Supplemental Information

# Size-dependent synthesis and catalytic activities of trimetallic PdAgCu mesoporous nanospheres in ethanol electrooxidation

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### 1. Chemicals

Palladium(II) chloride (PdCl<sub>2</sub>), chloroauric acid (HAuCl<sub>4</sub>), chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>), ruthenium(III) chloride (RuCl<sub>3</sub>), silver nitrate (AgNO<sub>3</sub>), copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>), Iron(III) nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>), commercial palladium black (PdB) nanoparticles, dioctadecyldimethylammonium chloride (DODAC), octadecyl trimethyl ammonium chloride (C<sub>18</sub>TAC), Pluronic F127, and L-ascorbic acid (AA) were obtained from Alfa Aesar. Nafion solution (5 wt% in alcohol and H<sub>2</sub>O) was purchased from Sigma Aldrich. Hydrochloric acid (HCl), ethanol, sodium hydroxide (NaOH) and potassium hydroxide (KOH) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). N-(2-carboxyethyl)-N,N-dimethyloctadecan-1-ammonium chloride (C<sub>18</sub>TAOC) was synthesized according to our previous report.<sup>1</sup> 10 mM (mmol/L) H<sub>2</sub>PdCl<sub>4</sub> solution was obtained by dissolving 0.355 g of PdCl<sub>2</sub> with 20 mL of 0.2 M HCl solution in a 200 mL volumetric flask and further bringing to volume by deionized H<sub>2</sub>O. All the reagents are of analytical reagent grade and used without further purification. Deionized H<sub>2</sub>O with the resistivity of 18.25 mΩ was used in all experiments.

#### 2. Synthesis of trimetallic PdAgCu mesoporous nanospheres (MNSs)

Trimetallic PdAgCu MNSs were synthesized by a one-pot solution-phase route with the structure-directing surfactant of DODAC, the co-metal precursors of  $H_2PdCl_4$ , AgNO<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>, the reducing agent of AA, and the co-solvents of ethanol and H<sub>2</sub>O at 25 °C. In a typical synthesis of the MNS-58, 3 mg of DODAC was first dissolved in 10 mL of co-solvents with ethanol/H<sub>2</sub>O volume ratio of 2 : 8. Then, 0.2 mL of NaOH (100 mM) was added to tune pH of reaction solution. After that, 0.48 mL of H<sub>2</sub>PdCl<sub>4</sub> solution (10 mM) was added to above homogeneous solution. After stirred for 10 min, 0.24 mL of AgNO<sub>3</sub> (10 mM) and 0.08mL of Cu(NO<sub>3</sub>)<sub>2</sub> (10 mM) were successively injected, and kept undisturbedly for an additional 30 min. Subsequently, 1.0 mL of freshly prepared AA (0.3 M) was rapidly injected into above solution under gentle shaking. After reacted for 30 min, PdAgCu MNS-58 was obtained by centrifugation and washed by acetic acid, ethanol and H<sub>2</sub>O for three times. We calculated the reaction yields via the real weight of obtained PdAgCu MNS-58 and acquired a conversion efficiency of nearly 80% (atomic percentage). Considering the loss of PdAgCu nanomaterials during the washing and centrifugation procedures for the removal of surfactants and other reactants, the real conversion efficiency would be higher than 80%. Similarly, PdPtAg, PdAgFe, PdPtCu and PdCuRu MNSs were synthesized using the above procedures by simply changing the species of metal precursors. Besides, pH, ethanol contents, concentrations and species of surfactants were also changed to tune the sizes and nanostructures of as-resulted trimetallic PdAgCu nanoalloys under the similar procedures.

## 3. Electrochemical ethanol oxidation reaction (EOR) measurements

Electrocatalytic EOR tests were carried out on the CHI 660E electrochemical analyzer at 25 °C. For all electrochemical tests, the three-electrodes system was employed with the working electrode of glassy carbon electrode (GCE, 0.07065 cm<sup>2</sup>), the counter electrode of the carbon rod, and the reference electrode of the saturated calomel electrode. Before electrocatalytic tests, all the nanocatalysts were first cleaned with acetic acid to remove the surfactants inside MNSs.<sup>2</sup> An ink of the nanocatalysts was prepared by mixing 1 mg of nanocatalysts, 4 mg

of Valcan XC-72 carbon, 1.5 mL of ethanol and 0.5 mL of H<sub>2</sub>O. After the sonication for 30 min, 50  $\mu$ L of Nafion solution was added and further sonicated for an additional 30 min. After that, 6  $\mu$ L of freshly-prepared ink solution was dropped on the GCE electrode and dried before test. CVs were then scanned until the stabilized curves were obtained for further removal of the surfactant in 1.0 M KOH.<sup>3</sup> The electrolyte solution was initially purged with N<sub>2</sub> for 30 min to remove O<sub>2</sub> and other gas before test. CVs were used to evaluate the ECSAs (1.0 M KOH) and activities (1.0 M KOH and 1.0 M ethanol) of the nanocatalysts at different scan rates.

## 4. Characterizations

TEM and high-resolution TEM studies were collected using a JEOL 2100 TEM with an accelerating voltage of 200 kV. STEM mappings and corresponding line scans were performed on FEI Talos F200X apparatuses equipped with STEM and EDS detectors. TEM and STEM samples were prepared by dropping a suspension of the samples (in ethanol and/or H<sub>2</sub>O) on carbon coated nickel grids (300 mesh). XRD patterns (both small-angle and wide-angle) were carried out on powder samples using a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite-monochromatized Cu K $\alpha$  radiation. XPS was collected on a scanning X-ray microprobe (Thermo ESCALAB 250Xi) that uses Al K $\alpha$  radiation, and C 1s peak (284.8 eV) was employed as a standard to calibrate the binding energies of other elements.

#### Reference

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Fig. S1 Chemical structures of the surfactants (DODAC,  $C_{18}TAC$ ,  $C_{18}TAOC$  and F127) used in this work.



Fig. S2 TEM images of trimetallic PdAgCu nanostructures synthesized with (a, b)  $C_{18}TAC$ , (c, d)  $C_{18}TAOC$  and (e, f) F127.



**Fig. S3** TEM images of trimetallic PdAgCu MNSs synthesized with different pH value of (a, b) 5.76, (c, d) 6.03, (e, f) 6.34, (g, h) 7.92, (i, j) 9.33 and (k, l) 10.61.



**Fig. S4** TEM images of trimetallic PdAgCu nanostructures synthesized with the lower pH value of (a, b) 4.18 and (c, d) 4.97.



**Fig. S5** TEM images of trimetallic PdAgCu nanostructures synthesized with the higher pH value of (a, b) 10.92, (c, d) 11.27 and (e, f) 11.45.



**Fig. S6** TEM images of trimetallic PdAgCu MNSs synthesized with different ethanol volume of (a, b) 0 mL and (c, d) 0.75 mL.



**Fig. S7** TEM images of trimetallic PdAgCu MNSs synthesized with different ethanol volume of (a, b) 1.5 mL, (c, d) 1.75 mL, (e, f) 2.25 mL, (g, h) 2.5 mL and (i, j) 3 mL.



**Fig. S8** TEM images of trimetallic PdAgCu nanostructures synthesized with different ethanol volume of (a, b) 4.0 mL and (c, d) 5 mL.



**Fig. S9** TEM images of trimetallic PdAgCu nanostructures synthesized with different DODAC concentration of (a, b) 0.06 mg/mL, (c, d) 0.15 mg/mL, (e, f) 0.6 mg/mL, (g, h) 1.5 mg/mL and (i, j) 2.0 mg/mL.



**Fig. S10** TEM images of trimetallic PdAgCu nanostructures synthesized with different precursor concentration of (a, b) 0.1 mM, (c, d) 0.4 mM, (e, f) 0.8 mM, and (g, h) 3.2 mM.



**Fig. S11** Supporting TEM images of trimetallic PdAgCu MNS-58 with different magnifications, indicating uniform and well-dispersed MNSs with cylindrically opened mesoporous nanochannels and continuous frameworks.



**Fig. S12** (a) Small-angle and (b) wide-angle XRD patterns of trimetallic PdAgCu MNS-58. The result indicated mesoporous nanostructure and trimetallic elemental compositions.



**Fig. S13** The selected-area electron diffraction (SAED) of trimetallic PdAgCu MNS-58. The result indicates the formation of PdAgCu nanoalloys (no phase separation).



**Fig. S14** STEM EDX and corresponded element compositions (inserted) of trimetallic PdAgCu MNS-58.



**Fig. S15** XPS survey and high-resolution XPS spectra of trimetallic PdAgCu MNS-58, indicating the presence of Pd, Ag, Cu elements and the formation of PdAgCu nanoalloys.



**Fig. S16** TEM images of trimetallic PdAgCu MNSs with different Ag content of (a, b) 0 wt%, (c, d) 9.4 wt %, (e, f) 18.9 wt%, (g, h) 27.9 wt %, (i, j) 36.7 wt% and (k, l) 45.1 wt %.



**Fig. S17** TEM images of trimetallic PdAgCu MNSs with different Cu content of (a, b) 0 wt%, (c, d) 5.4 wt %, (e, f) 9.7 wt %, (g, h) 13.8 wt%, (i, j) 19.6 wt % and (k, l) 24.5 wt %.



**Fig. S18** CV curves of the Pd-based nanocatalysts in 1.0 M KOH containing different ethanol concentrations: (a) MNS-21, (b) MNS-36, (c) MNS-49, (d) MNS-58, (e) MNS-71, (f) MNS-93, (g) MNS-104, and (h) PdB.



**Fig. S19** Dependence of mass activities on ethanol concentration for PdAgCu MNSs with different sizes at a scan rate of 50 mV/s.



**Fig. S20** CV curves of the Pd-based nanocatalysts in 1.0 M KOH and 1.0 M ethanol with different scan rates: (a) MNS-21, (b) MNS-36, (c) MNS-49, (d) MNS-58, (e) MNS-71, (f) MNS-93, (g) MNS-104, and (h) PdB.



**Fig. S21** The relationship between mass activities and scan rates (v) for PdAgCu MNSs with different sizes in 1.0 M KOH and 1.0 M ethanol.