Electrochemical Properties of Gold-Nanoparticle Ionic Liquid-Derived Polymer Composites

Sungwon Lee, Sönke Seifert and Millicent A. Firestone
Materials Science Division, Argonne National Laboratory
Argonne, IL 60439

In this work, we describe the design, synthesis and electrochemical properties of a nanostructured chemical (polymeric) gel formed by the spontaneous organization of a binary mixture of water and a polymerizable ionic liquid, 1-decyl-3-vinylimidazolium chloride, $[C_{10}VIm^{+}][Cl]^{-}$. Small-angle X-ray scattering has been used to probe the rich variety of structural motifs, including 1-D lamellar (LAM), 2-D hexagonal (HEX), and 3-D cubic (gyroid, G) phases, achievable by simply controlling the amount of water in the ionic liquid monomer. Furthermore, a large region of phase space has been identified in which the binary system adopts long-lived metastable structural states that are intermediate in character between lamellar and hexagonal, namely, hexagonal modulated layers (HML) and hexagonal perforated lamellae (HPL).[1- 4] These structures are of particular interest for the development of nanostructured templates or scaffolds for controlling the nucleation and growth or internal packing arrangement of in-situ synthesized metal (Au) nanoparticles. As an example, we describe the single-step synthesis of a robust, self-supporting (mechanically durable) gold nanoparticle-ionic liquid-derived polymer composite. Specifically, a gold nanoparticle-containing ionic liquid-derived polymer is synthesized in a single step by UV (λ = 254 nm) irradiation of a metal ion ($HAuCl_4$) precursor-doped, self-assembled ionic liquid ($[C_{10}VIm^{+}][Cl]^{-}$). The as-synthesized gold nanoparticle-IL composite prepared with 16 % (w/w) water adopts a HPL structure. The optical properties of the as-synthesized composite possesses a broad manifold of plasmon resonances positioned in the NIR (800-1200 nm), suggesting strong particle-particle interactions arising from matrix-promoted formation of aggregated 1-D clusters or chains of the gold nanoparticles (Figure 1).

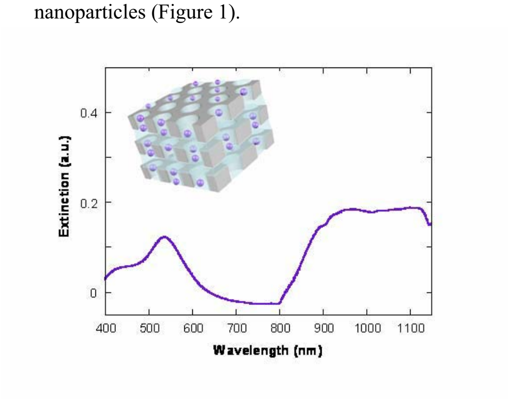

Figure 1. Vis-NIR optical spectrum collected on an as-synthesized 13 mM Au3+ - IL polymer composite. Inset schematic illustration of structure of polymer as determined by SAXS

Impedance spectroscopy (EIS) was used to characterize the electrochemical properties of the Au-polymer nanocomposite. The Nyquist impedance spectra for a composite prepared with 13 mM Au^{3+} is presented in Figure 2. Similar measurements made on the polymer composite that did not have gold nanoparticles show nearly identical behavior, suggesting that at low gold concentrations, the transport is primarily ionic conductivity and matrix mediated. EIS studies conducted on samples prepared with increasing gold concentration (55 and 165 mM) show a significant increase in composite conductivity, most likely arising from electronic transport through organized gold nanoparticles.

Ultimately, the ability to combine organized noble metal nanoparticles with semiconductor nanoparticles offers the possibility of forming an integrated, self-assembled, polymeric solar energy device that includes components for light harvesting, charge separation, and charge collection.

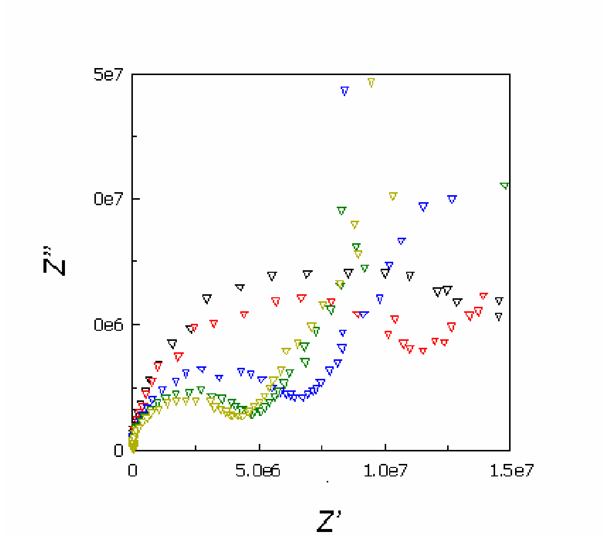

Figure 2. Nyquist impedance spectra collected on a Au nanoparticle (13 mM) – IL composite. Black data collected at 10°C, red data collected at 20°C, blue data collected at 30°C, green data collected at 40°C and yellow collected at 50°C.

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