Synthesis and Self-assembly of Metal and Semiconductor Nanoparticle-Polymer Composites

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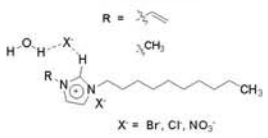
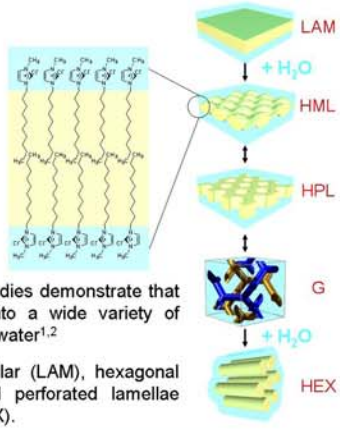
Motivation: Controlling the spacing (and thus, the communication) between metal and semi-conducting nanoparticles in a nanostructured ion-conducting framework offers considerable potential in fabricating "next-generation" optoelectronic or photovoltaic materials. To this end, we have synthesized polymerizable ionic liquids whose mesophase structure can be tuned via the controlled addition of water. Once the mesophase architecture is self-assembled, photopolymerization converts the physical gel into a robust polymeric (chemical) gel whose lattice dimensions can be expanded or contracted via control over solvent conditions. These subtle changes in the tiny channels that both trap and order nanoparticles have been shown to regulate the internal packing arrangement of the nanoparticles and hence their collective properties.

Physical Ionogel Formation

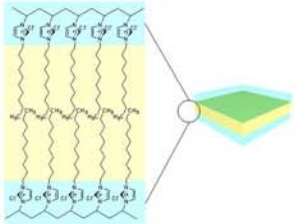




- Small-angle X-ray scattering (SAXS) studies demonstrate that C_{10} imidazolium salts self-assemble into a wide variety of mesophases upon controlled addition of water[1,2]
- The mesophases formed include lamellar (LAM), hexagonal modulated lamellae (HML), hexagonal perforated lamellae (HPL), gyroid (G) an 2-D hexagonal (HEX).

Chemical Ionogel Formation

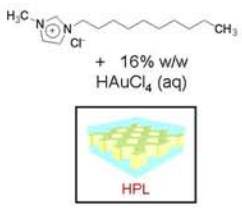
- Photopolymerization of a vinyl imidazolium salt, $[C_{10}vim^+][Cl^-]$ converts the physical gel into a robust polymeric (chemical) gel.

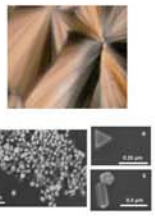


1. Firestone, M. A.; Dzielawa, J. A.; Zapol, P.; Curtiss, L. A.; Seifert, S.; Dietz, M. L., *Langmuir* **2002,** 18, (20), 7258.
2. Firestone, M.A.; Rickert, P.G.; Seifert, S.; Dietz, M.L. *Inorg. Chim. Acta* **2004**, 3991.

Results:

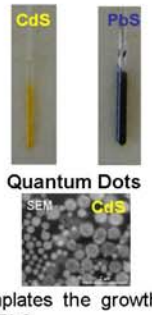
Physical Gel





- The 2-D HPL mesophase of $[C_{10}mim^+][Cl^-]$ selectively promotes the nucleation and growth of ***anisotropic*** gold (Au) nanoparticles.

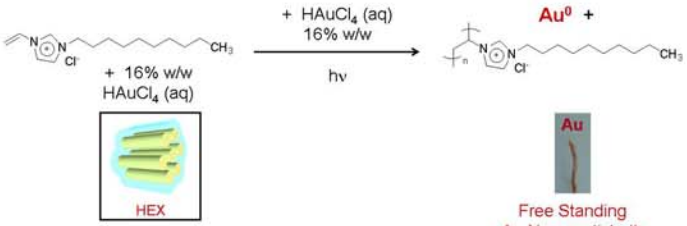
Firestone, M. A.; Dietz, M. L.; Seifert, S.; Trasobares, S.; Miller, D. J.; Zaluzec, N. J., *Small* **2005,** 1, (7), 754.



- The gyroid (G) mesophase of $[C_{10}mim^+][Cl^-]$ templates the growth of hollow, spherical semi-conducting nanoparticles, CdS and PbS.

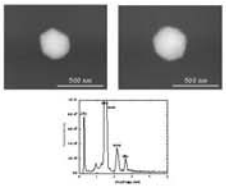
Batra, D.; Liu, A.C.Y.; Benitez, G.M.; Firestone, M.A. Manuscript in preparation.

Chemical Gel



Free Standing Au Nanoparticle-IL Composite

- Au nanoparticles can be grown with concomitant synthesis of a robust chemical ionogel, Poly $[C_{10}vim^+][Cl^-]$.

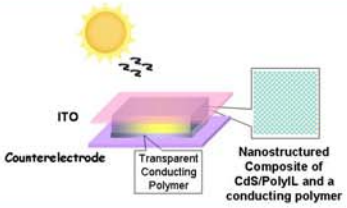


- SEM images show presence of Au nanoparticles whose spacing can be controlled within the nanoparticle-polymer composite.

Batra, D.; Liu, A.C.Y.; Miller, D.J.; Varela, L.M.; Firestone, M.A. *J. Am. Chem. Soc.*, submitted.

Future Direction:

- Fabricate an all 'solid-state' solar cell device using polymerized ILs as the electrolyte layer.
- Grow CdS and CdSe nanoparticles in polymerized-ILs and incorporate them with a conjugated polymer for a nanostructured solar cell and/or optoelectronic devices.



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