Supporting Information

Simultaneous Reduction-Etching Route to Pt/$ZnSnO_3$ Hollow Polyhedral Architectures for Methanol Electrooxidation in Alkaline Media with Superior Performance

Han Jiang, Baoyou Geng *, Long Kuai and Shaozhen Wang

College of Chemistry and Materials Science, Anhui Key Laboratory of Functional Molecular Solids, Anhui Laboratory of Molecular-Based Materials, Anhui Normal university, Wuhu, 241000, P. R. China. Fax: (+86)-553-3869303; E-mail: bygeng@mail.ahnu.edu.cn.

1. Experimental Section

All chemical reagent used as received without further purification. Zinc acetate dihydrate ($ZnAc_2$•$2H_2O$, AR), sodium hydroxide (NaOH, AR) and Stannic chloride pentahydrate ($SnCl_4$• $5H_2O$, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Cetyltrimethyl Ammonium Bromide (CTAB), Sodium Dodecyl Benzene Sulfonate (SDBS) and PolyVinyl Pyrrolidone (PVP, K30) were purchased from BASF (Germany). Chloroplatinic acid hexahydrate (H_2PtCl_6•$6H_2O$, AR) were purchased from JiNan LuLi Chemical Factory (Shan Dong, China). The Commercial Pt/C electrocatalyst (the loading of Pt is about 40 % and Pt nanoparticles is about 2.8 nm) are purchased from YiBang/RuiBang New Power Sources Technology Co. LTD.

Synthesis of $ZnSnO_3$ polyhedra. In a typical synthesis, a solution of $SnCl_4$· $5H_2O$ in water (0.5 M, 5 mL) was added to a solution of $ZnAc_2$·$2H_2O$ (0.5 M, 5mL) after adding 0.2275 g CTAB at room temperature with vigorous agitation, and a solution of NaOH (3 M, 10 mL) were added to the mixture, which was stirred for 15 min in a beaker. Then, the mixture was transferred to a microwave reaction device (WF-4000)

and heated at 85 °C for 1.5 h. Subsequently, the obtained mixture slurries were centrifuged and the products were washed with distilled water and absolute alcohol for several times, and dried at 60 °C for 6 h in a vacuum oven.

Synthesis of $ZnSnO_3$ hollow polyhedra. 0.05 g $ZnSnO_3$ 14-faceted polyhedron power was added to 7.5 ml water, then, 2.5 ml HCl solution (1.0 M) drop the suspension, stir for 4 h at 15 °C. The products were washed with distilled water and absolute alcohol for several times, and dried at 60 °C for 6 h in a vacuum oven.

Synthesis of the Pt/$ZnSnO_3$ hollow polyhedra composite catalysts. We used the L-ascorbic acid as reductant to reduce the $H_2PtCl_6 \cdot 6H_2O$ in the water environment. Briefly, 0.5 ml $H_2PtCl_6 \cdot 6H_2O$ (0.019 M) was added to 10 mL ice water rapidly under a strong agitation. Then, 10 mL L-ascorbic acid ice-water solution (0.1 M) was drop slowly to above mixture. Next, 0.005 g $ZnSnO_3$ polyhedra power was dropped to the above pale-yellow solution, and stirred for 10 minutes. Subsequently, the solution was placed in an ultrasonic cleaning instrument and treated for 1h, and then the solution was deposited for 24 h. The obtained products were washed with distilled water and absolute alcohol for several times, and dried at 60 °C for 6 h in a vacuum oven.

Synthesis of the Pt/$ZnSnO_3$ solid polyhedra composite. In this experiment, $NaBH_4$ was used as the reductant. Typically, 0.085 g $NaBH_4$ powder was dissolved into 10 ml ice water, then 0.5 ml $H_2PtCl_6 \cdot 6H_2O$ (0.019 M) and 0.025 g CTAB was added to above solution. After strong stirring 10 min, 0.05 g $ZnSnO_3$ hollow polyhedra product was added into above solution and stirred for another for 10 min; subsequently, the solution was ultrasonic treated for 30 min and then the solution was deposited for 24 h.

The obtained products were washed with distilled water and absolute alcohol for several times, and dried at 60 °C for 6 h in a vacuum oven.

Characterizations. X-ray powder diffraction (XRD) was carried out on an XRD-6000 (Japan) X-ray diffractometer with Cu-Kα radiation (λ=1.54060 Å). Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) micrographs were performed using JEM 2010F microscopes. X-ray Photoelectron Spectroscopy (XPS) was performed on the Thermo ESCALAB 250.

Electrochemical Measurements. The electrocatalysis activity experiments were controlled and recorded with CHI-660C electrochemical workstation. The modified electrode was prepared as follows: GC electrodes (3 mm diameter) were carefully polished with a diamond pad/0.3 μm polishing suspension, rinsed with distilled water and ethanol. 10 mg Pt/$ZnSnO_3$ polyhedra nanocomposite was dissolved in a mixture of Nafion and ethanol (0.5 %, 1 mL). Approximately 10 min of ultrasonication was necessary to obtain a uniformly dispersed nanocomposite catalyst. After dropping 10 μL of the nanostructure suspension onto the electrode surface, the electrode was dried in air. The electrochemical impedance spectroscopy was measured in 0.1 mol L^{-1} KNO_3 solution containing 5.0 mmolL^{-1} $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ (1:1). The cyclic voltammograms (CVs) experiments were performed in 0.5 M N_2-saturated KOH aqueous solution at a scan rate of 50 mVs^{-1}. Electrocatalytic properties for methanol oxidation of the product were measured in a mixture of 0.5 M methanol and 0.5 M KOH. Current-time curve of the product was recorded at -0.2 V.

2. Additional Images.

2.1. Figure S1

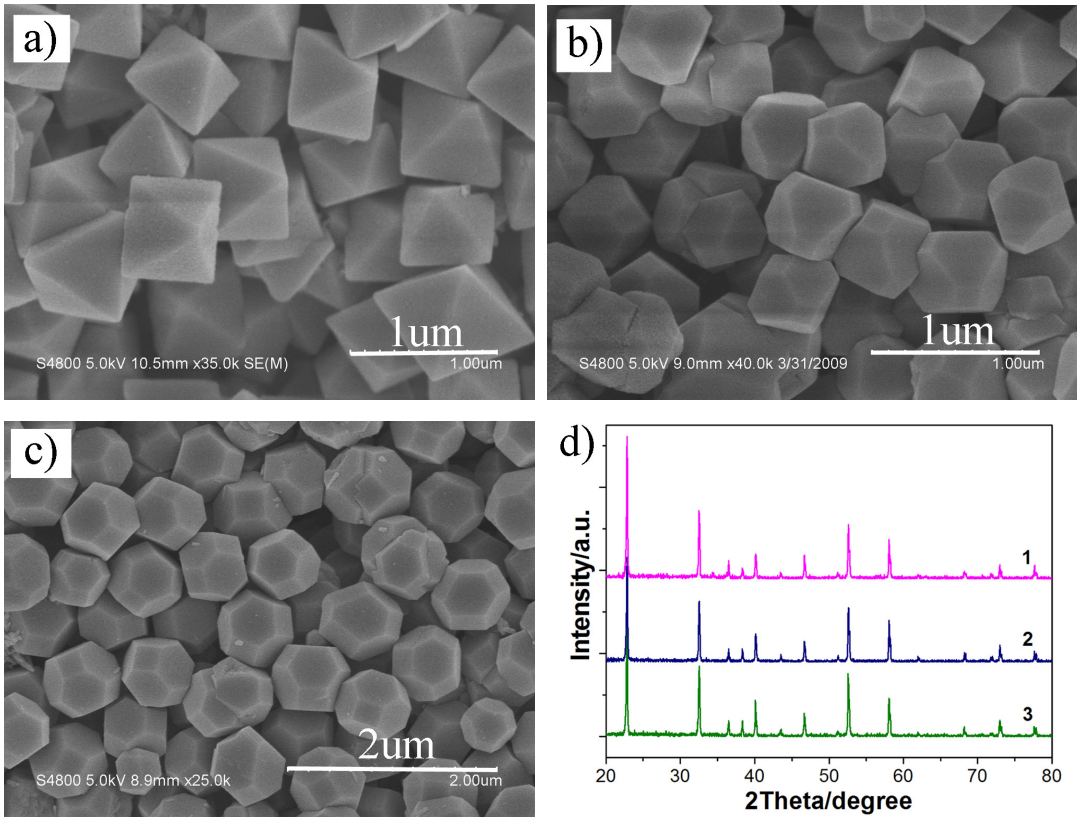

Figure S1. The SEM images of $ZnSnO_3$ polyhedra. a) Octahedral $ZnSnO_3$; b) truncated octahedral $ZnSnO_3$; c) 14-faceted polyhedral $ZnSnO_3$; d) the XRD patterns of the as-prepared $ZnSnO_3$ polyhedra (1, Octahedral $ZnSnO_3$; 2, truncated octahedral $ZnSnO_3$; 3, 14-faceted polyhedral $ZnSnO_3$).

2.2. Figure S2

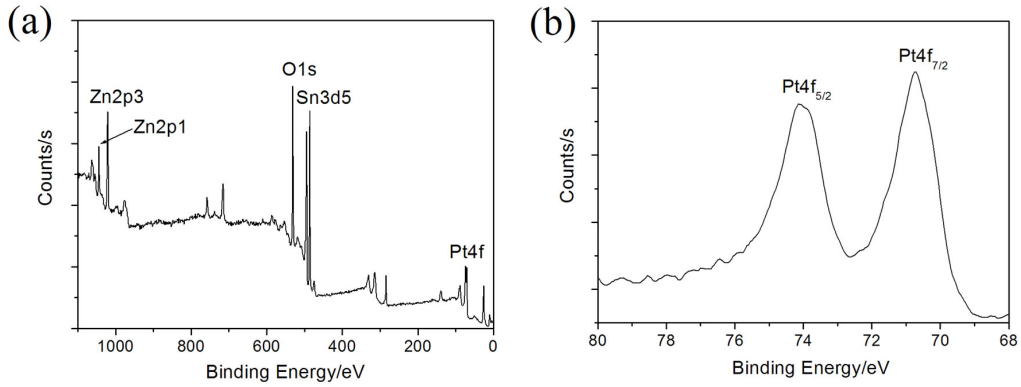

Figure S2. XPS spectra of the Pt/$ZnSnO_3$ hollow polyhedra composite. (a) Survey scan; (b) high-resolution XPS spectrum of the Pt 4f region. The main peaks found in the survey scan were Zn 2p (1017.75 ev), Sn 3d (486.82 ev) O 1s (531.5 eV) and Pt 4f (70-75 ev), all of which correspond to Pt/$ZnSnO_3$ hollow polyhedra composite. The high-resolution XPS spectrum of the Pt 4f region (Figure S3 b) revealed the existence of Pt with a binding energy of Pt $4f_{7/2}$=70.72 eV and $4f_{5/2}$=74.30 eV, which are in good agreement with the expected value for Pt^0.

2.3. Figure S3

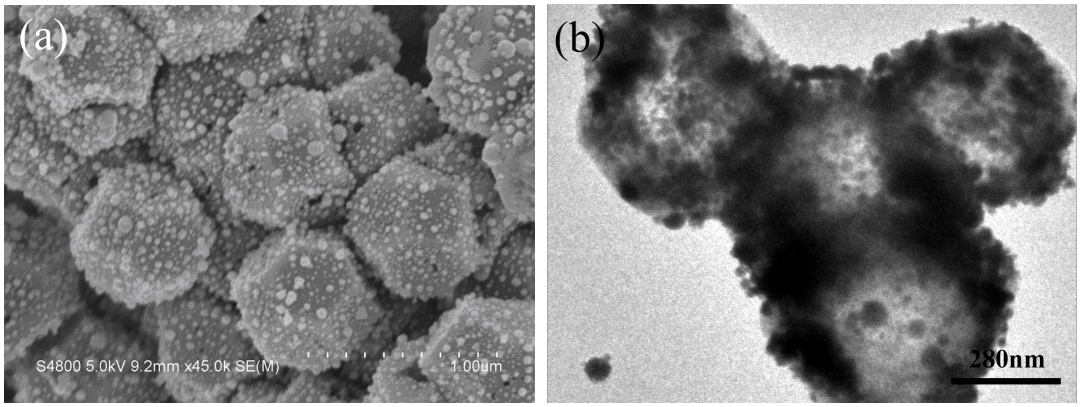

Figure S3. (a) SEM and (b) TEM images of Pt/$ZnSnO_3$ hollow polyhedra nanocomposite obtained by using HCHO or $NaBH_4$ as the reductant and hollow $ZnSnO_3$ polyhedra as precursor. The diameter of the as-prepared Pt NPs is biggish (~30 nm) and dispersed inhomogenously.

2.4. Figure S4

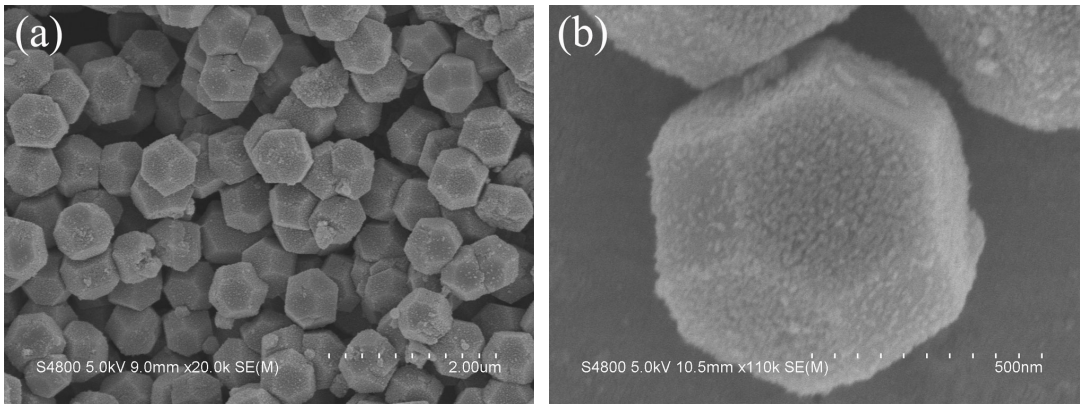

Figure S4. Low- (a) and high-magnification (b) SEM images of $Pt/ZnSnO_3$ solid polyhedra nanocomposite obtained by $ZnSnO_3$ solid polyhedra in the presence of a reductant HCHO or $NaBH_4$ and the diameter of Pt NPs is about 5 nm.

2.5. Figure S5

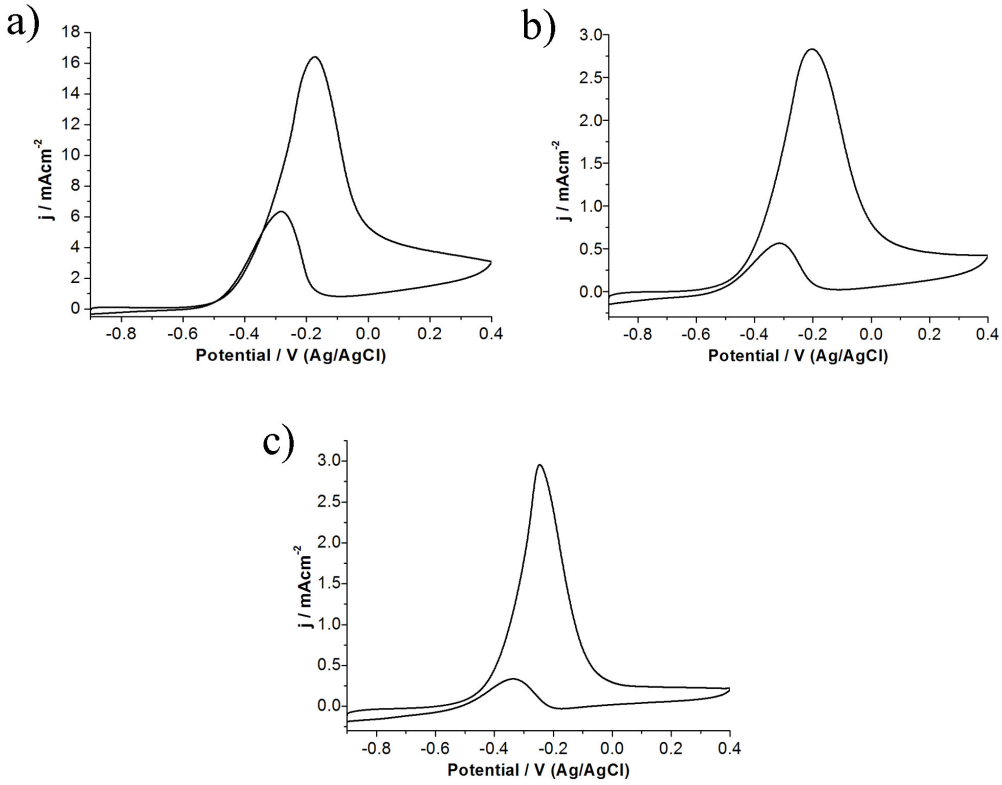

Figure S5. The methanol oxidation curves of the as-prepared products in a mixture of 0.5 M methanol and 0.5 M KOH (50 mVs^{-1}), a) $Pt/ZnSnO_3$ hollow polyhedra composite, b) $Pt/ZnSnO_3$ solid polyhedra composite, and c) Pt/XC-72 carbon composite.

2.6. Figure S6

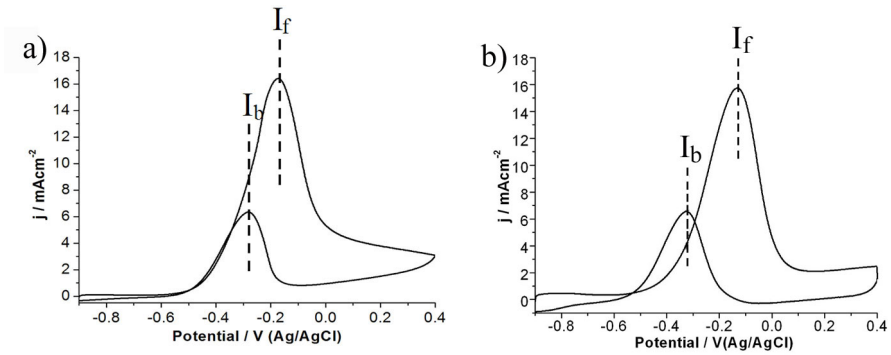

Figure S6. The methanol oxidation curves of a) $Pt/ZnSnO_3$ hollow polyhedra composite and b) the pure Pt nanoparticles in a mixture of 0.5 M methanol and 0.5 M KOH (50 mVs^{-1}).

Explanation of Figure S6:

The ratio of the two anodic peak current densities, I_f/I_b (I_f: forward scan, I_b: back scan), can be used as an indicator of the catalyst tolerance to the CO-like carbonaceous species. The lower ratio of I_f/I_b represents the poorer oxidation of CH_3OH to the final product (CO_2) during the forward anodic scan and more accumulation of carbonaceous species on the surface of catalyst [1-5]. That is, a higher I_f/I_b value indicates the known more excellent CO-tolerance. According to the calculation based on the Figure S6, the I_f/I_b of $Pt/ZnSnO_3$ hollow composite is 2.8, while that of the pure Pt nanoparticles is about 2.4, indicating that the obtained $Pt/ZnSnO_3$ hollow polyhedra composite exhibit better CO-tolerance than that of Pt nanoparticles, from which we deduce that the hollow $Pt/ZnSnO_3$ nanocomposite has a certain degree of alloy property through the complex of Pt with Sn in the $ZnSnO_3$.

Reference

[1] D. Villers, S. H. Sun, A. M. Serventi, J. P. Dodelet, *J. Phys. Chem. B* 2006, **110**, 25916.

[2] S. H. Sun, G. X. Zhang, D. S. Geng, Y. G. Chen, M. N. Banis, R. Y. Li, M. Cai, X. L. Sun, *Chem. Eur. J.* 2010, **16**, 829.

[3] M. M. Dimos, G. J. Blanchard, *J. Phys. Chem. C* 2010, **114**, 6019.

[4] J. B. Jia, L. Y. Cao, Z. H. Wang, *Langmuir* 2008, **24**, 5932.

[5] A. Halder, S. Sharma, M. S. Hegde, N. Ravishankar, *J. Phys. Chem. C* 2009, **113**, 1466l.