Nanoparticle- Metallopolymer Assemblies Charge Percolation and Redox Properties - L. Keane and R. Forster (Dublin City University)

Stable gold nanoparticles have been prepared by the chemical reduction of gold hexachloroaurate in the presence of PVP and the metallopolymer $[Os(bpy)_2 (PVP)_{10} Cl]^+$ films, where bpy is 2,2'-dipyridyl and PVP is poly(4-vinylpyridine). As illustrated in Figure 1, by systematically varying the mass ratio of polymer:gold from 25:1 to 0.1:1, gold nanoparticles of radii between 1.6±0.3 and 5.0±0.2 nm have been prepared.

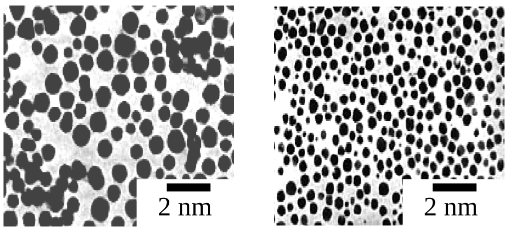

Figure 1. SEM images of gold nanoparticles formed in the presence of $[Os(bpy)_2 (PVP)_{10} Cl]^+$. In A the mass ratio of PVP:Au is 25:1 while in (B) it is 0.1:1.

As illustrated in Figure 2, the dependence of the electrical conductivity on the metal loading is described by the percolation theory describing a random distribution of the nanoparticles.

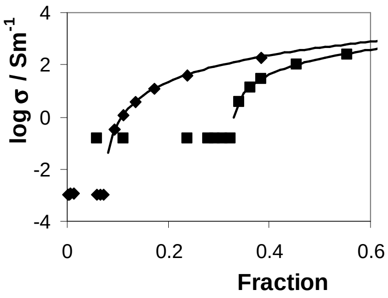

Figure 2. Dependence of the dry state electrical conductivity of $[Os(bpy)_2 (PVP)_{10} Cl]^+$ on the volume fraction of gold nanoparticles. The solid line indicates the best fit percolation theory for a randomly dispersed filler.

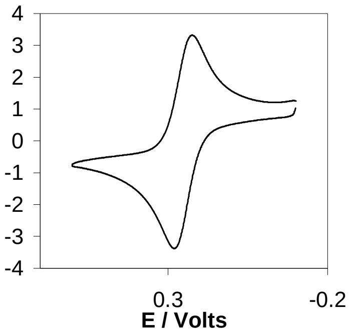

Figure 3. Cyclic voltammogram of $[Os(bpy)_2 (PVP)_{10} Cl]^+$ in the presence of gold hexachloaurate.

As shown in Figure 3, the voltammetric response corresponding to the $Os^{2+/3+}$ couple is nearly ideal for all nanoparticle loadings. The dependence of the cell resistance for electrodes coated with the composites on electrolyte concentration over the range 0.1 to 1.0 M suggests that the films contain rather large amounts of electrolyte and water, and that Donnan exclusion has failed. The effect of changing the concentration of $HClO_4$ and $NaClO_4$ as supporting electrolyte concentration on both the formal potential, $E^{o'}$, and charge transport diffusion coefficient, D_{CT}, have been investigated using cyclic voltammetry. The dependence of the formal potential on electrolyte concentration suggests that while the oxidized form of the metallopolymer is ion paired with an extra ion in the absence of gold nanoparticles, ion-pairing does not occur for the composite material suggesting that the nanoparticles may interact specifically with the redox centers. Alternatively, the behavior may arise because of an increased dielectric constant within the metal containing films. The apparent diffusion coefficient for charge transport D_{CT} has been evaluated using cyclic voltammetry. In $HClO_4$ media, D_{CT} is $5.7\pm0.4\times10^{-11}$ cm^2s^{-1} for $0.1 \leq [HClO_4] \leq 1.0$ M indicating relatively slow electron transfer dynamics between adjacent redox centres. In contrast, when the gold nanoparticle loading is above the percolation threshold, D_{CT} values that are almost two orders of magnitude are observed. These results are interpreted in terms of nanoparticle mediated oxidation of the polymer bound redox sites.