Supplementary Information

Butylphenyl-functionalized palladium nanoparticles as effective catalysts for the electrooxidation of formic acid

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1. Reagents and materials

Palladium chloride ($PdCl_2$, 59% Pd, ACROS), 4-butylaniline (97%, Aldrich), sodium borohydride ($NaBH_4$, 98%, ACROS), sodium nitrite ($NaNO_2$, 98%, ACROS), fluoroboric acid (HBF4, 50 wt% in water, ACROS), toluene (HPLC grade, Fisher Scientific), tetrahydrofuran (THF, HPLC grade, Fisher Scientific), sulfuric acid (H_2SO_4, Extra pure, 96%, ACROS), and formic acid (HCOOH, 99%, ACROS) were used as received. A commercial Pd black catalyst was purchased from Aldrich (#205834). Water was supplied by a Barnstead Nanopure water system (18.3 MΩ· cm).

2. Synthesis of butylphenyl-stabilized Pd (Pd-BP) nanoparticles

$PdCl_2$ (17.7 mg, 0.1 mmol) was dissolved in hydrochloric acid (0.5 mL) under heating condition. After most of water was evaporated, the product of H_2PdCl_4 was dissolved in THF (5 ml), and cooled with an ice-water bath. Butylphenyl diazonium was synthesized by following a literature protocol.[1] Briefly, to a beaker was added HBF_4 (0.5 mL) and 4-butylaniline (0.16 mL, 1 mmol). The solution was cooled in an ice-water bath, and stirred prior to the dropwise addition of a cooled $NaNO_2$ solution (69 mg, 1 mmol). After several minutes, the aqueous phase was removed, and the diazonium product was dissolved in ice-cold THF (20 mL). To the diazonium solution was added ice-cooled H_2PdCl_4 and toluene (30 ml). A yellow solution was formed, so no phase transfer of $PdCl_4^{2-}$ from aqueous to organic phases was needed in the present method, as compared with the previous synthesis.[2] Under magnetic stirring, $NaBH_4$ (saturated solution in THF, 20 mL) was then added dropwise to the above yellow solution. The solution color changed gradually from yellow to brown-green, and finally to dark brown, indicating the formation of Pd nanoparticles. Subsequently, the solution was washed with 0.1 M H_2SO_4 solution and water. After the solution was concentrated, the Pd nanoparticles were precipitated by ethanol, and further washed three times with ethanol to remove any excess of ligands and other impurities. Finally, the purified Pd nanoparticles were dissolved in toluene.

The exact Pd concentration in the final toluene solution was determined by a UV-Vis spectrophotometric method proposed by Morrow et al.[3] In this method, $PdCl_4^{2-}$ ions reacted with I^- in $HClO_4$, yielding a yellow-red PdI_4^{2-} complex ions with an absorption band at 408 nm. Prior to spectrophotometric analysis, Pd-BP nanoparticles were dissolved in aqua regia to form $PdCl_4^{2-}$, and the solution was carefully evaporated to a small volume in order to remove NO_3^- ions (note that NO_3^- must be removed completely; or else, it would oxidize I^- to colorful I_3^- during the formation of PdI_4^{2-}).

References

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3. J. J. Morrow and J. J. Markham, *Anal. Chem.*, 1964, **36**, 1159.