Sintering of Metal Nanoparticles through Repetitive Electrochemical Oxidation-reduction Cycles

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We describe the electrochemical sintering of 2, 4 and 15 nm Au nanoparticles (NPs) attached to (3-aminopropyl)triethoxysilane functionalized glass indium tin oxide (glass/ITO) in different electrolytes. Different sized NPs show different stability when treated with multiple oxidation-reduction cycles in cyclic voltammetry (CV). The stability of Au NPs during oxidation-reduction cycling was monitored by observing the peak potential shift in anodic stripping voltammetry (ASV) and measuring the surface area-to-volume ratios (SA/V) after a different number of CV cycles. After 1000 CV cycles, the peak potential for ~2, 4 and 15 nm diameter Au NPs was shifted positive by 230 mV, 90 mV and 120 mV, respectively, compared to the untreated NPs. The surface area decreased with an increase in the number of CV cycles. The diameter, as calculated from the electrochemically-measured SA/V ratio, increased by ~10, 8 and 3-fold for 2, 4 and 15 nm Au NPs, respectively, which is in good agreement with the scanning electron microscopy (SEM) determined sizes. This electrochemical sintering behavior of Au NPs is particle size dependent, where smaller sized NPs undergo a greater extent of sintering than the bigger ones under identical conditions such as pH, NP coverage, and CV scan rates. The mechanism of NP sintering was determined by monitoring the oxidation-reduction process for 4 nm diameter Au NPs which was completely dissolved after 1000 CV cycles in acidic electrolyte. This result suggests that the NPs grow larger during oxidation-reduction cycling by Ostwald ripening, which was further confirmed by observing the size histogram from SEM images.