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A Simple Water-Based Synthesis of Au Nanoparticle/PDMS Composites for Water Purification and Targeted Drug Release

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A Simple Water-Based Synthesis of Au Nanoparticle/PDMS Composites for Water Purification and Targeted Drug Release[a]

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AuNP/PDMS nanocomposites have been synthesized in the form of gels, foams, and films with distinctive structure and morphology. A simple in situ process in aqueous medium for the formation of such composite materials is described. The nanoparticles are held firmly within the PDMS while still being chemically accessible to substances soluble in PDMS. We demonstrate the utility of this property for water purification applications such as removing aromatic solvents and sulfur-containing contaminants from water. The contaminants can be freed from the composite with a simple thermal treatment, allowing the material to be reused. We also demonstrate chemically selective uptake and release of a fluorescent dye by the nanocomposite as a drug delivery model system.
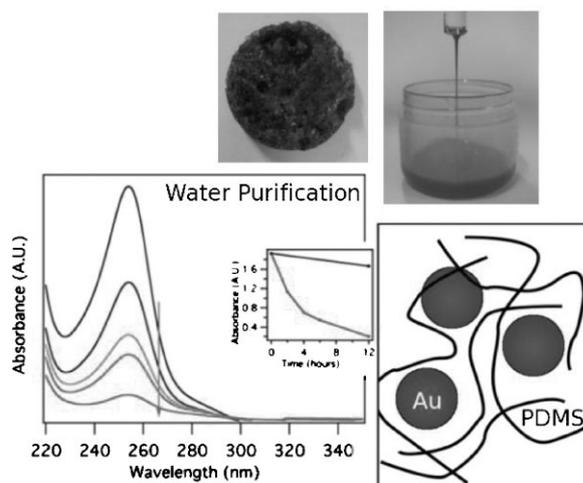
Introduction

Polymer composites with embedded metal nanoparticles are of great interest because the advantageous properties of the nanoparticles can be exploited for a wide variety of applications while the polymer matrix holds and stabilizes the nanoparticles. Using this strategy, it is possible to develop new materials with fine control over properties.[1,2] There are many reports of metal nanoparticle/polymer composites that use the unique optical properties of nanoparticles to obtain effects such as wavelength-tunable light attenuation, chemically-tunable luminescence, surface plasmon resonance, and lasing.[3–6] In addition to playing a passive, stabilizing role, polymers in many cases impart additional desirable properties to the nanocomposite. Opto-mechanical actuators and opto-thermal devices which utilize the photothermal properties of gold nanoparticles coupled with the elastic and thermal properties of polymers have been demonstrated.[3,4] Conductive nanoscale patterns have been formed using Ag/polystyrene nanocomposite as an electron beam resist and conductive microscale features have been patterned directly from metal-powder-loaded polymer.[5,6] Polymeric nanocomposite materials with novel electrical properties such as the tunable dielectric function and tunable conductivity can be engineered by the controlled inclusion of nanopar-

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ticles.[7,8] Cell adhesion and patterning, bio-electrochemical sensing, and antimicrobial materials combine specific metal nanoparticle properties with the bio-compatible nature of polymers, leading to advanced bio-functional materials.[9–11]

The choice of polymer thus plays an important role in determining the functionality of the nanocomposite. In this context, polydimethylsiloxane (PDMS) is an attractive polymeric matrix due to its many favorable properties such as chemical inertness, biocompatibility, mechanical flexibility and stability, high dielectric constant and breakdown field, optical clarity in the visible and ultraviolet region and importantly, due to ease of processing.[12] It has applications in many fields including microfluidics,[13] biomedical implants and devices,[14,15] chemical separation,[16] and microstructure fabrication.[17,18] Another important feature of PDMS is its solid solution nature and resulting high absorption ability for a range of aromatic materials.[19] The literature on Au nanoparticles is rich and abound with examples relating interesting electronic and optical properties to potential applications.[20,21] We consider it is interesting to synthesize and investigate Au-nanoparticle-incorporating PDMS (AuNP/PDMS) as nanocomposites.

During the last year, in situ synthesis of Au nanoparticles in PDMS leading to nanocomposite formation has been realized. Chen and coworkers first reported the preparation of AuNP/PDMS films where the curing agent itself acting as the reducing agent.[22] In this case, HAuCl$_4$ is reduced at the surface of cured PDMS in aqueous medium at room temperature over a period of several hours to days. Patterning of microelectrodes,[23] cell adhesion,[9] and polymer wettability[24] has been demonstrated using similar processes combined with oxygen plasma treatment. Ajayan and coworkers synthesized Au, Ag, and Pt nanoparticle/PDMS composite films by introducing the metal salt in organic solvents with the uncured PDMS and allowing the nanoparticles to reduce during curing.[25] The resulting materials show enhanced Young's modulus and exhibit antibacterial properties. In this paper, we introduce a simple, green method of preparing the nanocomposites that uses only plain water as the medium. The nanocomposite can be made in the form of a gel, foam, or a patterned flexible thin film with good control

over the particle loading. The resulting materials have been characterized using electron microscopy, optical microscopy, and UV-visible spectroscopy. We have examined its sorption ability with respect to organic solvents and sulfur containing molecules, properties important in waste water treatment.[26] The nanocomposite has also been tested for hosting and controlled release of molecules using the fluorescent dye rhodamine chloride (R6G) as a model system. The ability to selectively store and release the chosen molecules has great implications for applications such as targeted drug delivery.

Experimental Part

PDMS gel and foam were synthesized following the procedure illustrated in Figure 1a. A commercially available PDMS kit (Dow Corning, Sylgard 184), KAuCl$_4$ (Aldrich, 98%), Millipore water, and sulfur-free toluene (99%) were used in the synthesis. An uncured PDMS mixture was prepared by mixing thoroughly the prepolymer and the curing agent in a 10:1 v/v. The mixture was taken in a glass vial containing 0.02 M aqueous KAuCl$_4$ solution in a 200:1 m/v ratio and stirred below 70 °C for 2 h to form gel. At lower temperatures, the curing of the elastomer is extremely slow resulting in gel formation. The resulting gel can be cast into a mold or coated as a film and cured by exposing to vacuum (to remove air bubbles) and subsequently heating at 100 °C for 48 h or above 165 °C for 1 h. Figure 1c shows a scanning electron microscopy (SEM) image of a cured film patterned by molding using a compact disk (CD) as master. As seen from the figure, the patterned film is
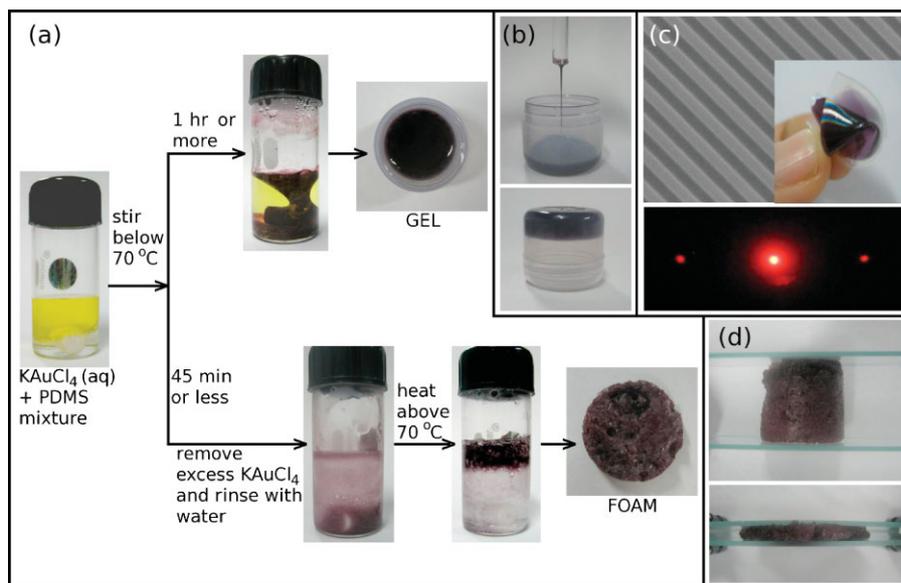

Figure 1. (a) Optical photographs illustrating the process used to synthesize AuNP/PDMS nanocomposite gel and foam. (b) Optical photographs showing viscous nature of gel (c) SEM image of a patterned AuNP/PDMS film. A photograph of the hand twisted patterned film exhibiting colors. Below is an optical diffraction pattern obtained in the transmission mode using a 633 nm diode laser. (d) Optical photograph depict a piece of cylindrical foam between glass slides, compressed using metal clips.
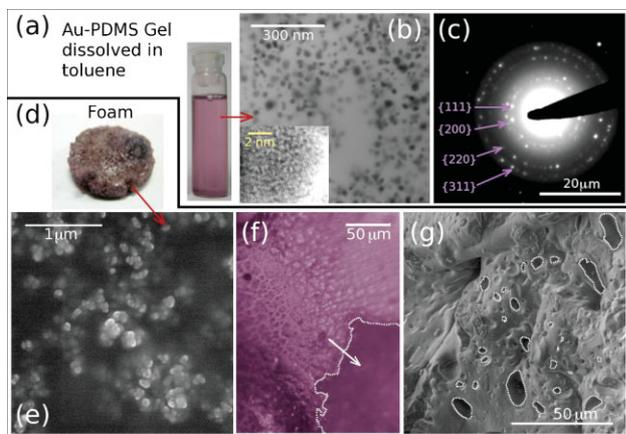
Figure 2. (a) AuNP/PDMS gel dissolved in toluene characterized using, (b) STEM and HR-TEM (inset), and (c) ED. (d) Optical photograph of the foam used, (e) SEM of a foam sample with high surface concentration of Au nanoparticles, (f) high resolution false color optical micrograph, and (g) SEM micrograph illustrating microporous nature of the foam.

optically diffracting in the transmission mode while at the same time, flexible. Foam can be synthesized using a similar process by stirring PDMS and $KAuCl_4$ (aq.) below 70 °C for up to 45 min and arresting the reaction by decanting off the unreacted $KAuCl_4$ solution and rinsing the remaining AuNP/PDMS mixture with copious amounts of water. When the mixture is further stirred and heated in plain water at temperatures above 70 °C, the elastomer cures. The AuNP/PDMS mixture in this case floats at the aqueous surface and cures into a sponge-like phase as seen from the bottom part of Figure 1a. In Figure 1d, an example is shown of highly compressible nanocomposite foam between two glass slides. Compression is achieved using metal clips to apply a nominal force.

AuNP/PDMS gels and foams were characterized using different microscopic techniques as shown in Figure 2. A solution of the gel in toluene (Figure 2a) drop-cast on a carbon-coated grid was examined using scanning transmission electron microscopy (STEM), high-resolution transmission electron microscopy (HR-TEM, Figure 2b) and electron diffraction (ED, Figure 2c). The STEM image shows that the particles are polydisperse with a size range of 5–50 nm. Lattice fringes in the HR-TEM as shown in inset in Figure 2b and the ED pattern in Figure 2c confirm the crystalline nature of the nanoparticles. The foam shown in Figure 2d was characterized using optical microscopy and SEM. We have observed that the foam contained large open pores in the size range 100 μm to 1 mm that are interconnected across the entire volume of the sample. One such pore is shown in the optical image in Figure 2f. The SEM image of the foam in

Figure 2g clearly reveals the presence of smaller pit-like structures, typically in the range, 10–100 μm all over the surface. Unlike the large open pores, these pits are essentially closed pores. Thus the foam exhibits two different microstructures which are relevant for adsorption. In addition, the embedded Au nanoparticles themselves offer another active interface.

In the case of gels, the particle loading can be controlled by varying the concentration of $KAuCl_4$ during synthesis while keeping a constant stirring time of 2 h. Higher precursor concentrations lead to more intense color of the resulting gel as clearly seen in the solutions of AuNP/PDMS in toluene shown in Figure 3a. The UV-visible spectrum from the 0.02 M preparation, exhibits a distinct peak around 534 nm due to Au surface plasmon absorption. This observation corroborates well with particle size obtained from electron microscopy (see Figure 3b and c). For lower precursor concentrations, not only the absorption peak intensity is diminishing and its position slightly is red-shifted (see Figure 3a) but also is seen a shoulder feature at ≈500 nm. This kind of modulation can be explained due to the local environment or size and shape of the nanoparticles which is known in the literature.[21] In the case of foams (Figure 3b), the visible intensity of the foam color and the measured intensity of the Au plasmon peak at 534 nm increase with increase in stirring time during synthesis.

Foams can also be realized by directly heating the PDMS and $KAuCl_4$ between 70 and 100 °C while stirring. Foams formed in this manner are found to have a non-uniform distribution of nanoparticles with an excess of Au particles at the surface because the $KAuCl_4$ continues to reduce at the surface even after the PDMS has cured to a semi-solid or solid phase. The nanoparticle
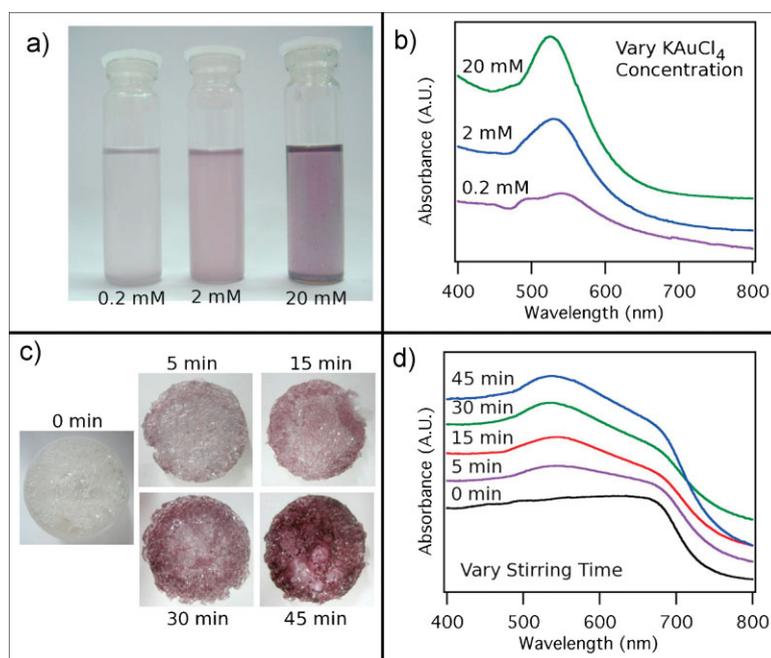

Figure 3. (a) Optical photographs of vials containing AuNP/PDMS gel solutions in toluene (10 mg · mL^{-1}) obtained with different concentrations of $KAuCl_4$ and (b) corresponding UV-visible spectra recorded in transmission mode. (c) Optical photographs of AuNP/PDMS foams formed by varying the pre-stirring time with 0.02 M $KAuCl_4$ and (d) corresponding UV-visible spectra obtained in reflectance mode. All UV-visible spectra are vertically offset for clarity.

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concentration can be controlled by varying the temperature. At higher temperatures, the PDMS cures into a solid very quickly and does not allow much Au incorporation whereas at lower temperatures, there is more time for Au to reduce and get into the PDMS matrix.

The AuNP/PDMS nanocomposites were tested for stability after high temperature treatment and robustness in different chemical environments as shown in Figure 4. When the AuNP/PDMS film is heated to temperatures of 200 and 300 °C, the surface plasmon peak position is almost unaltered (blue shifted by ≈5 nm, Figure 4a). PDMS is known to be minimally affected by such temperatures.[12] In Figure 4b, the plasmon peak is shown to be minimally affected following treatment with acids, bases, and chlorocarbons. The near constancy in the plasmon peak intensity also implies that the particles are prevented from leaching into the media.

Applications

Water Purification

PDMS is well known to swell extensively in non-polar solvents such as toluene.[27,28] When plain PDMS in the form of foam as well as film, was dipped in toluene for 1 h and taken out, its weight increased due to swelling to 200 and 196%, respectively (Figure 5a). These values may be compared with 131% reported for normally cured PDMS.[21]
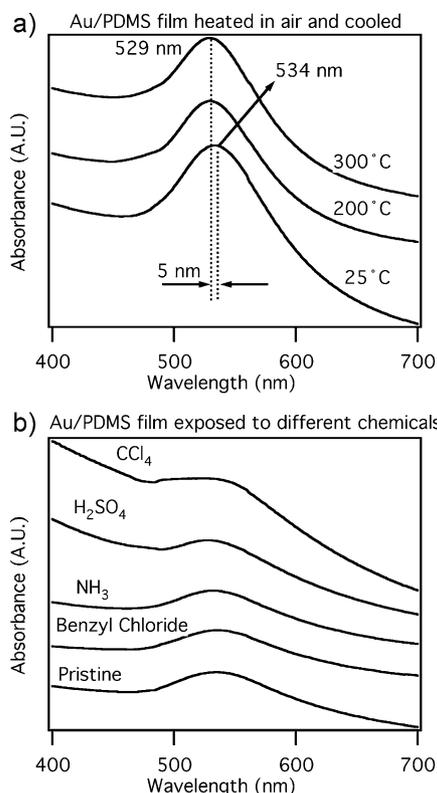

Figure 4. UV-visible spectra of AuNP/PDMS films after (a) heating to different temperatures for 1 h and cooling back to room temperature and (b) exposure to various acids, bases, and chlorocarbons.

The toluene uptake is slightly more in the case of the foam due to the presence of large density of micropores. More strikingly, AuNP/PDMS foam was able to swell more than 600% times its mass (Figure 5a), which is attributable to large surface area made available by the embedded Au nanoparticles. Indeed, volume expansion by toluene inclusion was vivid as shown in the photographs in Figure 5b. The mass change in differently swelled samples was monitored with time as the solvent evaporated under ambient conditions until each recovered to its original (deswelled) mass (Figure 5a). As can be seen from the figure, AuNP/PDMS is slower in giving up toluene by evaporation. The exceptional ability of AuNP/PDMS composite to take up and store toluene can be exploited for applications such as water purification. Figure 5c and d illustrate toluene removal from contaminated water. Toluene has very limited solubility in water, 500–627 ppm, but is a commonly occurring organic pollutant.[29,30] Starting with a saturated (500 ppm) solution of toluene (see Figure S1 of the Supporting Information), the extent of toluene removed was monitored using UV-visible spectroscopy in terms of spectral changes as shown in the mass-normalized plots in Figure 5c. Clearly, AuNP/PDMS composite is more effective in removing toluene; a small quantity (10 mg) of the foam is good enough to bring down the contaminant from 500 to ≈150 ppm within 8 h. Without Au nanoparticles, the latter value is ≈186 ppm. The removal is more gradual thereafter for both the foam samples. Toluene or in general, organic removal from water is however increasingly difficult but more critical at lower concentrations (below 100 ppm), as maximum contamination limit (MCL) is set to 7–10 ppm.[29] We have examined this region more carefully, using a 100 ppm solution of toluene in water as shown in the inset of Figure 5d. Again, the AuNP/PDMS foam is relatively faster at bringing down the contamination to ≈58 ppm with 100 mg of the nanocomposite.

We have also examined the ability of AuNP/PDMS composite to remove odorous contaminants such as sulfides, thiophenol, and thioether.[31–33] These contaminants are present in wastewater from crude oil and petroleum refineries, released from manufacturing sites, used as pesticide and mosquito larvicide, and are pharmaceutical intermediates. They are highly toxic in nature. In particular, this study examines removal of Na_2S, thiophenol, and thioanisole from water (Figure 6). We have used AuNP/PDMS films, as the spectral changes of the composite could be monitored more accurately in this form than in foams. The solution of Na_2S in water (6×10^{-4} M) is basic (pH $= 10.26$) because of its partial dissociation in water resulting in a high conductivity value of 63 $\mu S \cdot cm^{-1}$. The UV-visible spectra of a Na_2S solution (Figure 6a) exhibits diminishing intensity of the peak around 233 nm when treated with the AuNP/PDMS and the peak eventually vanishes after 12 h. The 233 nm peak corresponds to
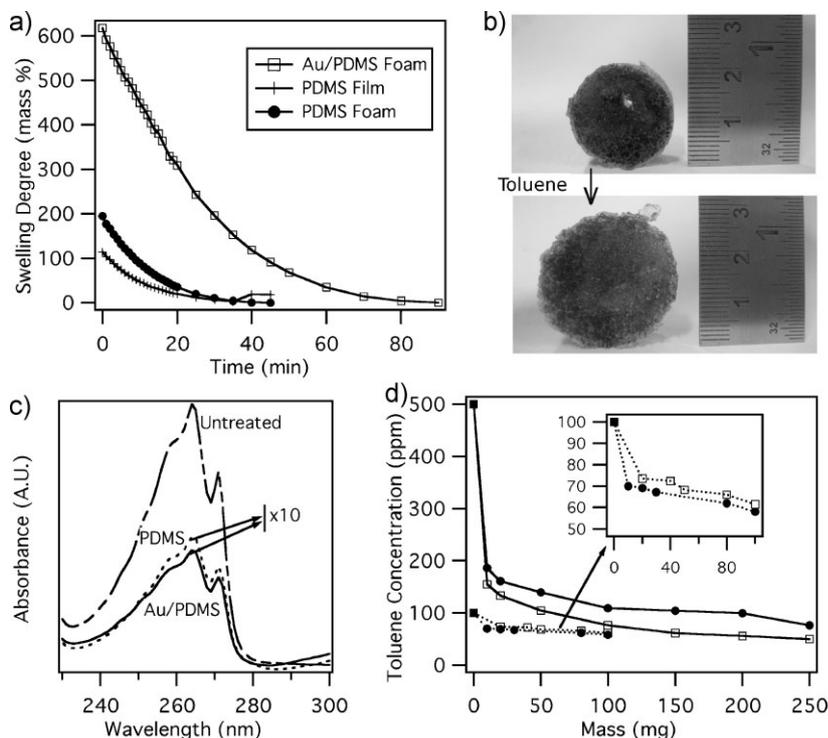
Figure 5. (a) Swelling and deswelling behavior of AuNP/PDMS foam, PDMS foam, and PDMS film over time after saturation with toluene. (b) Optical photographs of AuNP/PDMS as-synthesized (above) and after swelling with toluene (below). (c) UV-visible spectra of contaminated water (500 ppm toluene) showing reduction in intensity of toluene modes after treatment with 200 mg of PDMS and AuNP/PDMS foam. The spectra of treated water samples are multiplied by factor of 10 for clarity. (d) Concentration of saturated and 100 ppm (inset) toluene in water after treatment as a function of amount of AuNP/PDMS foam and PDMS foam used.

maximum at 240 nm with a side shoulder at 265 nm corresponding to thiophenolate species as seen in Figure 6e. When the solution was treated with a fresh AuNP/PDMS film (Figure 6f), the thiophenolate became the predominant species. This was also evident from the pH change from 6.93 to 6.03 as solution turned acidic. The change in the spectral weight is clearly seen as the isosbestic point in the spectra. The variation is rapid (see inset). The conductivity of the solution changed from 20 to 117 $\mu S \cdot cm^{-1}$ due to the ionization of thiophenol. After removing the odorous contaminants from the water into another substance, the removal of those contaminants from the sorption material to facilitate reuse or environmentally friendly disposal is a challenge.[34] The contaminants can be desorbed from the composite by applying a simple thermal treatment and the material can be reused. We observe spectral changes to the Au plasmon peak including broadening, reduction in intensity, and a small red shift on the adsorption of thiophenol. Heating the sample to 200 °C in air caused the Au plasmon peak to recover its original shape and position, as shown in Figure S2 of the Supporting Information. The adsorption-desorption process was repeated three times with no noticeable degradation of the Au plasmon signature from the UV-visible spectra, indicating that the material is robust and reusable.

HS$^-$, which forms when Na$_2$S is dissolved in water. The variation in absorbance with time is shown in the inset. When it is treated with the AuNP/PDMS film, the sulfide ions interact with Au specifically and get further reduced to bisulfide ions. The bisulfide ion does not exhibit any feature in UV region, as seen in Figure 6b, but changes in the Au plasmon peak are observed. The decrease in pH of the solution to 7.34 can be related to the increase in hydrogen ion species on dissociation of sulfide to give bisulfide ions. Concomitantly, the conductance increases to 85 $\mu S \cdot cm^{-1}$. In Figure 6c, the 253 nm peak corresponding to thioanisole in water (10^{-4} M) is seen to decrease to negligible intensity after 12 h of treatment with a fresh AuNP/PDMS film. The variation is quite rapid, as shown in the inset. Thioanisole is found to be chemisorbed on the surface of Au particles in AuNP/PDMS nanocomposite as seen from Figure 6d. The UV-visible spectra from films show that thioanisole chemisorbs on the Au nanoparticle surfaces resulting in a broad red shifted absorption at 257 nm. The pH change was minimal (6.5–6.3) while the conductivity increased from 8 to 82 $\mu S \cdot cm^{-1}$. The UV-visible spectrum corresponding to untreated thiophenol in water (10^{-4} M) exhibits absorption

Drug Delivery

One distinct property of our AuNP/PDMS nanocomposite material that distinguishes it from other materials is the physical stability of the Au nanoparticles inside the PDMS matrix while they are chemically accessible. Generally in polymer-based nanocomposite materials, particles are either chemically interacting with the polymer matrix, in which case their surfaces are not available for chemical reaction with other species, or they are weakly bound to the polymer and thus prone to leaching.[34]

To further probe the possibility of utilizing the Au nanoparticle surfaces within the composite, we studied the interaction of R6G, a fluorescent dye, with AuNP/PDMS composites. The adsorption and triggered release of R6G in the composite, shown schematically in Figure 7a, is used as a model system to probe specific chemical interactions between the embedded nanoparticles and small molecular
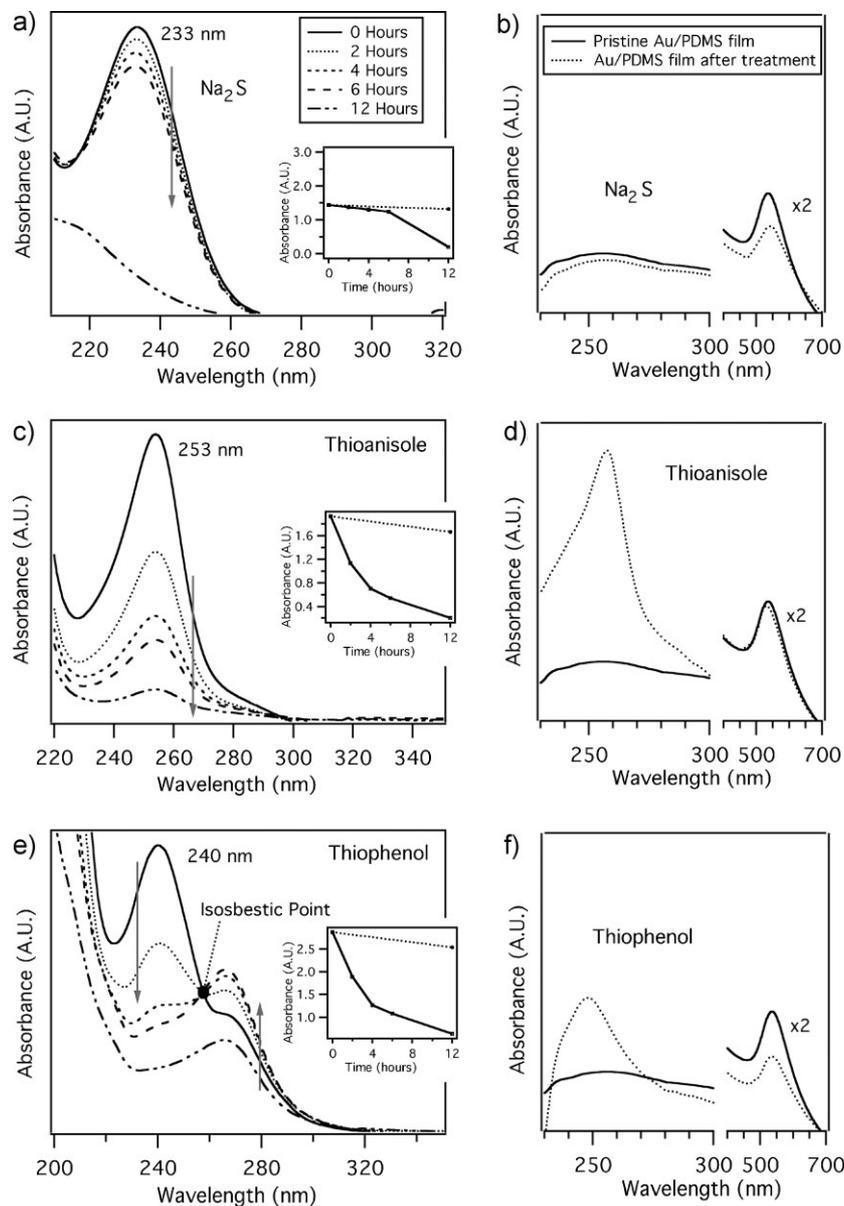
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Figure 6. UV-visible spectra recorded after different time intervals from solutions of (a) Na_2S (6×10^{-4} M), (c) thioanisole (10^{-4} M), and (e) thiophenol (1.28×10^{-4} M) in water. The gray arrows indicate increasing passage of time. The solutions of Na_2S, thioanisole and thiophenol were stirred for 24 h in sealed bottles before use. The inset in each plot shows the decrease in absorbance with time for treated samples (solid line) along with blank solution absorption (dotted line). UV-visible spectra of AuNP/PDMS films dipped in (b) Na_2S, (d) thioanisole, and (f) thiophenol show the interaction of these chemicals with the nanocomposite. The 450–700 nm regions of the spectra, corresponding to the Au plasmon peaks, are multiplied by a factor of two for clarity.

the excess R6G molecules from the film surface. As shown in Figure 7, the intensity of the characteristic R6G peaks at 508 and 543 nm are approximately two times greater for the AuNP/PDMS composite than for plain PDMS, suggesting that the Au nanoparticles facilitate additional uptake of the dye. The absorption spectra in Figure 7b show splitting of the broad absorption band of R6G into two peaks, the 508 nm peak is attributed to molecular R6G while peak at 538 nm is due to chemisorbed species on the Au nanoparticle surface. The absorption at 508 nm is attributed to a dye aggregation band and 538 nm is related to the Au surface plasmon.[37] We also observe a small peak at 714 nm arising from R6G far away from the main spectral features. Photoluminescence (PL) spectra of the films with R6G obtained with an excitation wavelength of 490 nm are shown in Figure 7b. In this case, the relative PL intensity of the dye in the case of AuNP/ PDMS composite is 17 times less than plain PDMS in spite of significantly higher absorption of dye. The low intensity of the PL peak is attributed to quenching due to the charge transfer interaction of the dye with the Au nanoparticle surface, which is consistent with the observations made in the literature.[38] R6G was released from the nanocomposite using hexadecylthiol (HDT) as a chemical trigger. HDT has a strong affinity to Au due to the presence of the sulfur in the thiol groups,[39] therefore it can displace the relatively weakly-interacting R6G from the nanoparticle surfaces and into the solvent medium, as shown schematically in Figure 7a. The R6G-incorporated films were soaked in a 2×10^{-3} M solution of HDT in toluene for 8 h. The relative release of R6G was characterized by performing PL on the resulting solutions. From the spectra in Figure 7c, it is clear

species. R6G is chosen because of its strong absorption in the visible region, high fluorescence yield, and easily characterized photo-physical properties which are relevant for biological studies. It is also soluble in PDMS and is known to interact well with Au nanoparticles.[35,36] AuNP/PDMS and pristine PDMS films were soaked in R6G solution in toluene (10^{-3} M) for 6 h and washed with toluene to remove

that the amount of R6G released is much higher in the case of AuNP/PDMS composite than plain PDMS. This is attributed to the higher capacity of the nanoparticle composite to hold the dye due to chemical interaction of the dye molecules with the nanoparticles. The significantly higher R6G release into HDT solution relative to toluene is consistent with the proposed mechanism. Thus, R6G
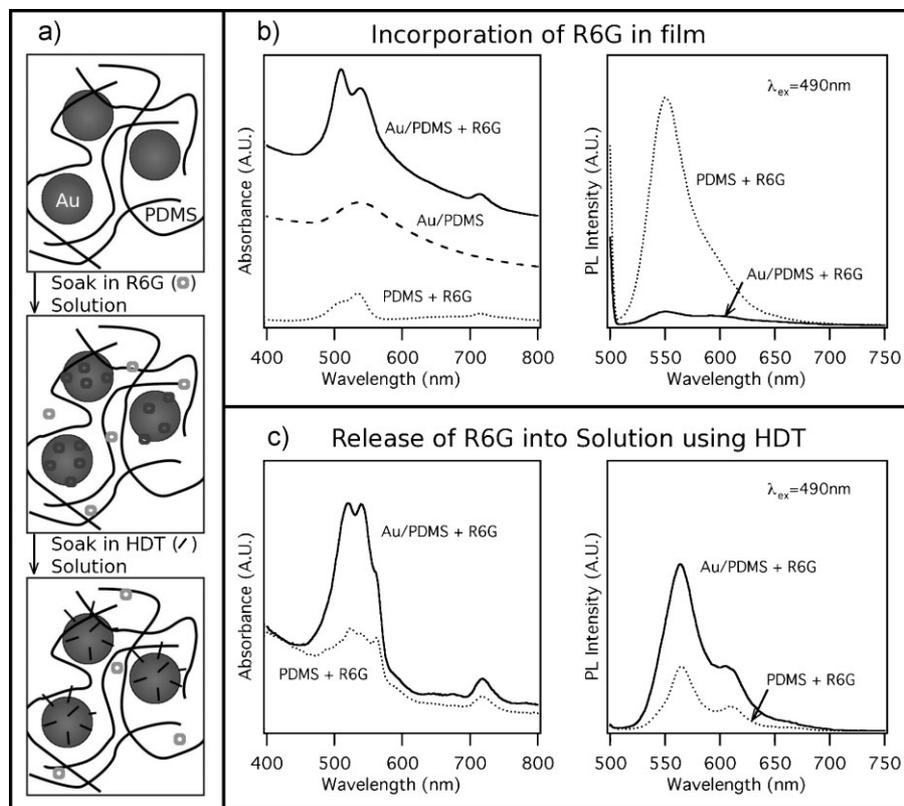
Figure 7. (a) Schematic representation of R6G incorporation and subsequent chemically-triggered release in AuNP/PDMS nanocomposite material. Spectral measurements from AuNP/PDMS and plain PDMS films upon adsorption of R6G (b) show that the composite takes up twice as much R6G as plain PDMS. The quenching of the PL in the nanocomposite shows the intimate interaction of the dye with the nanoparticles. (c) HDT solution is shown to release R6G into toluene from PDMS and AuNP/PDMS, as monitored by observing UV-visible absorption and PL emission (at 490 nm excitation wavelength) of the resulting solutions. UV and PL spectra in (c) are multiplied by 7 and 2, respectively, relative to (b) for clarity.

foams, and thin films with controlled nanoparticle concentration can be formed using this one-pot method by simple variation in process parameters such as precursor concentration, reaction temperature, and time. The unique solid-solution nature of PDMS has been exploited to realize a system where Au nanoparticles are mechanically stabilized within the matrix in a highly robust manner, yet the surfaces are chemically accessible to small molecules for specific interaction. These properties make the nanocomposite a highly promising material for drug delivery, water purification, and chemical sensing applications.

has enabled us to probe the microenvironment of the composite. The ability of this composite to release the dye molecules in the presence of a specific chemical environment shows promise for storage and chemically-induced release of specific compounds, which can be applied for targeted drug delivery.

Conclusion

In summary, AuNP/PDMS composites are of great current interest for applications including biomedical, optical, water purification, and microfluidic systems. We have presented a simple, novel, green technique for the synthesis of various AuNP/PDMS composite materials. This technique involves in situ reduction under mild conditions: stirring aqueous KAuCl₄ along with PDMS mixture at room temperature. It offers a good control over loading of Au nanoparticles with size in the range of 5–50 nm. Gels,

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