

Electronic Supporting Information

**Potential-Controllable Green Synthesis and Deposition of Metal Nanoparticles with
Electrochemical Method**

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S1 - Experimental Section

Chemicals and reagents

1-n-Butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆) was synthesized and purified as follows. Typically, 1-Butyl-3-methylimidazolium chloride was first prepared by reaction of equal molar amounts of 1-methylimidazole and chlorobutane in a round-bottomed flask fitted with a reflux condenser by heating and stirring at 70 °C for 48 h. The resulting viscous liquid was allowed to cool to room temperature and then was washed three times with 200 mL portions of ethyl acetate. After this, the remaining ethyl acetate was removed by heating to 70 °C under vacuum. To prepare the BmimPF₆ ionic liquid, hexafluorophosphoric acid (1.3 mol) was dropped added (slowly to prevent the temperature from rising significantly) to a mixture of 1-butyl-3-methylimidazolium chloride (1 mol) in 500 mL of water. After stirring for 12 h, the upper acidic aqueous layer was decanted and the lower ionic liquid portion was washed with water (5×500 mL) until the washings were no longer acidic. The ionic liquid was then heated under vacuum at 70 °C to remove any excess water.

Electrochemical experiments and characterization

Electrochemical experiments were conducted on computer-controlled BAS 100B/W electrochemical analyzer (BAS). The three-electrode system was used as shown in Scheme 1. Indium tin oxide (ITO) electrode was used as working electrode, and a platinum spiral wire was used as counter electrode, Ag wire was used as a quasi-reference electrode. The potential of the quasi-reference electrode was calibrated to be -0.30 V vs. Ag/AgCl (KCl-Sat.) electrode with ferrocenecarboxylic acid as the redox probe [1]. In a typical preparation, certain concentrations of H₂PtCl₆ precursor were dissolved into BmimPF₆ and the electrolysis was then carried out in the potential-controlled manner at room temperature with different potentials. All electrochemical experiments were carried at room temperature. The electrodeposited Pt nanoparticles were rinsed thoroughly with distilled water prior to characterization. Pt nanoparticles dispersed in the solution were isolated by centrifugating the dispersion at 5000 rpm for 5 min, washed with acetone (3×15 mL) and dichloromethane (3×15 mL), and finally dried under reduced pressure prior to characterization.

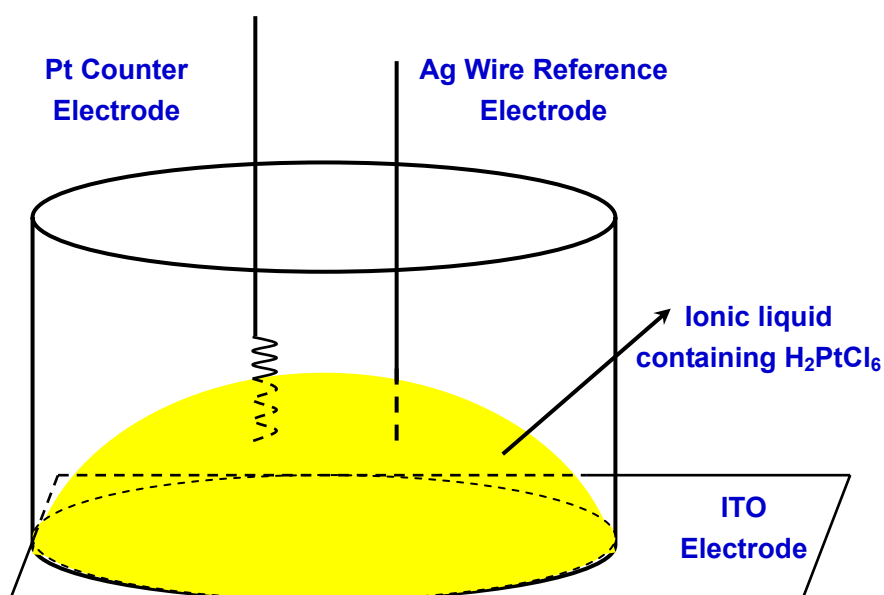
X-ray photoelectron spectroscopy (XPS) used for characterization of Pt nanoparticles was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al KR radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. The powder X-ray

diffraction (XRD) patterns of the synthetic Pt nanoparticles were recorded on Rigaku Dmax 2000 X-ray diffractometer with Cu K α radiation. Scanning electron microscopy (SEM) used for characterization of Pt nanoparticles electrodeposited from the IL droplet containing H₂PtCl₆ supported onto the ITO electrode was performed with Hitachi S4300-F microscope (Hitachi Inc., Tokyo, Japan). Transmission electron microscope (TEM) used for characterization the morphology of the Pt nanoparticles were performed with a JEM-1011.

References

- [1] V. M. Hultgren, A. W. A. Mariotti, A. M. Bond, A. G. Wedd *Anal. Chem.* 2002, **74**, 3151-3156.

S2 - Scheme S1 Schematic illustration of experimental setup for electrochemical formation of Pt nanoparticles with IL as the green medium supported onto ITO electrode.



S3 - XPS and XRD results of electrodeposited Pt nanoparticles

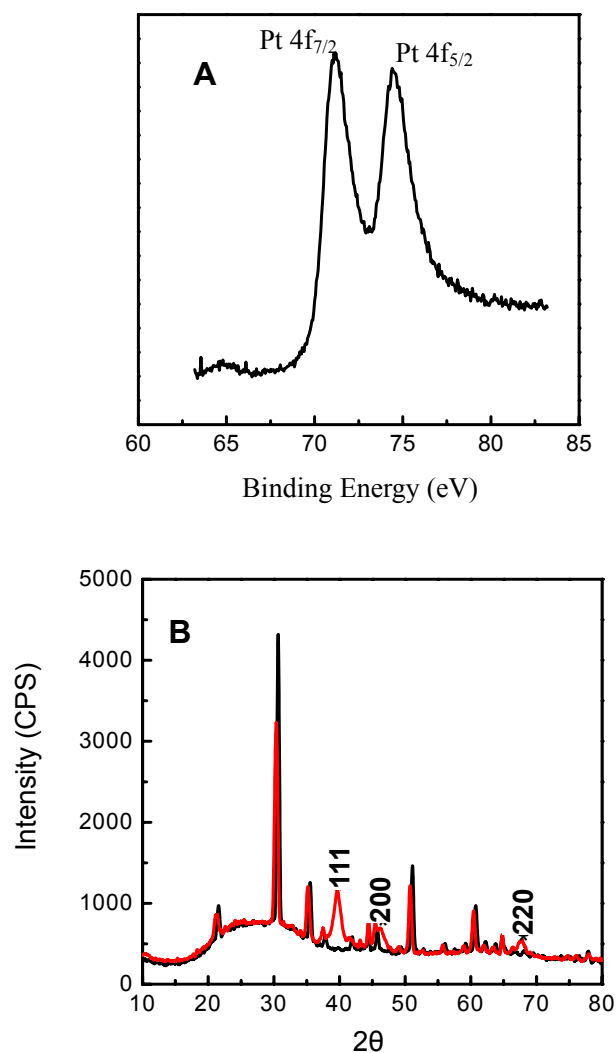


Figure S1. (A) XPS spectrum for Pt 4f of the Pt nanoparticles deposited onto the ITO substrate prepared by polarizing the substrate at -2.8 V vs. Ag/AgCl for 1000 s in ionic liquid containing 20 mM H₂PtCl₆. (B) XRD patterns of pure ITO substrate (black curve) and the substrate deposited with Pt nanoparticles (red curve) under the same condition mentioned above.

S4 - XPS and XRD results of electrosynthetic Pt nanoparticles

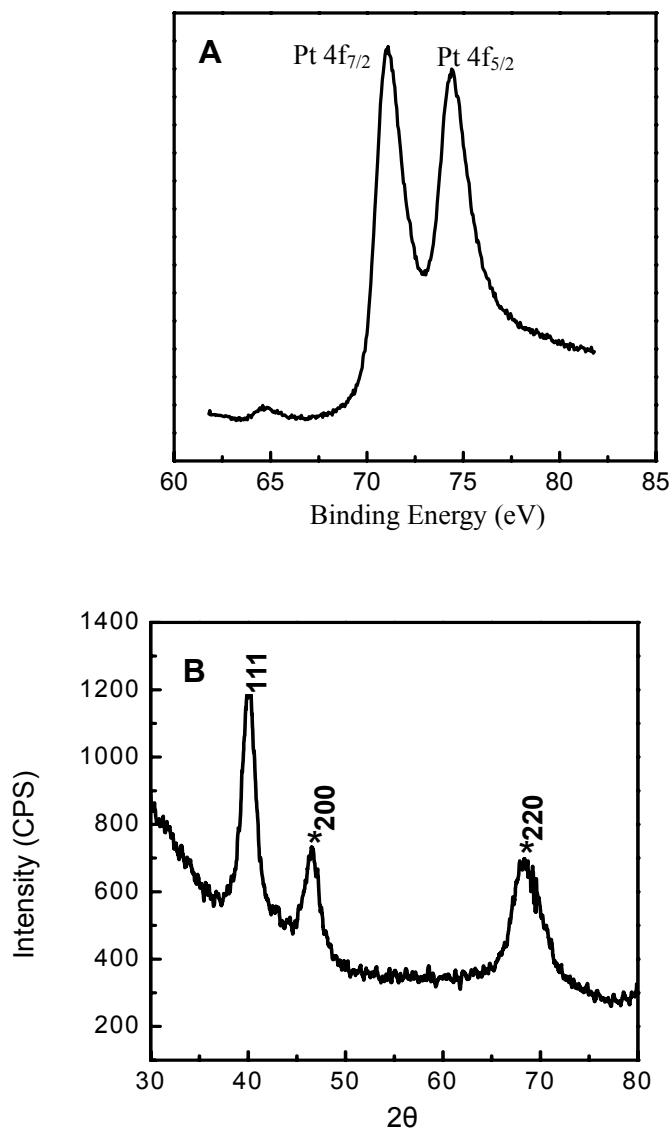


Figure S2. XPS spectrum for Pt 4f (A) and XRD pattern (B) of the synthetic Pt nanoparticles prepared by polarizing the ITO substrate at -1.8 V vs. Ag/AgCl for 4000 s in IL solution containing 20 mM H₂PtCl₆.

S5 - Cyclic voltammetric results in BmimPF₆ containing 20 mM H₂PtCl₆

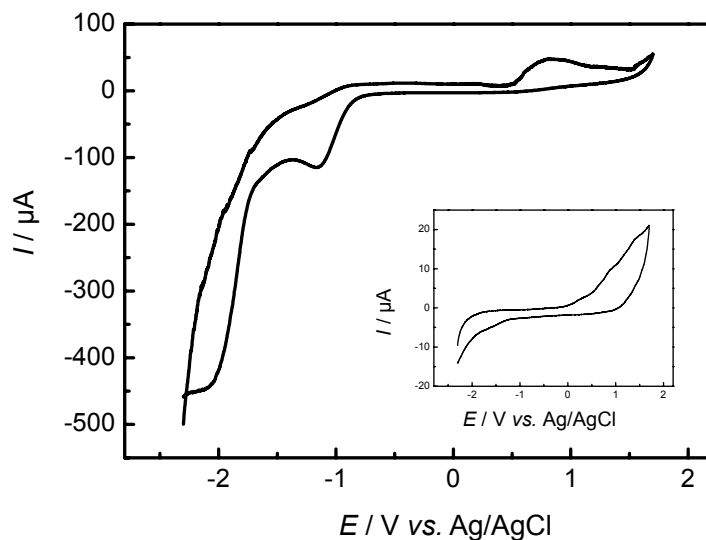


Figure S3. Cyclic voltammogram (CV) obtained at ITO electrode in BmimPF₆ containing 20 mM chloroplatinic acid hexahydrate. Inset, CV at ITO electrode in pure BmimPF₆ (i.e., containing no chloroplatinic acid hexahydrate). Scan rate, 100 mV/s.

As shown in Figure S3, two well-defined reduction peaks at *ca.* -1.0 and -2.0 V were obtained at ITO electrode in BmimPF₆ containing 20 mM chloroplatinic acid hexahydrate, which were ascribed to the reductions of platinum (IV) to platinum (II) and platinum (II) to platinum nanoparticles [2]. The onset potential for formation of platinum nanoparticles was *ca.* -1.6 V. This value was used as the reference for choosing the potentials for controllable electrodeposition and synthesis of Pt nanoparticles in this study.

References

- [2] P. He, H. Liu, Z. Li, J. Li *J. Electrochem. Soc.* 2005, **152**, E146-E153.