

Phase Transition Behavior of Hydrogels with *in situ* Generated Gold Nanoparticles

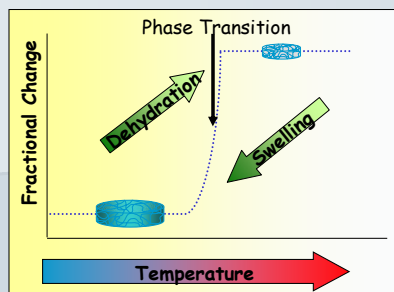
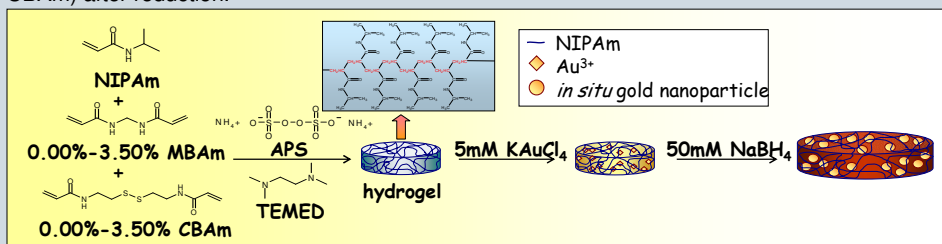
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Introduction

Hydrogels and metal nanoparticles are materials extensively researched because of their unique and useful properties. Hydrogels are cross-linked, hydrophilic polymer networks that undergo volume phase transitions in response to certain environmental stimuli. Metal nanoparticles, 1–100 nm in diameter, possess conductivity and optical properties strongly influenced by particle size and interparticle spacing. The addition of metal nanoparticles to hydrogels alters phase transition behavior. My research specifically investigates the effects of gel composition and the presence of *in situ* gold nanoparticles on hydrogel thermoresponsive phase transition. UV-Vis spectroscopy, gel diameter, and gel mass measurements were used to probe the phase transition.

Nanocomposite Synthesis

Gels were synthesized using the thermosensitive *N*-isopropylacrylamide (NIPAm) as the polymer backbone and varying concentrations of *N,N*-methylenebisacrylamide (MBAm) and/or *N,N*-cystaminebisacrylamide (CBAm) as crosslinking agents. CBAm has a disulfide linkage, in which can react with gold to form sulfur-gold chemical bonds. *In situ* gold nanoparticles were then formed in the gels. Depending on the concentration(s) of crosslinker(s) in the gel, the gels ranged from black (high MBAm, low/none CBAm) to red-brown (low/none MBAm, high CBAm) after reduction.

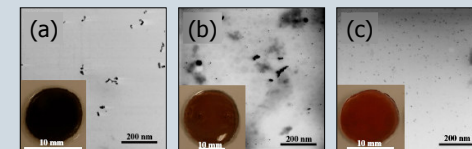
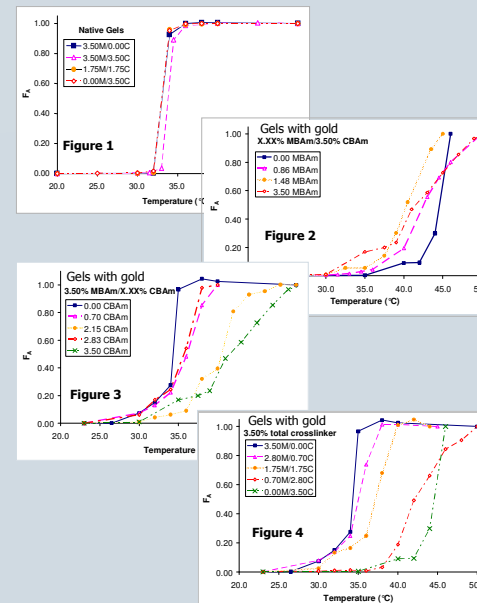


▲ During the phase transition, the initially clear and soft gel contracts and becomes hard and opaque, expelling its contents into its surroundings.

Results & Discussion

As shown in Figure 1, native gels of various compositions all possess narrow phase transitions in the temperature range of 32–34 °C. MBAm concentration has little effect on the phase transition; in Figure 2 where MBAm concentration is varied against 3.50% CBAm, phase transition temperatures widen and shift similarly. However, in Figures 3 and 4 where CBAm concentration is changed against 3.50% MBAm and varied MBAm concentrations respectively, phase transitions are sharp with high MBAm/low CBAm respectively, but progressively widen and shift to higher temperatures as CBAm concentration increases. This indicates that crosslinking density does not influence the change in phase transition as strongly as CBAm does.

Increased gel volume and elevated, widened phase transitions were expected with the high CBAm gels. Higher CBAm concentration increases the amount of sulfur-gold bonds present in the hydrogel, which prevent larger nanoparticles from forming during the *in situ* reduction. On the right are electron micrographs of nanocomposites with increasing CBAm content (a to c). The smaller nanoparticles have greater surface area and greater surface charge, thereby making the gel more hydrophilic and requiring more heat for the gel to contract and push out water.

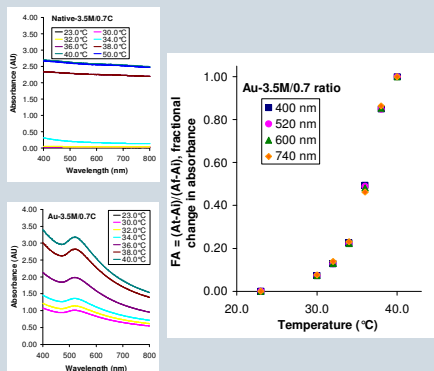


▲ Electron micrographs of *in situ* gold gels obtained with Scanning Transmission Electron Microscopy. All gels contain 3.50% MBAm and varying amounts of CBAm; a) 0.002% CBAm; b) 1.75% CBAm; c) 3.50% CBAm.

Wang, C.; Flynn, N.T.; Langer, R. *Adv. Mater.* 2004, 16, 1074.

UV-Vis Spectroscopy

Hydrogel phase transitions were examined using UV-Vis spectroscopy. For both native (non-gold containing) and gold gels, parallel shifts in absorbance across 400–800 nm were observed. Absorbance readings of gold gels showed a peak between 510–520 nm. To compare gels of different composition, the fractional absorbance change of the gels was determined using $F_A = (A_T - A_i) / (A_T - A_i)$. The wavelength used for the calculations was 600 nm.



Conclusion

Phase transition behavior was dependent on the amount of CBAm and the presence of *in situ* gold nanoparticles. Of the gels examined, samples with high concentrations of CBAm—regardless of MBAm concentration—which contain *in situ* gold nanoparticles displayed the largest upward shifts in and the widest broadening of the phase transitions. High concentration CBAm-gold nanoparticle samples—with little or no MBAm—were also substantially larger than gels that had lower concentrations of CBAm and/or higher concentrations of MBAm.

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