Controlling the Architecture and Properties of Nanocomposite Materials
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Introduction
Nanocomposite materials consisting of colloidal metal nanoparticles embedded in synthetic polymer hydrogels have attracted attention due to applications in catalysis, photonics, electronics, optics, and biomedicine. This work describes a method for generating nanocomposites of gold (Au) nanoparticles within thermoresponsive poly(N-isopropylacrylamide), poly(NIPAm), hydrogels. Altering the concentration of a reactive, disulfide-containing crosslinking agent (cystamine-bis-acrylamide, CBAm) used in hydrogel synthesis leads to dramatic alteration in the size and morphology of Au nanoparticles generated. Similarly, the bulk properties of equilibrium swelling and thermoresponsive phase transition of the hydrogel are strongly dependent on the presence of the Au nanostructures.

Synthesis and Infrared Spectroscopy
Poly(NIPAm) is polymerized in water with varying amounts of an unreactive (methylene-bis-acrylamide, MBAm) and reactive (CBAm) crosslinking agents. Au nanoparticles are then generated in situ through introduction of KAuCl₄ followed by NaBH₄ reduction. Infrared spectra of the 3.5% MBAm/3.5% CBAm hydrogels are shown. Peaks closely match those observed for other poly(NIPAm) systems with the addition of two new peaks at ~1000 cm⁻¹ and ~1045 cm⁻¹ (blue arrow). These peaks are only observed with the CBAm containing hydrogels after Au nanoparticle generation in situ. The origin of these peaks is under investigation.

UV-Visible Spectroscopy
UV-Visible spectra of hydrogel-Au nanoparticle composites in water. (Left) Large spectral changes caused by altering CBAm content with fixed 3.5% MBAm. (Above) Only minor spectral changes are seen with large variation of MBAm at fixed CBAm content.

Thermoresponsive Phase Transition
The poly(NIPAm) hydrogels undergo a thermoresponsive phase transition from a swollen hydrated state at low temperature to a shrunken dehydrated state at high temperature as illustrated below.

Equilibrium Swelling Behavior
Equilibrium swelling of native and Au-containing hydrogels. Values are the ratio of the hydrogel diameter to diameter after cutting the synthesized hydrogel films. Gels treated with dithiothreitol (DTT), which cleaves the disulfide bonds in CBAm, (B) are shown for comparison.

Electron and Optical Microscopy
Scanning transmission electron micrographs from hydrogel-Au nanoparticle composites with 3.5% MBAm and 0.002%, 2.1%, and 3.5% CBAm (left to right). At low CBAm content nanoparticles are large and irregularly shaped. At high CBAm content nanoparticles are significantly smaller and spherical. The intermediate CBAm content sample contains both types of Au nanostructures. These results demonstrate an ability to control nanoparticle size and morphology through altering the hydrogel composition. Insets show optical photographs from samples with the same composition.

Conclusion
In summary, we have synthesized Au nanoparticles with controlled structure inside thermoresponsive poly(NIPAm) hydrogels. The hydrogel samples contain varying concentrations of Au-reactive disulfide groups. Altering the relative amount of these groups enables control over the size and morphology of the Au nanoparticles generated within the hydrogel. The presence of the Au nanoparticles alters the equilibrium swelling properties of the hydrogels as well as their phase transition behavior.

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