In-Situ Formation of Gold Nano Particle/Conducting Polymer Nanocomposites
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Conjugated electroactive and electronically conducting polymers have received a great deal of attention because of their unique properties. These materials are much lighter than metals and easy to fabricate to various forms. However, they do not only exhibit limited conductivity compared to metal, but also their instability upon ultraviolet irradiation, heat, and other environmental conditions causes serious problems for practical applications.

In this research, conducting polymer/metal nanocomposites were prepared with an anticipation of these novel materials offering an answer to overcome the fundamental shortcomings of conducting polymers. In the preparation of composites, poly(3,4-ethylenedioxy thiophene) (PEDOT) and gold were selected for each component. PEDOT stands out for its high degree of visible light transmissivity and high environmental stability in the conducting state, along with a propensity toward multiple redox switches due to its ease of oxidation.

In order to prepare PEDOT/gold nanocomposites, neutral state PEDOT films react with AuCl₃ to yield oxidized PEDOT film in which Au nanoparticles are deposited by in-situ redox reaction. In the preparation of composite, PEDOT films were fabricated with inorganic silica network to provide good mechanical properties. The silica sol contains an optimum amount of aminopropyltrimethoxysilane or mercaptopropyltrimethoxysilane which has a amino- or mercapto-functional group for capturing gold particle. In the PEDOT/silica film formation, a suitable amount of EDOT and ferric toluene sulfonate (FTS) oxidant were added into silica sol, and the mixed solution was spin cast and finally baked in convection oven for 1hr at 130°C for complete gelation. These films were electrochemically or chemically reduced to yield neutral PEDOT and subsequently oxidized by the reaction of AuCl₃. AuCl₃ has sufficient power to oxidize PEDOT film in neutral state while it is reduced to form Au particles.

The electrochemical reduction process of PEDOT films was monitored by using UV-VIS spectra. Upon reducing, the absorption band developed at 580 nm while the charge carrying bipolaronic species at > 800 nm dissapeared. These films were immersed into the nitromethane solution of AuCl₃ for oxidation. The in-situ UV-Vis spectra are shown in figure 1. It is clearly seen that the oxidation of PEDOT film by AuCl₃ by monitoring the decrease in the absorption band at 600nm as well as the increase in the broad absorption band at >800 nm. In addition, a characteristic absorption band due to atomic gold formation was observed at ~520 nm. It was also revealed that the kinetics of oxidation reaction of AuCl₃ strongly depended on the reaction medium. Nitromethane allowed much faster reaction compared to acetonitrile.

The formation of gold particle was also confirmed by the X-ray photoelectron spectroscopy (XPS). XPS spectra of oxidized PEDOT film show the presence of single gold species of which binding energies are 83.3 and 87.5 eV. The formation of gold nanoparticles during the doping reaction of the PEDOT/silicate hybrid film containing MPS was demonstrated by SEM in Fig. 2. In the early stage of doping, it can be seen that the gold particles are small and well dispersed, but the small particles starts to coalesce after 100 sec. It was also revealed that the size of gold nano particle was dependent on the amount of mercapto functional groups in the silica matrix. The much smaller size of gold particle was monitored in the sample having higher amount of mercapto group. During the doping process, the rapid drop in resistance as well as enhanced light transparency were also monitored.

Figure 1. UV-Vis spectra of PEDOT during chemical oxidation by AuCl₃ (for 1000 sec)

Figure 2. SEM images of gold nanoparticles after 10 sec oxidation in nitromethane