

# Self-Assembled Films of Semiconductor and Metal Nanoparticles in Polyelectrolytes: Assembly Dynamics and Photo-induced Charge Transfer and Transport Processes

Lara Halaoui, Chemistry Department, American University of Beirut

Electrocatalytic and photo-induced charge transfer processes are investigated at metal and semiconductor nanoparticles in polyelectrolytes. These studies have implications for solar cells, fuel generation, fuel cells, and catalysis. Polyacrylate (PAC) surface-modified Pt nanoparticles (nano-Pt) and CdS quantum dots (Q-CdS) were assembled on oppositely charged poly(diallyldimethylammonium chloride), PDDA, as films of PAC-nano-Pt/PDDA, PAC-Q-CdS/PDDA, or heterostructures of nano-Pt and Q-CdS in PDDA; and the electrochemical and photoelectrochemical characteristics of the assemblies were explored to further our understanding of charge transfer at small size metals and semiconductors. Examples of these studies are presented. CVs in 1 M  $\text{H}_2\text{SO}_4$  in Fig. 1 show hydrogen underpotential deposition ( $H_{\text{upd}}$ ) at PAC-nano-Pt/PDDA at different surface coverage, varied on one layer by varying the adsorption time, or in multilayers using a layer-by-layer assembly; allowing catalytic site characterization and determination of real Pt surface area. The electrochemical behavior was studied in relation to surface coverage; for instance, the diffusion-limited peak current density for oxygen reduction normalized to real Pt surface area is shown in Fig. 2 to decrease with increasing nano-Pt coverage, while the reduction peak potential shifted positively with increasing the number of catalytic sites. The photoelectrochemical behavior of PAC-Q-CdS/PDDA was investigated with different redox couples ( $\text{Na}_2\text{S}$ , ascorbic acid, tartaric acid) and significant differences were observed relative to electrodeposited bulk CdS films. For example, Fig. 3 shows I-V curves under chopped illumination at 4 bilayers of Q-CdS/PDDA and bulk CdS (inset) in 0.1 M  $\text{Na}_2\text{S}/0.2$  M NaOH, showing cathodic and anodic photocurrents at the Q-CdS films. This behavior at Q-CdS depended on the redox species, electrode potential, and pH.

