Exploring the unique electrochemical and chemical reactivity of sub 2 nm diameter catalytic Au NPs

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We compare the electrochemical and chemical reactivity of amine functionalized glass/indium tin oxide electrode attached sub 2 nm diameter tetrakis(hydroxymethyl)phosphonium chloride-stabilized nanoparticles (THPC Au_{2nm} NPs) to 4 nm diameter citrate-stabilized Au nanoparticles (Cit Au_{4nm} NPs). We found that the potential for oxidative dissolution of THPC Au_{2nm} NPs in the presence of bromide is 250 mV more negative than that of Cit Au_{4nm} NPs and 450 mV negative of that of bulk Au, showing the very high reactivity of the tiny 2 nm NPs towards oxidative dissolution. In acid electrolyte, the surface Au oxide formation and reduction of THPC Au_{2nm} NPs occurs at a significantly more negative potential from that of Cit Au_{4nm} NPs on the first potential cycle. On the second scan, both NPs show very similar voltammetry because the THPC Au_{2nm} NPs undergo an electrochemical restructuring to a larger size, making them more resistant to oxide formation. The THPC Au_{2nm} NPs undergo Ostwald ripening in the presence of bromide at 0.3 V vs. Ag/AgCl after 35 minutes, increasing their size to ~4 nm in diameter. In contrast, Cit Au_{4nm} NPs remain very stable for the same potential and time. Exposure to ozone causes the THPC Au_{2nm} NPs to increase in size within 8 minutes through some type of ripening mechanism, while no noticeable change occurs to the Cit Au_{4nm} NPs during the same time. We found a 200 mv positive shift in the oxidation peak of THPC Au_{2nm} NPs after 3 min of galvanic exchange with 1 μM $PtCl_4^{2-}$. In contrast, Cit Au_{4nm} NPs do not show any noticeable change in their oxidation peak potential. After galvanic exchange with $PtCl_4^{2-}$, THPC Au_{2nm} NPs show better catalytic reactivity for bromide oxidation than Cit Au_{4nm} NPs under a similar condition, showing that the smaller NPs exchanged with Pt, but the larger 4 nm NPs did not significantly. Another remarkable difference is that the THPC Au_{2nm} NPs show a strong CO_2 reduction wave at about -0.45 V (vs. Ag/AgCl) which is non-existent for the Cit Au_{4nm} NPs or bulk Au. Similarly, the THPC Au_{2nm} NPs are more active as electrocatalysts for the hydrogen evolution reaction (HER) compared to Cit Au_{4nm} NPs. All of these differences are attributed to the Au NP size as opposed to the different ligands, since the ligands themselves are weakly adsorbed and do not appear to significantly perturb the reactivity of the NPs relative to bare Au.