

## CHARGE TRANSPORT IN MULTILAYER ASSEMBLIES OF METAL AND SEMICONDUCTOR NANOCLUSTERS

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The construction of mono- and multilayers of various materials with an ordered structure has attracted much interest because of the wide variety of possible applications and its significant importance in nanotechnology. The structurally controlled growths of mono- and multilayers of metal and semiconductor nanoclusters on solid surfaces have been attempted by many groups because these nanoclusters have various interesting characteristics different from those of bulk materials.

In this work, we have constructed the multilayer assemblies of metal (gold)<sup>1-3</sup> and semiconductor (CdS)<sup>4</sup> nanoclusters by the processes at solid/liquid interfaces, i.e., wet processes and investigated their charge transport property, which is a key process in many applications.

Various kinds of multilayers of gold nanoclusters (GNCs) were constructed on Au(111) and ITO surfaces using two types of GNCs, one covered by self-assembled monolayers (SAMs) of mercaptoundecanoic acid (MUA), hexanethiol (C<sub>6</sub>SH), and ferrocenylhexanethiol (FcC<sub>6</sub>SH), MHF-GNC, and the other with MUA and C<sub>6</sub>SH, MH-GNC, based on electrostatic interactions using an ionic polymer (poly(allylamine hydrochloride) (PAH)) as a binding layer. Electrochemical measurements of the multilayers of MHF-GNCs showed a pair of waves corresponding to the redox of the ferrocene group and the charge of these peaks, i.e., the amount of adsorbed GNC, linearly increased with the construction cycles. Quasi-reversible redox response of the ferrocene moiety was observed even at the gold electrodes with GNC multilayers of two different sequences in which MHF-GNC exists as the layer closest to the gold electrode or as the outermost layer with MH-GNC in the other layers. These results show the facile transfer of electrons, which takes place through the GNC cores by hopping, and ions through the multilayers of the SAM-covered GNCs.

Nanoclusters of CdS were prepared in Aerosol OT (AOT)/H<sub>2</sub>O/heptane reversed micelles and their cluster size was controlled by the [H<sub>2</sub>O]/[AOT] ratio. These nanoclusters showed size dependent absorption spectra. The multilayers of the CdS nanoclusters were constructed on a Au(111) surface using PAH as a binding layer. Photoinduced anodic current was observed when the nanocluster-modified electrode was immersed in an electrolyte solution containing triethanolamine as an electron donor. The photocurrent increased with the increase of the number of CdS layers, suggesting that all the CdS clusters were electrochemically active. The action spectra of CdS-nanocluster multilayers were in good agreement with the absorption spectra of respective colloidal solutions, indicating that the nanoclusters were immobilized on substrate without changing their cluster size, as far as the size of the nanoclusters were not too small. Visible pump IR absorption probe measurements were carried out to investigate the charge transport dynamics.

### References

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