Electronic Supplementary Information (ESI)

Effect of Metal Precursor on the Growth and Electrochemical Sensing Properties of Pt-Ag Nanoboxes

A. Popa and A.C.S. Samia*

[a]*Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio, 44106 USA*
E-mail: anna.samia@case.edu; Fax: +1 (216)368-3006;Tel: +1 (216)368-3852

Experimental Methods

Synthesis of Ag NCs. Anhydrous ethylene glycol (EG, 6 ml) was heated at 150 °C for 1 h, which was followed by the addition of sodium sulfide (Na_2S, 80 µl, 3 mM in EG). The resulting reaction mixture was further heated at 150 °C for an additional 10 min, after which polyvinylpyrrolidone (PVP, MW 55,000, 1.5 mL, 0.18 M in EG) was added, which was immediately followed by the addition of silver nitrate ($AgNO_3$, 0.5 mL, 0.28 M in EG). The resulting reaction mixture was heated for 15 min, and the Ag NCs were separated through centrifugation and subsequently washed with acetone and water a total of five times. The resulting Ag NC sample was re-dispersed in 4 ml of deionized H_2O and stored in a refrigerator at 4 ^oC until it was used for the galvanic replacement reaction to form the Pt-Ag NBs.

Synthesis of Pt-Ag NBs from Ag NCs. To prepare Pt-Ag NBs from Ag NCs through galvanic replacement, a PVP solution (10 ml, 9 mM) containing 200 µl of Ag NCs was heated to boiling in a round bottom flask under vigorous stirring. The reaction mixture was refluxed for 10 min after which the Pt precursor (H_2PtCl_6 or Na_2PtCl_4, 0.1 mM) was added slowly (~0.75 ml min^{-1}). The mixture was further refluxed for an additional 10 min and then cooled down to room temperature. To remove AgCl by-product, NaCl was added until a saturated salt solution was obtained. The resulting Pt-Ag NB sample was centrifuged for 30 min at 7000 g and washed five times with deionized H_2O. The Pt-Ag NB sample was then re-dispersed in a 1:1 ethanol/ water solution and centrifuged, and subsequently dispersed in ethanol at a concentration of 0.75 mg/mL for the succeeding sample analyses.

Preparation of Pt-Ag NBs/G composites. The Pt-Ag NB sample (0.75 mg/mL) in ethanol was mixed with equal volumes of graphene - dimethylformamide solutions (0.5 mg/mL) and sonicated for 2 h. The Pt-Ag NB/G mixtures were then centrifuged at 13,000 rpm for 15 min, and washed with ethanol three times. Prior to the electrode deposition, the Pt-Ag NB/G sample was vacuum dried and re-suspended in acetic acid overnight, after which it was washed three times with deionized water, dried and re-dispersed in deionized water+isopropanol+5% Nafion (volume ratio of 4:1:0.025) to reach concentrations of 2 mg mL^{-1}. Twenty µL of these dispersions are deposited on the surface of the GC electrodes and allowed to air dry before they were used for electrochemical measurements.

AAS sample preparation. Pt-Ag NB samples were divided for Pt and Ag elemental analyses in a 9:1 ratio since the AAS sensitivity for Pt is much lower than that for Ag. The portion for Pt analysis was digested overnight in aqua regia then diluted with water and HCl to obtain a 10% HCl solution, which is required for the solubilisation of AgCl. To eliminate the interferences from Ag and HCl, which depress the Pt signal, copper sulphate was added to result in a 2% Cu solution (20,000 Cu ppm). The sample portion for Ag analysis was digested in nitric acid overnight and diluted with water to result in 7% nitric acid solution. The presence of Pt does not interfere with the detection of Ag, thus no additional treatments were necessary.

Amount of Pt Precursors Added (µmol)	%Pt Incorporated in Pt-Ag NBs using PtCl$_4^{2-}$	%Pt Incorporated in Pt-Ag NBs using PtCl$_6^{2-}$
0.125	**16%**	**18%**
0.250	**24%**	**37%**
0.500	**38%**	**49%**
0.750	**54%**	**77%**

Table S1. Elemental analysis data showing the difference in Pt content of Pt-Ag NBs prepared using two precursors with different oxidation states (Pt^{2+} and Pt^{4+}).

Figure S1. Schematic illustration of the growth of the platinum-silver nanobox with increasing amounts of Pt precursor.

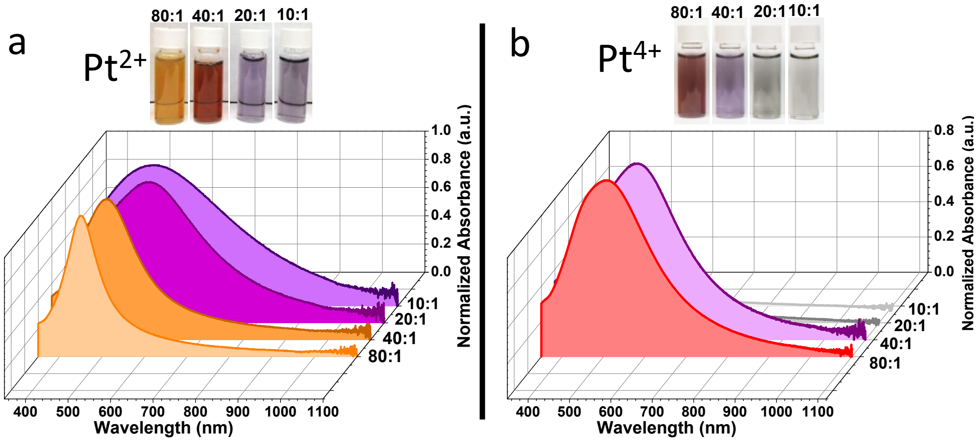


Figure S2. Photographs of Pt-Ag NB sample solutions and their corresponding absorption spectra obtained using Pt precursors with different oxidation states for Pt: a) Pt^{2+} and b) Pt^{4+}.

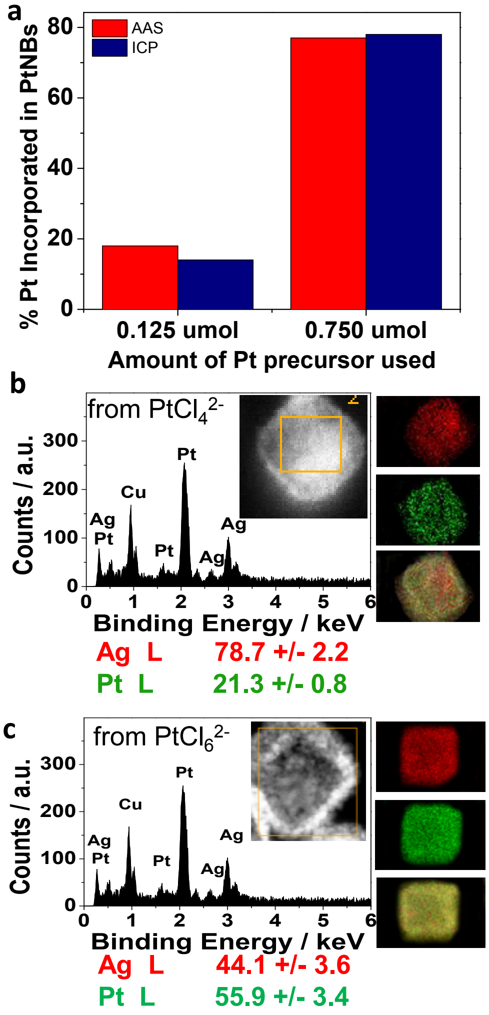


Figure S3. Comparison of Pt elemental analysis using AAS and ICP-AES methods (a), and x-ray energy-dispersive spectroscopic (EDX) analysis of the metal content of individual Pt-Ag NBs prepared using a 0.750 μmol of (b) Pt^{2+} and (c) Pt^{4+} based platinum precursors. The right-side panels represent the elemental maps for Ag (red), Pt (green) and an overlay for each Pt-Ag NB sample.

.

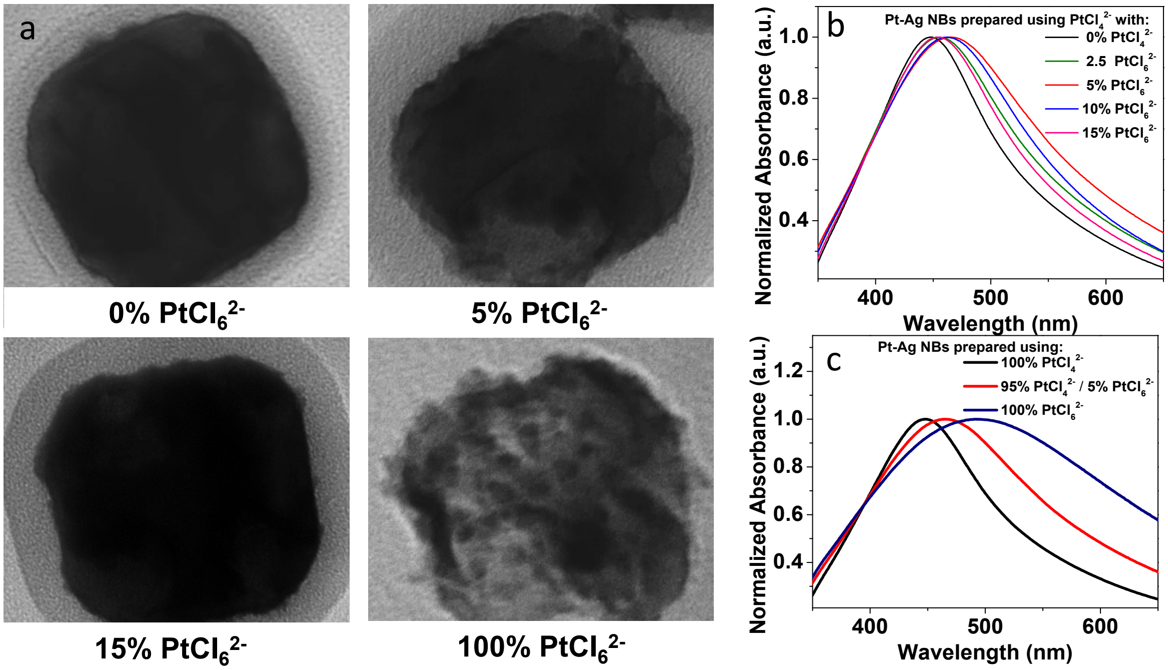
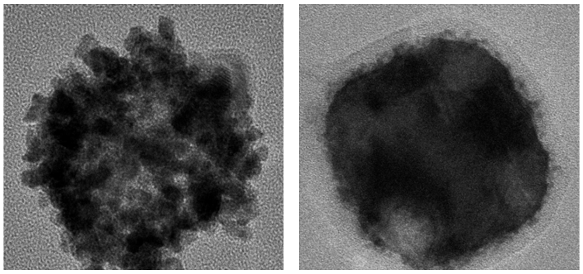


Figure S4. TEM images showing the morphology of Pt-Ag NBs prepared using different proportions of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ (a), and absorption spectra showing the plasmon band shift in the synthesized NBs (b and c).



1x molar concentration $PtCl_6^{2-}$

2x molar concentration $PtCl_4^{2-}$

Figure S5. High-resolution TEM images of Pt-Ag NBs prepared with $PtCl_6^{2-}$ and double the molar concentration of $PtCl_4^2$ showing the difference in morphology.

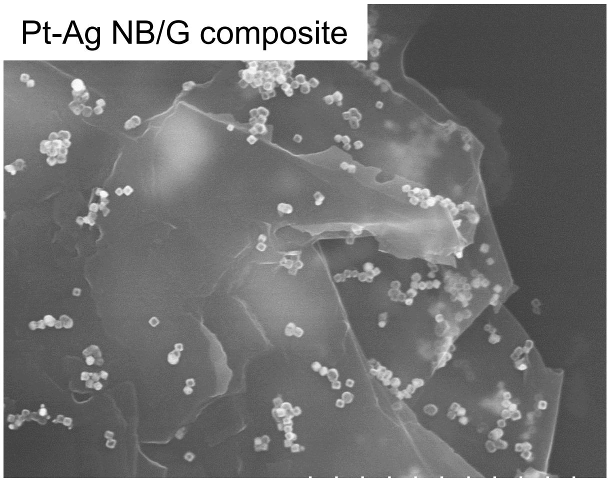


Figure S6. SEM image of a Pt-Ag NB/G composite.

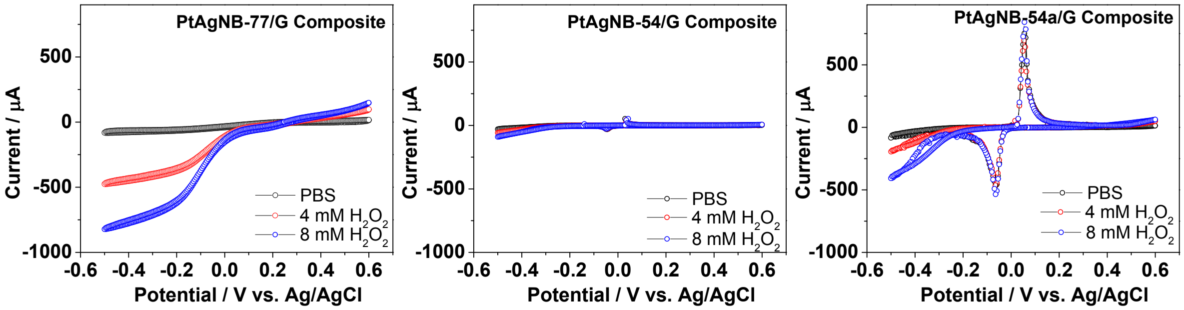


Figure S7. CVs obtained using a) Pt-Ag NB-77/G, b) Pt-Ag NB-54/G and c) Pt-Ag NB-54a/G (sample normalized for comparable Pt content to Pt-Ag NB-77/G) modified rotating disk glassy carbon electrodes in 10x PBS (pH 7.4) at 1200 rpm for different concentrations of H_2O_2. The Pt-Ag NB-77/G and Pt-Ag NB-54/G composites contain the same amount of Pt-Ag NBs by weight, while the Pt-Ag NB-77/G and Pt-Ag NB-54a/G composites contain the same amount of Pt by weight. The higher sensitivity of the Pt-Ag NB-77/G to hydrogen peroxide indicates that the difference can be also due to the suface morphology of the Pt-Ag NB-77sample rather than the total amount of Pt in the modified electrodes. The large oxidation and reduction features observed in the CV obtained using the Pt-Ag NB-54a/G modified electrode is due to the presence of large amounts of Ag from the increased amount of Pt-Ag NBs, which interacts with the Cl^- in the PBS solution. A AgNC/G modified electrode was previously prepared and tested and a similar profile was obtained.

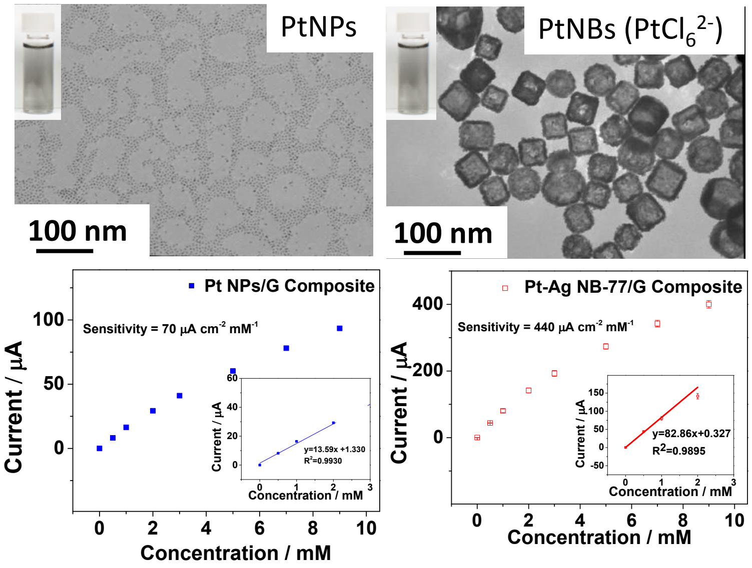


Figure S8. TEM images of small Pt nanoparticles and Pt-Ag NBs and the respective comparison of the electrocatalytic efficiency of modified GCE electrodes prepared using Pt NPs/G and Pt-Ag NB-77/G composites, respectively.