

Synthesis and Applications of Micro- and Nanostructured Hydrogel Composites

Hariharasudhan D. Chirra, J. Zach Hilt
University of Kentucky, Lexington, KY 40506

Statement of Purpose: Spatially functionalized ‘smart’ hydrogel micro- and nanostructures find many point of care diagnostic and therapeutic applications. The incorporation of nanoparticles with unique chemical and physical properties to these structures renders a synergistic effect, thereby amplifying potential applications in the biomedical field. Herein, in-situ precipitation of nanoparticles (e.g., gold, iron oxide, etc) was carried out inside responsive hydrogel (poly(N-isopropyl acrylamide), PNIPAAm; poly(methacrylic acid), PMAA) micropatterns and nanopatterns. Characterization of the hydrogel nanocomposite response was also completed.

Methods: Microcontact printing (μ CP) of a hydrophobic thiol over gold followed by initiator thiol assembly is used to obtain XY control^[1]. Polymerization (e.g., UV, atom transfer radical polymerization, ATRP; etc) of PNIPAAm hydrogels is then carried out (figure 1). Subsequent in-situ precipitation of particles is carried out to form nanocomposite structures. Characterization of structure and response was done using FTIR, SEM, AFM and optical microscopy.

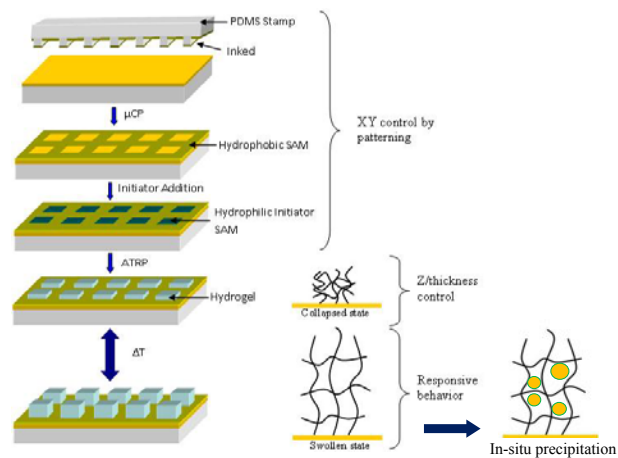


Figure 1. Scheme of ATRP followed by in-situ precipitation

Results/Discussion: SEM, and optical microscopy analysis revealed that the patterns were confined only to the initiator square regions as controlled by μ CP (XY control). AFM analysis of dry thickness revealed that ATRP led to a controlled Z growth of the hydrogels. The response behavior of thin hydrogels was studied using liquid cell setup AFM imaging. From figure 2, it can be observed that, poly(ethylene glycol n dimethacrylate) crosslinked PNIPAAm hydrogels collapse with increase in temperature. The amount of crosslinker and the molecular weight of the crosslinker can be employed to tailor the response behavior of the hydrogel patterns. Further instantaneous response was

observed from QCM-D analysis makes them viable for various biomedical applications.

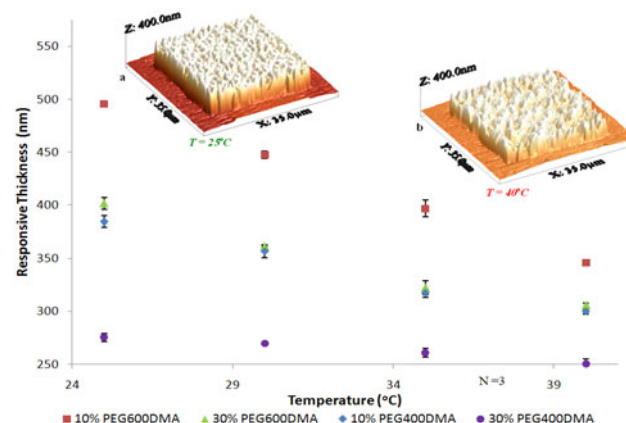


Figure 2. Effect of crosslinking density and molecular weight on the response behavior of different PNIPAAm hydrogels (squares, 24 hours ATRP). Inset is 3-D AFM images of the 10% crosslinked PEG400DMA system at 25 and 40°C respectively.

In other structures, gold nanoparticle (GNP) loading was done via in-situ precipitation in pH responsive PMAA patterns grown via UV photopolymerization. GNP hydrogel composites (figure 3) responded to pH stimuli with no leaching of particles observed. Functionalization of GNPs with biomolecules that can provide the necessary environmental stimulus for the hydrogel nanocomposites can be used for diagnostic sensing and therapeutic delivery.

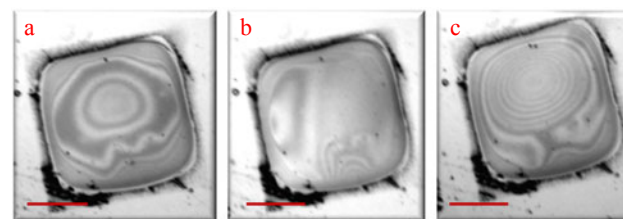


Figure 3. pH responsive behavior of GNP precipitated nanocomposites. (a) Swollen nanocomposite in water, (b) collapsed nanocomposite with the acidic stimulus (pH = 2.5), and (c) swelling back to original state with basic stimulus (pH = 8.7). Scale – 250 μ m

Conclusions: We have successfully demonstrated a route for forming spatially controlled patterned hydrogel surfaces using μ CP, followed by polymerization. Results show that crosslinker molecular weight and density can be used for tailoring the hydrogels response behavior. In-situ precipitated nanocomposites were synthesized with ease and have potential applications in instantaneous point of care diagnostic and therapeutic biomedical applications.

Reference:

[1] Chirra, H.D., Biswal, D., Hilt, J.Z., Polym. Adv. Tech., *in press*.