Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Gold nanoparticles as photo-switchable inhibitors and promoters for rapid, on-demand curing of polydimethylsiloxane (PDMS)

R. Joseph Fortenbaugh, Benjamin J. Lear

Contents

Synthetic and Experimental Details

In situ synthesis of gold nanoparticles (AuNPs) in polydimethylsiloxane (PDMS)

We began by adding an 0.02 M aqueous solution of tetrachloroaurate (III) trihydrate ($HAuCl_4$ $3H_2O$) (Alfa Aesar, Ward Hill, MA) in a 0.15% w/v ratio to the elastomer part of PDMS (Sylgard 184, DOW Corning, Midland, MI) and stirred for five minutes. The mixture was then heated to 100°C with mixing for an additional fifteen minutes to induce formation of AuNPs and remove excess water. The elastomer/AuNP colloid has been stable (i.e. without aggregation of AuNPs) for at least 9 months and likely much longer. Figure S1 shows the possibility of adding different concentrations of AuNPs to the PDMS elastomer precursor. For all experiments reported in this communication, we used the far right mixture.

Figure S1. Image of PDMS elastomer precursor mixed with different concentrations of gold. Weight percent of gold, from left to right, are 0.04, 0.08, 0.12, and 0.15%. The 0.15% weight solution was used for all experiments reported in this paper.

PDMS and AuNP film formation

When desired, an aliquot of the PDMS elastomer/AuNP colloid is taken and added to the PDMS curing agent precursor in a 7:1 ratio and then mixed for 5 minutes. Following this, the mixture is sonicated for three minutes to remove air bubbles. The mixture is then irradiated with 8 ns pulses (20, 50, and 100 mJ per pulse) at 10 Hz for 4 minutes with vertically polarized 532 nm light from a QuantaRay 130 Nd:YAG laser.

Additional Characterization Details

The extent of crosslinking was determined with infrared (IR) spectroscopy by following the absorbance of both the vinyl stretch (1597 cm^{-1}) and Si-H stretch (2162 cm^{-1}) over time using a Perkin Elmer Spectrum 400 FT-IR/FT-NIR spectrometer with a liquid transmission cell attachment (KBr windows, 0.1mm path length).

The relative rates of curing were obtained from the loss of intensity of the Si-H band. This intensity was normalized to the loss found for a 24-hour cure. Thus, for each sample, the starting intensity is 1, and an intensity of 0 indicates the intensity expected if the polymer had cured to the same extent as a 24 hour ambient cure, arrived at using the data shown in Figure 1 of the manuscript.

Scanning transmission electron microscopy (STEM) images were captured with a Tecnai G2 20 XTWIN, and scanning electron microscopy (SEM) images were taken on an FEI Nova NanoSEM 630 FESEM with a Helix detector. Samples were sputter coated with carbon to minimize charging. Figure S2 shows STEM images of the uncured elastomer/AuNP colloid and a microtomed sample of the cured AuNP and PDMS film, respectively. The uncured mixture exhibits a variety of different shapes but with relatively consistent sizes of 42 ± 4 nm.

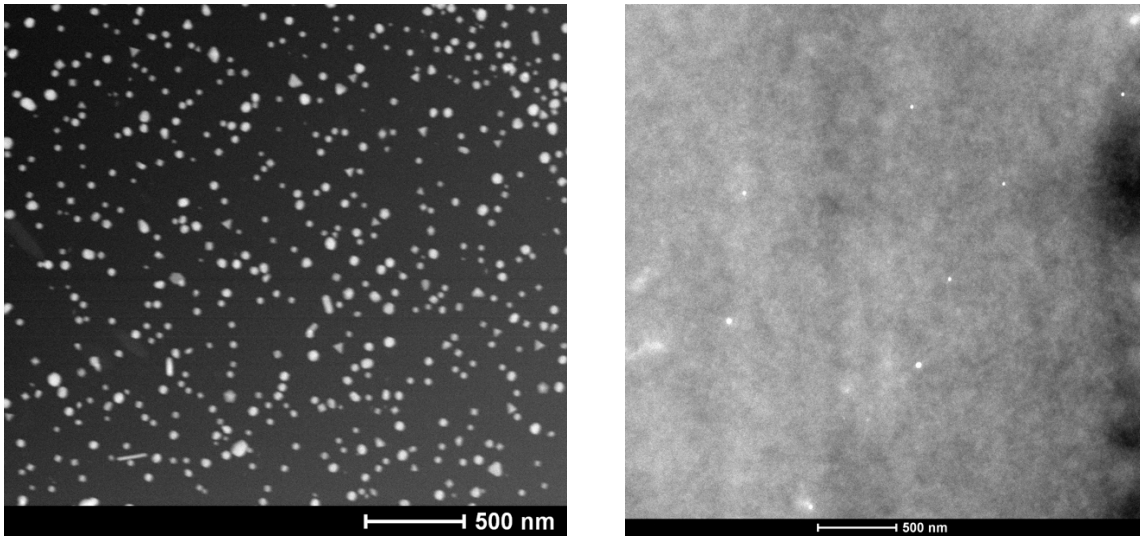

Figure S2. STEM images of uncured elastomer/AuNP colloid (left image) and cured PDMS and AuNP film (right image).

UV-Vis spectra were collected on a Hitachi U-3010 UV/Vis spectrophotometer. Figure S2 shows the UV-Vis of the cured PDMS and AuNP film. The surface plasmon of the AuNPs absorbs at 562 nm.

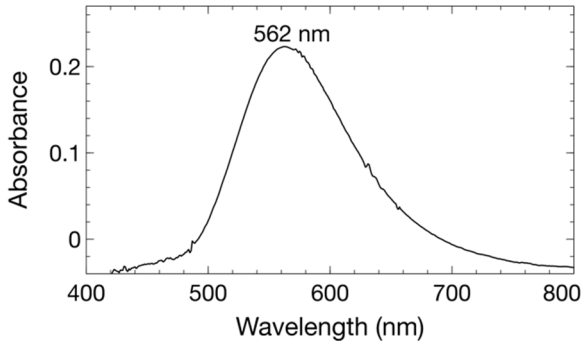

Figure S3. UV-Vis spectra of cured PDMS and AuNP film.

Using a program written by Prof. Jensen of Penn State,[1] we calculated the expected extinction coefficient, assuming all particles are spheres of the mean size, as obtained by STEM. This approximation allows us to estimate the concentration to be 8.63×10^{13} AuNPs/L. This is in good agreement with the concentration that is estimated by accounting for the mass of gold salt added to the elastomer and the mean size of the particles – which yield an estimated concentration of 1.15×10^{14} AuNPs/L.

Electrospray ionization, time-of-flight mass spectrometry (ESI-TOF MS) data was collected on a Waters Q-TOF Premier.

Bulk Temperature Measurements

Measurement of the bulk temperature changes were made using a thermal camera (Raytek TermoView Ti30). Samples of pure PDMS, or PDMS containing AuNPs, were cured in small vials under illumination, and the temperature was monitored during the curing. The maximum temperature changes (from room temperature) are recorded below (Table S1).

Table S1. The observed maximum change in temperature for pure PDMS and PDMS with AuNPs under irradiation.

AuNPs	Light /MW·cm^{-2}	ΔT_{max} /K
no	8.0	2.5
Yes	8.0	12.5

References

1. Bala Krishna Juluri, Jun Huang, Lasse Jensen [Online], version 1.3UQ; https://nanohub.org/tools/nmie/session?sess=996386 (Accessed August 2016).