

## Electronic Supplementary Information (ESI)

### Detailed Preparation Procedure:

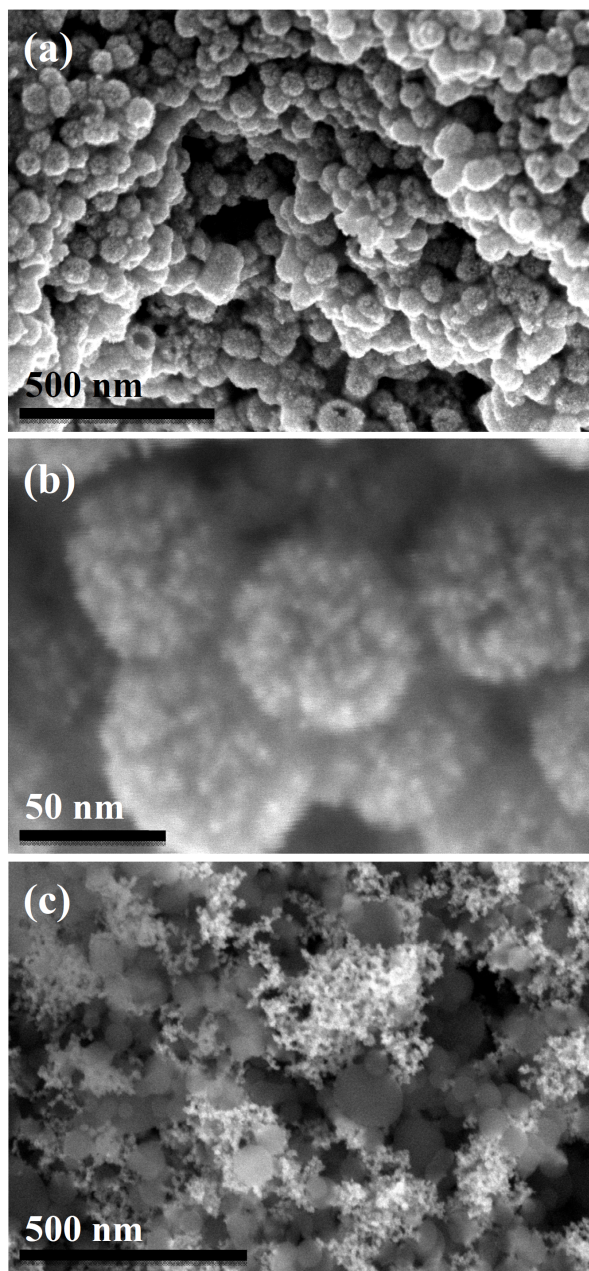
For the preparation of the Pt hollow spheres, the surface of the silica particles was modified with aminopropyltriethoxysilane (APTES) firstly. The suspension of silica nanoparticles (Average particle diameter: 100 nm, Nissan Chemical Industries, Ltd.) was added to 50 ml tetrahydrofuran (THF) solution including 10 wt% APTES. After stirring for 12 h at room temperature, the APTES-modified silica particles were precipitated. Then, the modified silica particles were washed with THF and water in consecutive washing/centrifugation cycles for three times in order to remove excess APTES and form a smooth and homogenous layer of APTES on silica particles. Since the amount of modified APTES on the silica surface was not sufficient, it was difficult that the APTES was detected by IR and NMR measurements. So, here the modification of APTES was confirmed by ninhydrin reaction (not shown). In a typical synthesis, the organically modified silica particles (6.0 mg) was ultrasonically dispersed in 20 mM  $K_2PtCl_4$  solution (7.5 ml) containing 0.05 g Pluronic F127. Then, 0.1 M ascorbic acid (AA) (5 ml) was added, and the mixture was sonicated for 15 min. After washing three times with water, the product was added to 10 wt% hydrofluoric acid solution (20 ml) and placed for 3 days at room temperature in order to completely remove silica template. The removal of silica was checked by ICP analysis. The final product was washed five times with water and dried at 45 °C.

### Electrocatalytic Experiment:

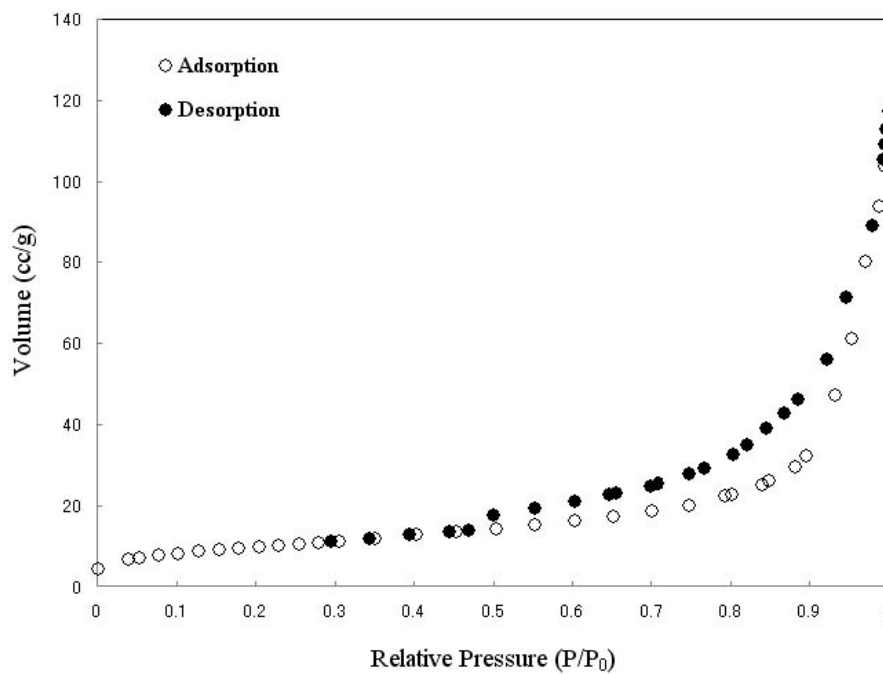
All cyclic voltammetry (CV) experiments were performed using a CHI 842B electrochemical analyzer (CHI Instruments, USA). A conventional three-electrode cell was used, including an Ag/AgCl (saturated KCl) electrode as a reference electrode, a platinum wire as a counter electrode, and a modified glassy carbon electrode (GCE) (3 mm in diameter) as a working electrode. The modified GCE was coated with the samples and dried at room temperature before each experiment. The loading

amount in all of the samples was 3.0  $\mu\text{g}$ . Methanol electro-oxidation measurements were performed in a solution of 0.5 M  $\text{H}_2\text{SO}_4$  that contained 0.5 M methanol at a scan rate of 50 mV/s.

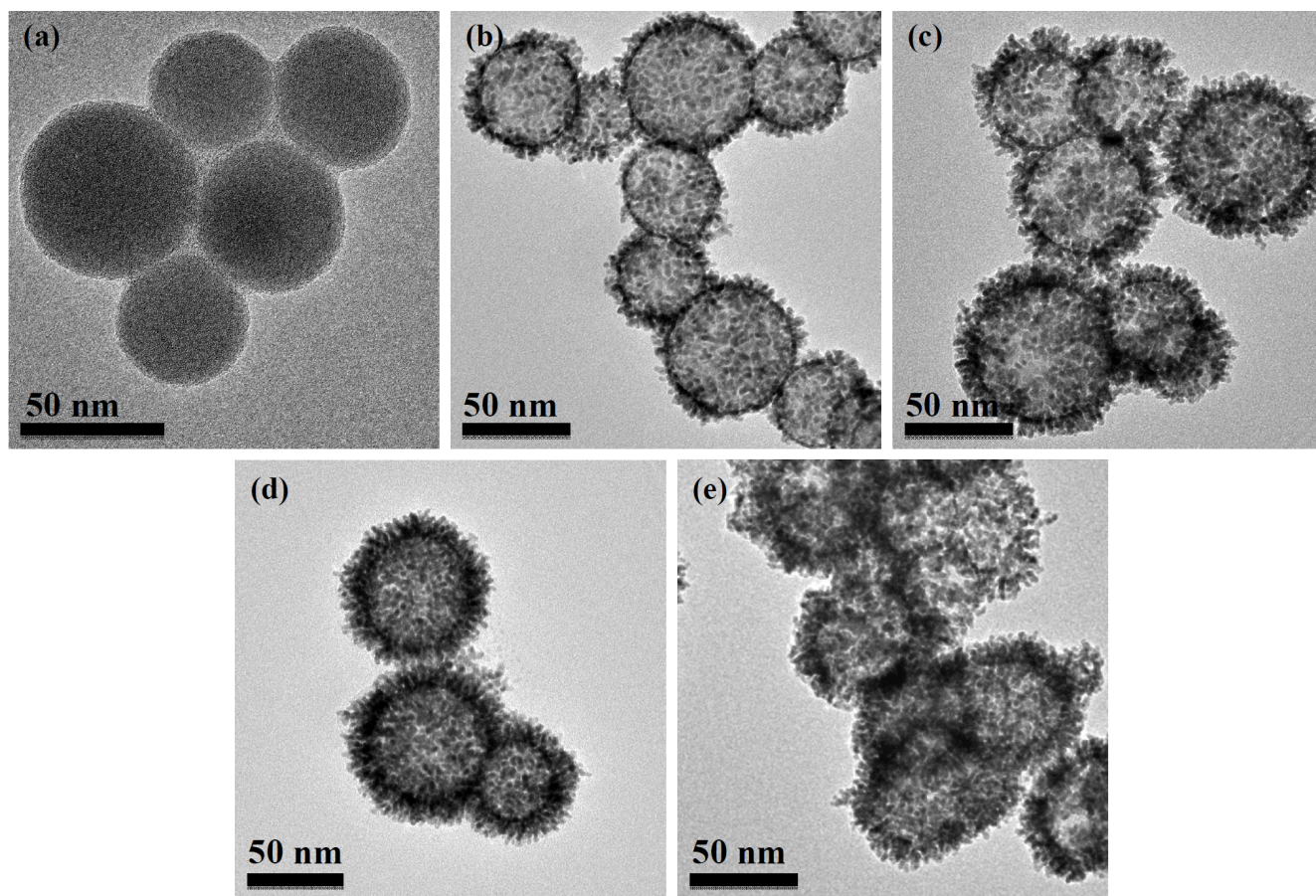
**Figure S1**



**Figure S1** (a) Low-magnification and (b) high-magnification SEM images of hollow Pt spheres (after silica removal) prepared using amino-functionalized silica particles under a typical solution containing 5 7.5 ml Pt solution. (c) Low-magnification SEM image of the deposited Pt obtained by using non-functionalized silica particles.



**Figure S2** N<sub>2</sub> adsorption-desorption isotherm of hollow Pt spheres prepared from a typical solution containing 7.5 ml Pt solution.



**Figure S3** TEM images of (a) the original silica template and (b~e) the obtained Pt products (before silica removal) prepared from precursor solutions containing different Pt amounts. The amounts of added Pt solution are (b) 2.5 ml, (c) 5.0 ml, (d) 7.5 ml, and (e) 10 ml, respectively.