Nanocomposites

Based on “Take-Home Nanochemistry: Fabrication of Gold- or Silver-Containing Cling Film, Campbell, D. et al.

This lab will go over three weeks. Experimental Part A will be done during the Ferrofluids lab, Experimental Part B during the ZnO lab and Part C during the Gold Nanolayer lab.

The purpose of this laboratory experiment is to introduce aspects of nanocomposites using a polymer matrix and developing gold nano-reinforcement in situ within the polymer. There are essentially two ways to incorporate metal nanoparticles into a polymer matrix, in situ; where the metal nanoparticles are formed in the matrix and ex situ; where metal nanoparticles are added to the polymer. Both have advantages/disadvantages and will be discussed in lectures later in the semester.

The matrix material, polydimethylsiloxane (PDMS) can be produced as a colourless, transparent elastomer that is used for a variety of applications, such as encapsulation of electronic components to protect them from moisture and dirt.

When the liquid kit components are mixed together (Fig 1) silicon–hydrogen bonds attached to PDMS oligomers (species 2) oxidatively add to a platinum catalyst (possibly Karstedt’s catalyst formed by the reaction of chloroplatinic acid, H₂PtCl₆, and divinyltetramethyldisiloxane). The carbon-carbon double bonds, attached to short polymer chains (Species 1), react with the silicon-hydrogen single bonds attached to other short polymer chains (Species 2). Vinyl groups attached to PDMS oligomers (species 1) insert into the platinum–hydride bond and then the alkyl and silyl groups reductively eliminate to produce –Si–CH₂–CH₂–Si– cross-links within the PDMS.

After the cross-linking is essentially complete, however, some of the leftover silicon–hydrogen bonds can still reduce some metal-containing ions, such as tetrachloroaurate- (III), tetrachloropalladate(II), tetrachloroplatinate(II), and silver(I), that are carried into the elastomer by organic solvents. The metallic particles produced by this reduction reaction are embedded within the polymer matrix, which restricts particle aggregation. The PDMS is transparent to visible light wavelengths, so the colours of the nanoparticles can be examined both by the eye and by visible light spectroscopy.

Fig. 1. Hydrosilylation Cross-Linking Reaction of PDMS
Experimental Part A Casting a thick sheet of polydimethylsiloxane (PDMS)

1) Obtain a plastic Petri dish from your lab instructor. This dish will be a mould for making a disk-shaped PDMS window cling.

2) You can use dry-erase markers to write a message or picture onto the bottom interior of the dish. Use some mark to identify your group but do not cover the whole surface as we need to do UV-VIS on the sample later on.

 NOTE: Any written markings that transfer from the dish to the PDMS will be reversed (a mirror image).

3) Weigh 3.0 g (no more than 4.0 g) of PDMS base into a plastic weigh boat. Use a disposable plastic pipette with the tip cut away to dispense the viscous liquid. Clean up any spills with paper towels immediately.

4) Weigh 0.3 g (no more than 0.4 g) of PDMS curing agent into the same plastic weigh boat. Use a different disposable plastic pipette with the tip NOT cut away to dispense this less-viscous liquid. Clean up any spills with paper towels immediately. DO NOT place the pipet back into the curing agent, you will need it for the next step.

5) Mix the PDMS precursors together thoroughly in the weigh boat using the plastic pipette from the previous step. Stir for at least 100 strokes.

6) Pour the mixed PDMS into the Petri dish so that the entire bottom of the dish is covered. Use the plastic pipette to scrape as much of the PDMS from the weigh boat into the Petri dish as possible.

7) Let the mixed polymer stand in the dish for at least 15 minutes to allow some of the trapped air bubbles to rise to the surface of the polymer. These bubbles can be popped by gently blowing on the surface of the mixed PDMS.

8) Place the Petri dish on a bench as instructed by the demonstrator. The films will be dried in a drying oven set to at least an hour and be ready for your next lab session.

Experimental Part B – Growth of gold or silver nanoparticles within the PDMS

1) Remove the cross-linked PDMS from the Petri dish without tearing the elastomer. This is best accomplished by inserting a spatula between the PDMS and the edge of the dish. Carefully move the spatula around the inside edge of the dish, the PDMS should release from the dish relatively easily. When this is accomplished, carefully use the spatula to pry the PDMS away from the bottom of the dish. The dry-erase marker markings should have been encapsulated into the elastomer. You now have a PDMS window cling!

2) Place the cross-linked PDMS into a soaking solution of 5 mM sodium tetrachloraurate(III), Na[AuCl₄], dissolved in ethyl acetate in a beaker for one hour. Place
aluminium foil over and around the beaker to minimize evaporative losses and photoreduction of the metal species in solution.

4) After an hour the PDMS will have swollen due to the absorbed ethyl acetate. In the Na[AuCl₄] solution the polymer will have taken on a pinkish-purple tint. Gently remove the PDMS sample from the soaking solution with a forceps, dip it in clean ethyl acetate to rinse it, and then place it between two sheets of aluminium foil to dry in a fume hood. Leave the PDMS in the fume hood at least overnight.

**Experimental Part C – Optical characterization of gold nanoparticles within the PDMS**

1) Place the PDMS in the light beam of the visible light spectrometer. As mentioned above, the valence electrons in each metal nanoparticle collectively absorb light (via plasmon resonance). The specific wavelengths of light that each particle absorbs depend on such factors as particle size, shape, and composition. To obtain the best spectrum from the nanoparticles in PDMS, avoid shining the beam through the ink markings at the surface of the polymer. Record the wavelength corresponding to the maximum absorbance of the nanoparticles in your sample. The absorption of light due to the gold nanoparticles should have a maximum absorbance wavelength between 500 and 600 nm.

**Questions**

1) You can estimate the average particle size from the position of the surface plasmon resonance (SPR) peak on your UV-VIS spectra. (see table and graphs in appendix) What would a very broad peak mean in reference to a very narrow peak? Was there much difference in peak position between groups? Comment

2) Write the redox reaction between the silicon-hydrogen bonds in polydimethylsiloxane and the metal compound. Which is the oxidizing agent?

3) The redox reaction within the PDMS has also been used to produce gold and silver nanoparticles from ionic species, but not nickel or iron nanoparticles from their metal ions. Would you expect PDMS to be used to produce zinc nanoparticles from zinc(II) ions? Why or why not?

4) Na[AuCl₄] and AgBF₄ dissolve readily in water. Why was ethyl acetate used as a solvent to carry these species into the PDMS instead of water?

5) What is the wavelength of the maximum absorbance of the nanoparticles? To what colour of visible light does this correspond? Estimate a size for the gold nanoparticles formed.

6) The absorption of light by the collective oscillation of the gold or silver nanoparticles is referred to as plasmon resonance. What type of bonding exists between gold or silver atoms in these particles?
APPENDIX Gold nanoparticle properties as a function of diameter.

<table>
<thead>
<tr>
<th>Diameter, nm</th>
<th>Peak SPR Wavelength, nm</th>
<th>Molar Ext $\text{M}^{-1}\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>515-520</td>
<td>$1.10 \times 10^7$</td>
</tr>
<tr>
<td>10</td>
<td>515-520</td>
<td>$1.01 \times 10^8$</td>
</tr>
<tr>
<td>20</td>
<td>524</td>
<td>$9.21 \times 10^8$</td>
</tr>
<tr>
<td>30</td>
<td>526</td>
<td>$3.36 \times 10^9$</td>
</tr>
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<td>40</td>
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</tr>
<tr>
<td>50</td>
<td>535</td>
<td>$1.72 \times 10^{10}$</td>
</tr>
<tr>
<td>60</td>
<td>540</td>
<td>$3.07 \times 10^{10}$</td>
</tr>
<tr>
<td>80</td>
<td>553</td>
<td>$7.70 \times 10^{10}$</td>
</tr>
<tr>
<td>100</td>
<td>572</td>
<td>$1.57 \times 10^{11}$</td>
</tr>
</tbody>
</table>
HAZARDS

The polymers used in these experiments are messy and can be mild irritants; wear gloves and goggles.

The steps involving volatile solvents such as ethyl acetate or tetrahydrofuran should be performed in a fume hood and away from potential ignition sources. Tetrahydrofuran has been known to form potentially explosive peroxides.

The crosslinked PDMS is chemically quite unreactive in a dry, room-temperature-type environment, but will degrade when subjected to high temperatures or highly acidic, basic, or oxidizing conditions.

SYLGARD(R) 184 SILICONE ELASTOMER BASE OSHA HAZARDOUS COMPONENTS

None present. This is not a hazardous material as defined in the OSHA Hazard Communication Standard.

Acute Effects

Eye: Direct contact may cause temporary redness and discomfort.
Skin: No significant irritation expected from a single short-term exposure.
Inhalation: No significant effects expected from a single short-term exposure.
Oral: Low ingestion hazard in normal use

ETHYL ACETATE

2 Hazards identification

- Hazard description:

- Information concerning particular hazards for human and environment:
  Repeated contact with skin may cause dermatitis due to the degreasing effect of the solvent. Vapours of the product are heavier than air and may accumulate on the ground, in the sump of pits, drains or cellars with higher concentrations. Ground level ventilation is recommended. May have a narcotizing effect after prolonged exposure (see R67) R11 Highly flammable. R36 Irritating to eyes. R66 Repeated exposure may cause skin dryness or cracking. R67 Vapours may cause drowsiness and dizziness.