Understanding the Role of Nanoparticle Assembly Method and Electrode Material on the Electrochemically-determined Surface Area-to-Volume Ratio

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In this work we describe the effect of the type of assembly method and electrode material on the electrochemically-determined surface area to volume ratio (SA/V) ratio of Au nanospheres (NSs) of different diameters. The SA/V was approximately 10% and 34% smaller for 4 and 15 nm diameter Au NSs, respectively, assembled by electrophoretic deposition (EPD) directly onto glass/ITO electrodes as compared to those attached electrostatically to glass/ITO through aminopropyltriethoxysilane (APTES). Surprisingly, the SA/V was 80-90% smaller for 32 nm, 50 nm, and 70 nm diameter Au NSs deposited by EPD as compared to those deposited electrostatically onto glass/ITO/APTES. The lower SA/V suggests that the Au NSs attach more flattened on Au NSs deposited by EPD, making the full NS surface less accessible. This also leads to a more positive shift in the oxidation potential for these Au NS compared to those deposited on glass/ITO/APTES. Drop-cast deposition and deposition with carbon black also leads to a large decrease in accessible surface area of the NSs as compared to deposition onto glass/ITO/APTES. Au NSs attached through amine (Ethylene diamine) and thiol (Aminoethanethiol) terminated linkers to glassy carbon and Pt disk electrodes respectively, also showed variations in the electrochemically determined SA/V of Au NSs of similar sizes attached through APTES to glass/ITO. The observed trend for SA/V for 15 nm Au NPs for these different assembly methods was GC/ED > glass/ITO/APTES > Pt Disk/AET. Knowing the SA/V for different NS assembly methods and different electrode materials is useful for selecting the proper method and material

for different applications and plays an important role in the reactivity and stability of the surface-attached NSs.