isotropic shapes. It has been shown that the surface conditions play a crucial role in GNR reshaping, and changes with the mode of heating: conventional (inwards) or photothermal (outwards heat diffusions).\textsuperscript{190} While reshaping is an inevitable effect of photothermal heating, its rate depends on the energy being applied, for example pulse energy and width if a laser used.\textsuperscript{180}

**Applications**

Photothermal heating has several advantages over conventional heating: 1. It is non-contact mode of heating so as long as the nanoparticle heat source receives the light pulse, it will generate heat. 2. The heat can be precisely controlled with the intensity and time of light pulse. 3. Since photothermal heating generates a large amount of localized heat, it is very useful in site-specific heating applications. This has been showed by Maity et al., where they used gold nanoparticles as heating sources and incorporated them in nanofibers prepared via electrospinning.\textsuperscript{191} Furthermore if anisotropic nanoparticles like GNRs are used, it provides
another parameter to control the selectivity of photothermal heating. Using a light source at the particular wavelength (LSPR), in conjunction with a polarizer; for a sample containing aligned GNRs causes photothermal heating only when alignment is parallel to the polarization direction leaving other regions unaffected. Alignment of GNRs in bulk films is even easier, where shear stresses can be used. By simply stretching a thermoplastic film containing randomly oriented GNRs to an appropriate strain levels, GNRs can be aligned in the strain direction. Since the heat is generated inside out, and if the surface is relatively free of these nanoparticle heaters, it allows an otherwise thermally-degradable material to hold its shape until the function is performed. Photothermal heating using gold nanoparticles can cause melting/decomposition of polymer in close proximity to the gold, enabling focused and selective melting using a laser.

Several drug release systems inside the human body perform based on temperature, and therefore are niche application areas for photothermal heating. Using GNRs for triggered release of drug molecules, which has been shown to be reproduced over several cycles. Also since the size restriction are much smaller, a regular drug sized formulation is a feasible design. Combining the photothermal heating drug release with nanofiber mats for increased surface area, makes a system suitable for biomedical patch-type drug release applications.

**Shape memory polymers**

Shape memory materials, as the name suggests, are those that are able to return to a preprogrammed shape, after a specific stimulus. While shape memory occurs in several different classes of materials, their underlying principles could be entirely different. For this work, we would restrict to shape memory polymers (SMPs), particularly thermally-activated SMPs. In the simplest terms, a typical two stage thermally-activated SMP has two different
morphological components: soft part and hard part. These components could be two entirely different polymers, two phases of the same polymer, different crystalline structure, amorphous or crystalline phases, or even different sections of the polymer chains. Often, these structural components are large enough to be observed in the polymer microstructure. The hard component serves as the backbone of the SMP, typically with better mechanical properties (higher modulus, higher yield strength), and remains unaffected over a wider temperature range. The soft component, however, undergoes dramatic changes in the mechanical properties over a smaller range of temperature. This temperature could be the melting point of the soft phase, or the glass transition temperature of the SMP. Once heated beyond this transition temperature, the more fluid soft component allow the material to be temporarily reshaped, while the unaffected hard segments prevent it from flowing. A typical cycle of such a SMP is shown in figure 5-8.

![Figure 5-8. Typical steps in single stage one way shape memory effect (SME)](image-url)
The permanent shape is prepared by conventional polymer processing methods: solvent casting, melt processing. Further permanent shape changes are possible if the deformation and/or annealing is done close to the melting/decomposition temperature of the hard phase. Once the permanent shape is set, and the sample heated above the transition temperature, but well below decomposition temperature, any deformation will be accommodated by the soft phase. As such, the hard phase conforms but does not change its structural characteristics. Cooling the SMP well below transition temperature, under this constrained deformation, then ‘locks’ the soft segments in place, to create a temporary shape. At this low temperature (typically RT for most practical SMPs), the temporary shape will hold for a reasonably long time, after the constraints are removed. To regain the permanent shape, the SMP then has to be heated above the transition temperature. The soft phase becomes fluid again, but without any external stress are moved back into original position by the hard segments. While this is for the simplest of SMPs, two stage one-way transition, by using the more than 2 structural components, the SME can be achieved between different stages and/or in both directions.

Plasmonic nanoparticles, when incorporated in SMPs, can cause transitions from glassy to rubbery state, above $T_g$ and therefore photothermal heating has been successfully used for shape memory applications,\textsuperscript{197} which allows for remote actuations of films.\textsuperscript{198} Some SMPs are also thermally self-healing materials. Since the melting/glass transition due to photothermal heating occurs at numerous locations over the entire volume, the healed material can go back to before-fracture condition, that too within few seconds.\textsuperscript{199} For a SMP-gold nanoparticle sample deformed over a larger area, the size of the light probe for photothermal heating, dictates the recovery region. As such, it allows for controlled shape change in a pattern and order that can be controlled in situ. Also by controlling the percentage of area that is
photothermal heating and allowed to recover, it allows for virtually infinite configurations of deformed SMP.\textsuperscript{200} As with melting, polarization control of the shape recovery is also possible when GNRs are used. Simple stretching can be used to obtain good alignment, and by introducing the polarizer along/cross with the GNRs alignment direction, the photothermal heating can be triggered.\textsuperscript{201} If the polymer is amenable to both SME and thermal healing, gold nanoparticles can be used to perform both or either of those functions with good control over the location selectivity.\textsuperscript{202}

Another approach to obtaining photothermal heating selectivity is by using different sets of plasmonic nanoparticles and their corresponding light sources. While several of the methods discussed above are good candidates for selective photothermal heating for SME, using nanoparticles that respond photothermal heating to different wavelengths of light has certain advantages:

1. The nanoparticle distribution can be arbitrary; it could well defined in some sections of the sample, or there could be several patches of different nanoparticles, which could produce interesting topological effects.
2. If the SPRs of these nanoparticles sufficiently separated, the selectivity can be very precise, unlike in case of polarization selectivity.
3. The recovering shape may reorient in different directions but still can be photothermally heated.

**GNRs synthesis and processing**

GNRs were synthesized on a 1000 mL scale according to a method developed by Kozek et al.\textsuperscript{205} A schematic of the process is shown below. Succinctly, two different solutions are
prepared: a seed solution and a growth solution. The seed solution, which contains very small gold nanoparticles, is added to the growth solution, where they evolve into GNRs primarily through preferential growth caused by cetyltrimethylammonium bromide (CTAB).

**Figure 5-9.** Schematic for large scale gold nanorod synthesis

**Growth solution:** For the growth solution, the following solutions were made by dissolving the corresponding chemical in deionized water. Typically, for each of the solutions, final solution volume was maintained between 12-20 mL. The Table below shows the volumes and masses of the chemicals used for preparation of the growth solution for GNR synthesis on 1000 mL scale. For smaller volumes, the weight and volume of water was scaled by the appropriate factor e.g. for 200 mL (divide all numbers by 5)
Table 5-1. Concentrations of various solutions for GNR synthesis

<table>
<thead>
<tr>
<th>Chemical</th>
<th>MW (g/mol)</th>
<th>Weight (g)</th>
<th>Water (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>364.45</td>
<td>34.309</td>
<td>450</td>
</tr>
<tr>
<td>Note: from Amresco</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KBr (Potassium bromide)</td>
<td>119.002</td>
<td>1.12</td>
<td>10</td>
</tr>
<tr>
<td>AgNO₃ (Silver nitrate)</td>
<td>169.87</td>
<td>0.03255</td>
<td>10</td>
</tr>
<tr>
<td>HAuCl₄ (Hydro Chloroaurate)</td>
<td>411.85</td>
<td>0.3789</td>
<td>18.95</td>
</tr>
<tr>
<td>AA (ascorbic acid )</td>
<td>176.12</td>
<td>0.18565</td>
<td>15</td>
</tr>
</tbody>
</table>

1000 mL GNR synthesis: 36.3 g of CTAB was dissolved in 450 mL of deionized water in a 1000 mL solvent bottle. Complete dissolution was achieved by gently heating using a heat gun and keeping the entire solution bottle in water bath for at least 1 hr. 10 mL of KBr solution was added to the CTAB solution, followed by 10 mL of AgNO₃. Afterwards, 18.95 mL of HAuCl₄ solution as added to a 500 mL deionized water in a separate container. The resulting dilute gold precursor solution (g/mL) was slowly added to the growth solution, stirring it carefully all the time. Then 15 mL (2x7.5 mL) of ascorbic acid solution was added to the growth solution quickly and bottle was gently stirred, until the growth solution turned colorless. The bottle was then promptly transferred to water bath, to maintain at the synthesis temperature of 30 °C.

Seed solution: 0.364 g of CTAB was dissolved in 8 mL of deionized water. Complete dissolution was ensured by keeping the solution in water bath maintained at 30 °C for at least 30 minutes. The water bath also prevents the CTAB from recrystallizing at room temperature. 0.106 mL of the KBr solution (prepared earlier for the growth solution) was then added to the
seed solution and further diluted by 0.894 mL of deionized water. HAuCl₄ solution was further diluted to 20 times (0.5 in 9.5 mL of deionized water), 1 mL of this solution was then added to the seed solution. The seed solution was then transferred to water bath, to be maintained at 30 °C. NaBH₄ solution was freshly prepared by the adding ca. 0.1g of NaBH₄ to appropriate amount of deionized water (0.0378 g/mL). The solution was further diluted using ice cold water to 100 times. (1 mL in 10 mL and repeated) to give a final concentration of 0.000376 g/mL. 0.6 mL of this diluted NaBH₄ was added to the seed solution, under vigorous stirring. The solution turned dark brown immediately, indicating formation of small gold nanoparticle seeds. Stirring was stopped after 3 minutes, and the seed solution was allowed to stand for 2 more min. Then, 1.275 mL of the seed solution was added to the growth solution and gently shaken to completely disperse it. The growth solution was then allowed to stand in water bath for 60 minutes, over which the GNRs start to form and grow indicated by a growing pale pink color. Optical absorbance measurements have confirmed that the growth essentially reaches a plateau after 50 minutes, where without any further reduction, the GNRs are expected to stay at constant size.

According, to Kozek et al., at this stage the GNR growth solution (called the primary growth solution) are about 57 x 15 nm in size. But almost 80% of Au ions are still present in the solution. As such, to increase the efficiency of the process, it is required to further reduce these ions onto the existing GNRs. Therefore, a second growth step has to be performed.

Ascorbic acid solution was prepared with a concentration of 0.002773 g/mL. 35 mL of this ascorbic acid solution was loaded in a syringe pump. 30 mL of the solution was then injected into the FG slowly and continuously, by using a syringe pump. The rate was adjusted such that the injection took place over a time of 173 minutes. For synthesis on different volume
scale, the volume and the rate of AA addition was decreased by the same factor, such that the total time of addition is still 173 minutes. The growth solution was gently stirred during this addition. During this injection, the growth solution gradually turned dark red, and as Kozek et al. determined, all of the Au ions have been reduced at this point. The GNRs in this second growth solution (SGS) after completing the reaction typically measure 80 x 22 nm and have an LSPR near 800 nm.

The SGS cannot be used directly for composite preparation since:

a. It is an aqueous solution, while many polymers are soluble in organic solvents.

b. It contains a large amount of excess CTAB.

c. The concentration is too low.

Therefore, further processing is necessary. To remove the excess CTAB, the SGS (ca 1030 mL) was divided into centrifuge tubes of 60 mL volume each. 6 of these tubes were put in a high speed centrifuge, spinning at 12000 rpm for 12 minutes at 30 °C sample temperature. After the centrifugation, GNRs were deposited on the side walls of the tube. The supernatant was carefully decanted, and the GNR concentrated solution was collected. The process was repeated was each of the 6 tubes, and for the entire volume of SGS. The concentrated GNR solution (typically 70-100 mL) was then pooled together and centrifuged for a second time with the same parameters. After decanting the supernatant, a high concentration GNR solution was obtained. Typical concentrations achieved at this stage are between 3-10 mg/mL of processes GNRs.

The thermoplastic polyurethane (TPU) shape memory polymer used for the experiments is soluble in tetrahydrofuran (THF). To disperse GNRs in THF, another step for ligand exchange was performed. PEG is suitable for stabilizing GNRs, as it is soluble in water and a number of
other organic solvents, including THF. A small portion of the processed GNR solution was then PEGylated as follows: an excess of PEG-2000 was added to GNRs present in the processed solution. The mixture was then stirred for 24 hours. During this process, the PEG slowly displaces CTAB as the capping agent (ligand). After 24 hours, the solution was centrifuged at 10000 rpm (g) for 5 minutes, and the excess water was decanted. The sedimented GNRs are collected in form of pellet near the bottom. The GNRs are then redispersed in THF, with same volume of water as before, and re-centrifuged with same parameters. After decanting, the GNRs are redispersed in measured amount of THF, to get a desired concentration (0.5-5 mg/mL) of PEGylated GNR in THF solution (PEG-GNR-THF solution).

**LED setup:** For the photothermal experiments, an LED was used instead of the laser, as is more common. While there are certain advantages/disadvantages for each one of them, the main reason for using the LED is that the spot size is of the order of centimeters. This allows simultaneous photothermal heating and therefore actuation of larger, practically feasible samples, which is the closer to the motivation of these studies. To that end, a commercially available infrared LED was appropriated and assembled into a flashlight (Osram Golden Dragon SFH 4750, with peak at 860 nm, FWHM of 30 nm, and power of 3500 mW). The assembled LED was also fitted with potentiometer to adjust the output power. The power spectrum of the LED provided by Osram is shown in figure 5-10. To properly evaluate the power characteristics of the LED, additional experiments were performed to measure the power spread of the LED in 3 dimensions. As expected, the axial power of the LED decreases
as the distance increases. Interestingly, the radial spread of the power is not perfectly symmetric, as shown in figure 5-11.

Figure 5-10. Relative spectral emission of the LED. Source: Osram
Figure 5-11. 3D map of the power output of the LED a. axial variation b. radial variation

An initial experiment for evaluating the photothermal heating efficiency of these concentrated GNRs in water was carried out using the LED. Approximately, 5 mL of concentrated GNR solution was put inside a glass vial and was constantly stirred, while the LED was pointing horizontally towards it. The corresponding temperature rise was monitored using a wire probe thermometer against time. As seen in figure 5-12, the solution showed a sharp increase in the temperature initially, which gradually plateaus over time. The maximum
temperature reached was close to 48 °C. Optical absorbance measurements were performed on the solution before and after the experiment. As the figure 5-12 shows, the GNRs showed a marked decrease in SPR intensity, but minimal shift in the SPR after the heating step.

**Figure 5-12.** Photothermal heating of GNRs in water **a.** Temperature rise vs time **b.** Absorbance spectra of the GNR before and after the heating experiment

Thermoplastic polyurethane Diaplex MM5520 was purchased as the shape memory polymer. The advantages are two-fold:

a. It has a transition temperature at 55 °C, which is well above room temperature, to cause any uncontrolled spontaneous or gradual shape changes.

b. It is a single component polymer that dissolves readily in THF, so the PNC solution can be prepared from same solvent.
Diaplex has three components: methylene diphenyl diisocyanate (MDI) as the hard segments; polyethylene adipate glycol as the soft segments and 1, 3-butanediol as the chain extender. Their chemical structures are shown below in figure 5-14.\textsuperscript{203,204}

\textbf{Figure 5-13.} Chemical composition of the thermoplastic polyurethanes used\textsuperscript{203,204}

Composite films are prepared by dissolving Diaplex in THF. Typically, 0.2 g of Diaplex is dissolved in 5 mL of THF and stirred for 2 hours to give a homogenous, viscous solution. For composite preparation, PEG-GNR-THF solution was diluted with THF to get the desired final concentration (0.1 – 6 wt. %). Diaplex is then added while stirring to create homogenous dispersed GNR-Diaplex solution. For ex: to prepare a 0.5 wt. % sample, 2 mL of 5 mg/mL PEG-GNR-THF solution was added to 2 mL to THF. 0.2 g of Diaplex was then added to create the final solution.
While preparing samples for photothermal heating several factors have to be considered:

a. Concentration of GNRs: Low concentrations of GNRs reduce the SPR intensity and therefore photothermal heating output. Higher concentrations of GNRs causes agglomeration which shifts and broadens the SPR peak. Several concentrations (0.1-10 wt. %) of GNR in Diaplex were prepared as films and tested. For our experiments, 0.5 wt. % was found to give the best results.

b. Thickness of the sample films: For out-of-plane deformation, thickness controls the volume of the stressed material. Also, incorporating GNRs reduces the transparency of the films, affecting the photothermal heating on the side away from the LED. While a thicker sample is practical in handling and therefore preferable, too thick of a sample will cause unequal heating, leading to undesired recovery.

Once the solution was ready, a composite film was prepared by pouring it in a PTFE mold, and letting it sit in a fume hood to evaporate the THF. The mold was covered with only a few holes to suppress any bubble trapping due to low boiling point of THF. The mold was then left overnight, and the film was easily removed from it the next day. To further remove any trace THF, which might affect the SM or the mechanical behavior, the sample was annealed afterwards. The sample was wrapped in Al foil to prevent any warping and maintain the flat shape and then placed in an oven at 120 °C for 30 min. Annealing times can vary, depending on temperature and the sample volume. For example, if a temperature of 80 °C is used, the annealing time can be as long as 6 hr.
Polarization selective photothermal heating

A special jig was designed to prepare the aligned GNR sample with two sets of moveable Al grips. Each end of the sample was clamped on one of the aluminum grips. The initial sample length, measure as the separation between the grips, was kept as 20 mm for all samples. Stretching the sample, especially to high strains, creates residual stresses in the material, which drastically affects its shape memory properties. To prevent this, stretching was performed slowly and at higher temperature, which anneals the residual stresses. The entire assembly (jig and the samples) was placed inside the oven at 120 °C and allowed to heat for 10 minutes. Afterwards, the jig separation was increased by 10 mm every 2 minutes resulting in a strain rate of 5 mm/min. Typically, strains were between 300-400% with final sample length as 80-100 mm. After the desired strain was achieved, the sample was left for additional 2 min in the oven, and then kept at RT for 30 minutes. This resulted in a permanent stretched, annealed sample, which was used for photothermal heating experiments. The shear forces produced during this stretching have been shown to align the GNRs incorporated within the polymer matrix along the stretching direction. If the incident light (at the LSPR wavelength) is polarized, it will interact with the GNR length (or diameter) according to its component in that direction. This gives maximum absorbance when the polarized light is parallel to alignment direction, and conversely is minimum when it is perpendicular (ideally 0). This is the basis for polarization-selective photothermal heating. Our goal was to use this for selective shape recovery in SMP-PNCs.

For these studies, the permanent shape (as prepared or stretched) was rolled into the temporary cylindrical shape using aluminum foil as a constraint, it was left in oven at 80 °C for 4 min. and then at RT for 6 min to fix the temporary shape. If the sample is now heated by
conventional heating (water bath or oven) to the temperature 55 ºC or higher, it reverted to its original film shape. The sample was rolled in two different directions, lengthwise and breadthwise. Following the concept mentioned above, if the incident light is polarized parallel to one of the rolling directions (and therefore perpendicular to the other), that particular cylinder should heat up and reverts back to a flat film. Moreover, if these cylinders were nested inside each other (like Russian dolls), the inner one could not be opened unless the outer one opens first, dictating a correct combination of polarization direction to be used to “unlock” the system.

A polarizer selected was obtained from Thorlabs with an extinction ratio of 1000:1 in 600-950 nm. The polarizer was positioned just below the LED, and the sample stage was at a fixed distance. For initial experiments, each rolled cylinder was placed on the stage in the same direction, while the polarizer was rotated by 90°. The observations are shown in figure 5-15. While at this point the results have not been reproducible, this issue may be resolved in the future by inserting filters to better ensure selective heating can be conducted.
Figure 5-14. Selective heating using polarized light of a stretch annealed GNR/Diaplex sample a. parallel case: heating causes shape recovery b. perpendicular case: no heating occurs

**Wavelength-selective photothermal heating**

Another approach to selective heating is using particles with different SPR wavelengths. The SPR results in remarkably high absorbance over specific wavelength ranges, and since these ranges depend on the size and shape of the particle, it is possible to employ them for selective high absorption leading to selective heating. For our experiments, we selected GNRs with SPR peak around 800 nm and gold nanospheres (GNSs) with SPR peak around 525 nm, as the two heating nanoparticles.
Gold nanoparticle synthesis: 15 nm gold nanoparticles were synthesized according to method by Osterloh and coworkers.\textsuperscript{206} 50 mg of the gold precursor was added to a mixture of 0.6 mL of toluene and 0.5 mL of oleylamine, to prepare the gold precursor solution. Separately, 24 mL of toluene and 1.6 mL of oleylamine were mixed and heated to 110 °C at room temperature. Once boiling started, evident by vapors of toluene condensing in the container, the gold precursor solution was quickly injected. The solution changes from bright orange to colorless within few seconds. The solution was held at this temperature for 2 hours, after which it appears dark wine red, indicating formation of gold nanoparticles. An excess (about 1.5X) of methanol was added to an aliquot of the solution and centrifuged at 4500 rpm for 120 s. The sedimented nanoparticles were redissolved in THF for future use. TEM samples were prepared from these solutions, and the average size was found to be 15 nm.

\textbf{Figure 5-15.} Normalized absorbances SPR for GNRs and GNSs
The SMP-PNC film was prepared by solvent casting similar to before. Several different concentrations of gold nanoparticles were tested for heating. Diaplex was dissolved into THF first, and then the correct amount of gold nanoparticles-THF solution was added to it. The mixture was vortexed for homogenous distribution and then immediately cast into the PTFE mold. Covering the mold prevents formation of bubbles in the film but takes much longer to dry. This increases the possibility of aggregation, and associated SPR shift and broadening. To achieve a balance between the two, the mold was left uncovered in the fume hood, but a smaller amount of THF was used for the sample preparation (total solvent volume 3.5 mL). Once dried, the sample was annealed as before (30 min at 120°C).

For photothermal heating with GNSs, a green LED was provided by Prof. Michael Dickey’s lab, with high power output in the range of 510-530 nm. For these experiments, identical pieces of GNR-TPU and GNS-TPU were cut from the films with dimensions: 10 mm x 5 mm. These pieces were folded in half at RT, and pinched to create a stressed crease. This is the temporary shape.

To test for wavelength selectivity in photothermal heating, 20 x 10 mm samples were prepared from the GNSs composite films and folded at RT into a temporary zigzag shape. The sample was then positioned on a stage. First the 850 nm LED was positioned at a distance of 30 mm above the stage. After exposure time of 4 minutes, negligible change in shape is observed, indicating no heating. But when a 530 nm LED is used instead, the sample unfolds within few seconds. This selectivity was verified with different concentrations: 0.5, 1, and 3 wt. % of GNSs.
To further test LED and nanoparticle selectivity, the two samples were positioned on the stage next to each other. First the 860 nm LED was positioned above the stage at distance of 60 mm. As shown in figure 5-17, only the GNR sample unfolds and flattens down, indicating
selective heating. When the same experiments are repeated with 530 nm LED at a distance of 30 mm (relative distances for the two LEDs to achieve same power at sample height), the GNS sample heats faster and unfolds. It is important to note that 530 nm still absorbed by the GNR sample where TSPR is within that range which leads to some heating. However, by controlling that relative concentrations of GNRs and GNSs, it is possible to cause higher and faster heating in GNS, whereas the GNRs unfolding occurs over an order large time scale or to a lesser extent.

It should also be noted that as the samples unfold, they move further away from the LED, which leads to decreased heating. Therefore, in their initial position both samples receive the maximum power, which confirms the selectivity. If the experiments were to be performed in the opposite direction, flat to folded, then the initial selective power would be small, and any further selectivity would be aided by the sample moving towards higher power zone and therefore subjected to more heating.

Figure 5-17. Wavelength selective photothermal heating GNS/Diaplex. Samples do not heat under 860 nm light (center column) but heat and recover shape under 530 nm light (right column).
The following set of experiments were performed to show the exclusivity for both sets of plasmonic nanoparticles: i.e. shape recovery occurs only when the 860 nm light is shining on the GNR-Diaplex sample and 530 nm light is shining on the GNS-Diaplex sample, and not the other way around. Samples were prepared according to the method presented earlier, with each sample containing 0.5 wt. % of plasmonic NPs in Diaplex. Figure 5-18 shows the absorbance spectra of these samples.

Each sample was folded into a temporary shape (according to method mentioned previously) and placed on a single long stage, as shown in figure 5-19. Each sample has one of the two LEDs pointing downwards from top at a fixed distance. In first case (left panel in figure 5-19), when the correct combination of light and particles (GNR-Diaplex with 860 nm; and GNS-Diaplex with 530 nm light) is used, for both the samples, the folded sample heats up and recovers its permanent flat shape. While the GNR-Diaplex sample responded and recovered in few seconds, the GNS-Diaplex sample required 2 minutes to become flat. In the

Figure 5-18. Absorption spectra of Diaplex-GNR and Diaplex-GNS samples with 0.5 wt. % concentration
second case (right panel), the folded structures were exposed to the incorrect light for 2 minutes. As is evident from figure 5-19, very little shape recovery and consequently little heating occurs. To further improve the response time for recovery, particularly for GNS-Diaplex samples, another sample with a higher GNS loading (3 wt. %) was prepared. The absorbance is shown in figure 5-20.

Figure 5-19. Shape recovery for correct combination of light (860 nm: GNRs and 530 nm: GNSs) and no recovery for the other case

Figure 5-20. Absorption spectra of 0.5 wt. % Diaplex-GNR and 3 wt. % Diaplex-GNS samples
The next set of experiments were designed to show selectivity in shape memory response when both sets of samples were present. GNR-Diaplex and GNS-Diaplex samples were folded into temporary shapes and placed centered together on a stage. LEDs were mounted vertically on top of the stage, pointing down on the samples (Figure 5-21). The distance of the 530 nm and 860 nm LEDs were 41 mm and 45 mm respectively from the stage. As shown in figure 5-21, only the GNS-Diaplex sample heats and recovers back to the flat shape, when the 530 nm LED is used, while the GNR sample remains unchanged. The reverse happens when 860 nm LED is used: the GNR sample recovers to a flat shape while GNS sample remains folded. In each case, recovery occurs in few seconds. This experiment successfully showed the proof of concept for wavelength selective photothermal heating.
Additional experiments

Effect of various factors on the shape, size and LSPR of GNRS:

1. Seed making process: Dilution of NaBH₄ to prepare the seed solution is the critical step. On addition to the seed solution, NaBH₄ turns it into a dark brown color. Subtle differences in the preparation method or the waiting time before addition, causes changes in the seed. This is observed in the seed spectra as well, as shown in figure 5-19. If the diluted solution is allowed to sit for 10 minutes, before adding to the seed solution the LSPR for the first growth is at a lower wavelength.

![Graph showing absorbance analysis of different seeds](image)

**Figure 5-22.** Absorbance analysis of different seeds synthesized for GNRs

2. Volume of the seed added: The seed controls the initial number of gold nanoparticles that eventually grow into the GNRs when added to the growth solution. As such, by
changing the volume of seed solution (and therefore the number of seeds), the number of GNRs grown can be controlled. Since the amount of precursor is fixed for the growth solution, the GNRs can be bigger/smaller depending whether the seed solution was less/more than the standard procedure. Figure 5-21 shows the effect on the GNR shape and the LSPR on addition of 0.17x of the standard seed volume. As expected, fewer seeds grow into larger GNRs with smaller aspect ratio, with a corresponding decrease in LSPR.

Figure 5-19. Effect of different volumes of seed addition on the SPR of the GNRs first growth
Figure 5.23. GNRs synthesized by using 0.17x of standard seed volume.
3. Rate of addition of AA during second growth: Anisotropic growth of the GNRS occur because CTAB causes the reduced Au to preferentially deposit at the ends. If however, the rate of addition of AA (also the rate of reduction of Au) is slowed down, the LSPR shifts to the left indicating rods with lower aspect ratio, as shown in figure 5-22 and 5-23.

Figure 5-24. Effect of AA addition rate on the LSPR
Figure 5-25. GNRs with different AA addition rate during second growth.
4. PEGylation: Figure 5-26 shows the effect of PEGylation on the LSPR. After the centrifugation steps in PEGylation a red shift is observed in the LSPR peak. Usually this shift is small, of the order of 10-15 nm.

![Figure 5-26: Effect of PEGylation on LSPR of GNR](image-url)
5. Annealing the Diaplex sample shifts the LSPR to higher wavelengths. This could be an effect of the GNR reshaping that may occur at these temperatures. The LED output wavelength was chosen to have maximum overlap between the power and the absorption spectra, and therefore the photothermal heating.

![Figure 5-27. Effect of annealing on the absorbance spectrum of the GNR/Diaplex films](image-url)
Anisotropicity of stretch annealed Diaplex films: Samples were prepared and stretched by the standard protocol. The concentrations, final strain values and absorbance values of the samples are in Table 5-1. Polarization absorption measurements were performed on each of these samples using a polarizer in the spectrometer. The polarizer was mounted on an optical stage between the light source and the sample. For these experiments, the sample was fixed, while the polarizer was rotated between parallel and perpendicular to stretching (and therefore the GNR alignment) directions. The results are shown in figure 5-25.

![Graph showing absorbance measurements](image)

**Figure 5-28.** Absorbance measurements of Diaplex films with different strains and concentrations for parallel and perpendicular orientation of GNRs to polarized light.
As evident from the measurements, the LSPR absorbance was much higher when the light was polarized parallel to the GNR alignment, as compared to perpendicular. Absorbance values were used to calculate the alignment order parameter, according to the formula:

\[
OP = \left( \frac{A_{\parallel}}{A_{\perp}} - 1 \right) \left( \frac{A_{\parallel}}{A_{\perp}} + 1 \right)
\]

As observed from the absorbance data, that higher strains lead to better alignment (indicated by the higher value of order parameter). The effect is more prominent at higher concentrations though the relative absorbances do not scale linearly.
6. Electrospinning

Electrospinning or electrostatic spinning is a simple technique that utilizes large electrostatic forces to produce fibers. Typically, high voltages (about 3–30 kV)\textsuperscript{207} are used to electrically charge the polymer solution and ultra-fine fibers can be produced with diameters ranging from a few nanometers to larger than 5 μm.\textsuperscript{208} Figure 6-1 shows a schematic illustration of the basic electrospinning setup, which essentially consists of a pipette or a syringe filled with polymer solution, a high voltage source and a grounded conductive collector screen. In addition, a metering syringe pump can be used to control the flow rate of the polymer solution. The needle of the syringe also serves as an electrode to electrically charge the polymer solution and the counter-electrode is connected to the conductive collector screen.

![Diagram of electrospinning setup](image)

**Figure 6-1.** Schematic of an electrospinning setup

A schematic of the electrospinning process is shown in Figure 6-2. Under the influence of a strong electrostatic field, charges are induced in the solution and the charged polymer is accelerated towards the grounded metal collector. At low electrostatic field strength, the
pendant drop emerging from the tip of the pipette is prevented from dripping due to the surface tension of the solution. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone (the base region) and the induced charges on the liquid surface repel each other and create shear stresses. These repulsive forces act in a direction opposite to the surface tension, which results in the extension of the pendant drop into a conical shape and serves as an initiating surface. A critical value is attained when the repulsive electrostatic force overcomes the surface tension and a charged jet of fluid is ejected from the tip of the Taylor cone.

**Figure 6-2. Formation of Taylor’s cone**

The jet undergoes a transition from pressure-driven flow to electrically-driven flow. The change of shape of the Taylor cone from convex to concave is in accord with changes in charge density as the field strength is varied. Taylor studied the electric field used in electrospinning process and identified a critical or threshold voltage at which electrostatic repulsion overcomes the surface tension as:
where $V_c$ is the critical voltage, $H$, the distance between the tip-target, $L$, the length of the capillary, $R$, the radius of the capillary (inner diameter of the needle), and $\gamma$ is the surface tension of the polymeric solution. Balancing the capillary and Maxwell stresses, it is possible to obtain an estimate of the critical voltage $V_c$ which must be exceeded before a jet can emanate from the meniscus tip:

$$V_c = \frac{4H^2}{L^2} \ln\left(\frac{L}{R-3}\right) / (0.117\pi\gamma R)$$

Typically, $\gamma \sim 10^{-2} \text{ kg/s}^2$, $d \sim 10^{-2} \text{ m}$, $\varepsilon \sim 10^{-10} \text{ (J/m)}^{-1}$ and $R \sim 10^{-4} \text{ m}$, thus suggesting that extremely large voltages on the order of 10 kV are required to form a jet from the meniscus.\(^{209}\) The discharged jet diameter decreases in size with concomitant increase in length before being deposited on the collector.

**Instabilities**

This process can be explained by the three types of physical instabilities experienced by the jet. These instabilities influence the size and geometry of the deposited fibers. The first instability, also known as the Rayleigh instability is axisymmetric and occurs when the strength of electric field is low or when the viscosity of the solution is below the optimum value. Use of very low viscosity solutions causes jet break-up and leads to the bead-on-fiber morphology. Beading is attributed to the poor chain entanglement density in the solution and insufficient resistance to the electrostatic field. The Rayleigh instability is suppressed at high electric fields (high charge densities) or when using higher concentrations of polymer in the solution.
Following the initial straight path of the jet, which is controlled by the Rayleigh instability, the polymer jet is influenced by two other instabilities: the bending and whipping instabilities. These instabilities arise owing to the charge-charge repulsion between the excess charges present in the jet which encourages the thinning and elongation of the jet. At high electric forces, the jet is dominated by bending (axisymmetric) and whipping instability (non-axisymmetric), causing the jet to travel in an “inverse cone” manner. It produces wave or dumb-bell shaped patterns in the jet. At higher electric fields and at sufficient charge density in the jet, the axisymmetric (i.e., Rayleigh and bending) instabilities are suppressed and the non-axisymmetric instability is enhanced. The whipping instability produces a bending force on the jet, resulting in a high degree of elongation of the jet. During this process, the solvent evaporates and finally leads to the deposition of ultra-fine fibers on the conductive ground electrode.

Splaying occurs in a region in which the radial forces from the electrical charges carried by the jet, become larger than the cohesive forces within the jet, and the single jet divides into many charged jets (with approximately equal diameters and charge per unit length) before fibers ‘landing’ on the collector (the collection region). Splaying is thought to be one of the phenomena responsible for the unusually small diameter fibers which can be produced by electrospinning.\textsuperscript{210}

Process parameters

Deitzel et al. have systematically evaluated the effects of two important process parameters: spinning voltage and solution concentration, on the morphology of the fibers formed. They also investigated beading and found that the spinning voltage influences mainly the formation of beads while the polymer concentration has effect on the fiber size.\textsuperscript{211} Spinning
voltage was strongly correlated with the formation of bead defects in the fibers, and their measurements could be used to signal the onset of the processing voltage at which the bead defect density increases substantially. Solution concentration has major impact on the fiber size, with fiber diameter increasing with increasing solution concentration according to a power law relationship. In addition, electrospinning from solutions of high concentration has been found to produce a bimodal distribution of fiber sizes. The higher the solution viscosity, the fewer beads are formed. As long as no splitting is involved, one of the most significant parameters influencing the fiber diameter is the solution viscosity. A higher viscosity results in a larger fiber diameter. Wilkes has studied the effect of solution concentration, capillary–screen distance, electric potential at the tip and flow rate on electrospinning Esthane 5720 (a segmented polyetherurethane supplied by Goodrich). It was found that bead-like structure appeared when the tip-collector distance (TCD) decreased, while the average fiber diameter was increased. When increasing the concentration, the average diameter raised and the bead-like structure turned into blobs at lower capillary–screen distance. A too high concentration leaded to failure of the fibers instead of being drawn, as the viscosity was too high. This can also be caused by a too high flow rate at lower concentration. Finally, increasing the potential decreased the fiber diameter. Higher flow rates can lead to a faster removal of the ions at the orifice side of the polymer bath. However, this effect seems to be rather insignificant.

**Characteristics of fibers**

Typically, in most semi-crystalline polymers, the fibers produced by electrospinning display structural hierarchy. During the fiber formation process, a fraction of the chains crystallizes to form lamellae consisting of small crystals and the remaining fraction forms the amorphous phase. The lamellar structures determine the crystallinity of the fibers. In between
the stacks of lamellae are the relaxed amorphous tie molecules. Due to the shear forces
experienced by the jet during electrospinning, the lamellae orient along the fiber axis.\textsuperscript{213–215}
The process of electrospinning alters the intrinsic structural properties of the material. The
orientation extent can be quantified by using X-ray diffraction analysis on the samples.
Alternatively, the draw ratio can be used to obtain an estimate of the molecular orientation. It
quantifies the amount of extension the jet experiences during the electrospinning process. The
draw ratio for spun fibers can be calculated as the ratio of the spinning velocity of the collected
fiber to ejection velocity of the polymer solution from the pipette. High draw ratios experienced
by the jet are capable of aligning the macromolecular chains along the fiber axis, thereby
influencing the formation and structure of the crystallites.

The diameters of electrospun polymeric fibers are typically between 50 nm and 10
microns. Deitzel et al.\textsuperscript{211} have reported that the fiber morphology is strongly dependent on the
various physicochemical parameters (solution viscosity, surface tension, concentration and
dielectric permittivity) and the electric field. Changes in these parameters give rise to different
spray modes or instabilities, hence different final fiber morphologies.

**Electrospraying**

Electrospraying, or electrohydrodynamic atomization, makes use of same principle as
electrospinning. A minimum solution concentration is required for electrospinning, below
which electrospraying occurs. This transition from electrospinning to electrospraying can be
explained on the basis of chain entanglement density. Studies have been made to associate
electrospraybility with the molecular weight, entanglement number and the concentration of
various polymer/solvent systems.\textsuperscript{216} As in electrospinning, electrospraying consists of a
syringe needle, which is connected to high voltage of the order of few kVs and a grounded
collector or vice versa. The charged liquid that is forced through the needle is acted upon by electrical forces and broken down into a number of droplets. The size of these droplets may vary from few micrometers down to few nanometers with a narrow size distribution. The size of the droplets can be controlled by parameters like flow rate of the solution, applied voltage, viscosity, needle orifice size. This coupled with the high deposition efficiency, low tendency for agglomeration and the control on the direction of deposition associated with electrospraying makes it an important process in field of nanotechnology, especially device fabrication. The importance of electrospraying in formation of polymeric microspheres has been demonstrated in a recent study. 217

**Merits**

Electrospinning, has emerged as a versatile technique for production of polymer nanofibers, and consequently found applications in numerous fields like filtration,218 drug delivery,219,220 tissue engineering,221–223 sensors,224–229 and energy generation.230,231 An advantage of the electrospinning process is the fine control over the fiber diameter that can be achieved by tuning its process parameters like applied voltage, tip-to-collector distance (TCD), solution flow rate needle diameter, and the solution parameters like polymer concentration and viscosity.232 Some of these unique features cannot be otherwise achieved by conventional fiber processing techniques. Another merit is that under the influence of an electric field, electrospinning self-assembles dispersed fillers along the axial direction such that composites can be formed by imposing additional spatial confinement to the polymer chains. These reinforced fibers display superior properties and function as basic building blocks for the fabrication of high strength structures using a bottom-up approach. For example, carbon nanotubes (CNTs) and carbon black (CB) particles are among the commonly used fillers which
are dispersed within the fibers to mimic the functionality of silk fibers for high strength and toughness applications. Tailoring different assemblies of non-woven fibers viz. random or aligned is also possible by using various configurations of the electrospinning setup.\textsuperscript{233}

\textbf{Figure 6-3.} Electrospinning setup design and fabrication
Figure 6-4. Electrospinning of different materials
Collaborations:

Electrospinning is a very effective technique for incorporating particles in fibers. As collaborative efforts, we have electrospun fibers containing particles made by other research scientists in an effort to integrate the high surface area properties of nanofibers with the intrinsic properties of these particles.

i. Prof. Benjamin Wiley, Duke University

Nanowires of silver and copper were obtained from Prof. Wiley’s group. PEO was added to stirring dispersion of the nanowires in water, such that the final PEO concentration was 5% w/v of water, with Ag and Cu nanowires about 7.92 and 3.33 wt. % respectively with respect to PEO. Electrospinning was carried out with the following parameter: Voltage: 12kV, TCD: 15 cm; Flow rate: 5 μl/min. Nanowires were found to be partially enclosed in the PEO fibers, with some nanowires breaking out.
Figure 6-6. Electrospinning of Ag nanowires in PEO
Figure 6-7. Electrospinning of Cu nanowires in PEO

ii. Prof. Benjamin Martin, Texas State University

Nanoplateletes of Zirconia (ZrO$_2$), and zeolite in 3 different morphologies were provided by Daniel in Prof. Martin’s research group. These platelets have a very high surface energy and therefore, tend to stack together as shown in figure 11. Since the particles were dispersed in water, PEO was chosen to be the carrier polymer for electrospinning. PEO was added to stirring dispersion of these platelets in water, such that the final PEO concentration was 6% w/v. Electrospinning was carried out with the following parameter: Voltage: 10kV, TCD: 12 cm: Flow rate: 10 µL/min. The platelets dispersed well within the PEO fibers, and were also
separated into single platelets on many occasion. Figure 6-5 shows the SEM and TEM images of these hybrid structures.

![Figure 6-5. SEM and TEM images of ZrO₂ hybrid structures.](image)

**Figure 6-8.** Electrospinning of ZrO₂ nanoplatelets

### iii. Prof. Christopher Rhodes, Texas State University

We also attempted dispersing nanoplatelets of Vanadium pentoxide in PEO synthesized by the Prof. Rhodes’ and group in order to disperse them evenly over the substrate and observe the changes in the properties. However, the V₂O₅ aggregated aggressively even at very low concentrations in the PEO solutions. PEO was added to stirring dispersion of these platelets in water, such that the final PEO concentration was 6% w/v. Electrospinning was carried out
with the following parameters: voltage: 10kV, TCD: 12 cm: Flow rate: 10 µL/min. The aggregation of platelets in the solution before electrospinning, led to clear clumping of these particles within the fibers. This led to significant difficulty in continuous electrospinning.
7. References


<http://www.nature.com.prox.lib.ncsu.edu/nature/journal/v126/n3173/abs/126274a0.html>


36. Chiang, Y.-L. et al. Mechanically tunable surface plasmon resonance based on gold
nanoparticles and elastic membrane polydimethylsiloxane composite. *Applied Physics

37. Liu, S.-D. & Cheng, M.-T. Linear plasmon ruler with tunable measurement range and

38. Sönnichsen, C., Reinhard, B. M., Liphardt, J. & Alivisatos, A. P. A molecular ruler
based on plasmon coupling of single gold and silver nanoparticles. *Nature

metal nanoparticle. in *2010 IEEE 23rd International Conference on Micro Electro

40. Haes, A. J. & Van Duyne, R. P. A Nanoscale Optical Biosensor: Sensitivity and
Selectivity of an Approach Based on the Localized Surface Plasmon Resonance
(2002).


42. Lee, J.-H. et al. Artificially engineered magnetic nanoparticles for ultra-sensitive

43. Liong, M. et al. Multifunctional Inorganic Nanoparticles for Imaging, Targeting, and


212. Wilkes, G. electrospinning. *electrospinning* at

<http://www.che.vt.edu/Faculty/Wilkes/GLW/electrospinning/electrspinning.html>

213. Tashiro, K., Kotaki, M., Chirachanchai, S. & Kongkhlang, T. Electrospinning as a new technique to control the crystal morphology and molecular orientation of polyoxymethylene nanofibers. *Journal of the American Chemical Society* **130**, 15460–15466


224. Wang, X. et al. Electrospun Nanofibrous Membranes for Highly Sensitive Optical

225. Wang, X. et al. Electrostatic Assembly of Conjugated Polymer Thin Layers on


227. Aussawasathien, D., Sahasithiwat, S. & Menbangpung, L. Electrospun camphorsulfonic
acid doped poly(o-toluidine)-polystyrene composite fibers: Chemical vapor sensing.


229. Zampetti, E. et al. Biomimetic sensing layer based on electrospun conductive polymer

230. Choi, S. W., Jo, S. M., Lee, W. S. & Kim, Y. -R. An Electrospun Poly(vinylidene


232. Theron, S. A., Zussman, E. & Yarin, A. L. Experimental investigation of the governing

233. Teo, W. E. & Ramakrishna, S. A review on electrospinning design and nanofibre