Supporting Information

Template-free Synthesis of Multiple-shell MgO/Pt Hollow Spheres as Enhanced Electrocatalysts

Tao Wang, Weihao Cui, Meiling Peng, Shenshen Ouyang and Sheng Wang*

Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China.

*Corresponding author: Tel: +86-571-86843624; E-mail: wangseng571@hotmail.com

Table of Contents

S1. Experimental
S2. Characterization of yolk-shell MgO spheres
S3. XRD pattern and nitrogen adsorption–desorption isotherm plot of the sample
S4. Reduction of Pt precursor to Pt NCs
S5. Controlled experiment without glucose
S6. Controlled experiments by using water-insoluble salt replace MgCO₃
S7. Solubility of MgCO₃
S8. Controlled experiments by using Au and Pd precursor replace Pt precursor
S9. Controlled experiments by using HCl replace chloroplatinic acid
S10. Controlled experiments by using HNO₃ and H₂SO₄ replace chloroplatinic acid
S11. Data for the electro-oxidation of CH₃OH catalysed by the catalyst samples
S12. TEM images of the MgO/Pt MSHS composite after CA test for 3600 S
S1. Experimental

Chemicals

Chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O) was analysis reagent (A.R.) and purchased from Aladdin Industrial Corporation. Chloroplatinic acid (H$_2$PtCl$_6$·6H$_2$O) was purchased from Aladdin Reagents. Methanol (CH$_3$OH) and KOH were A. R. and purchased from Hangzhou Gaojing Fine Chemical Co., Ltd. All reagents were used as received without further purification. Nafion (5 wt. %) was purchased from Sigma-Aldrich. Commercial Pt black was purchased from Johnson Matthey Company. The water used in all experiments was ultrapure (Millipore, 18.2 MΩ).

Preparation of yolk-shell MgO spheres: MgCO$_3$·3H$_2$O microrods were prepared using the process described in our previous works. Certain amount of MgCO$_3$·3H$_2$O microrods (0.06 g) were added to glucose aqueous solution (0.3 M, 40 mL) with vigorous stirring for ten minutes. The resultant solution was transferred to a 100 ml Teflon-lined autoclave and maintained at 160 °C for 10 h. After the autoclave cooled to room temperature naturally, the precipitate was isolated by centrifugation, washed thoroughly with deionized water and ethanol several times, and dried in a vacuum oven at 80 °C for 12 h. Finally, the product collected was subsequently calcined in air at 500 °C for 2 h to remove the carbonaceous species, leaving the white yolk-shell MgO spheres sample.

Preparation of MgO/Pt MSHS: certain amount of MgCO$_3$·3H$_2$O microrods (0.06 g) was added to glucose aqueous solution (0.3 M, 40 mL), and then with vigorous stirring chloroplatinic acid hexahydrate H$_2$PtCl$_6$·6H$_2$O (1.09 M, 0.01 mL) was added and stirred for ten minutes. The resultant homogeneous solution was transferred to a 100 ml Teflon-lined autoclave and maintained at 160 °C for 10 h. After the autoclave cooled to room temperature naturally, the precipitate was isolated by centrifugation, washed thoroughly with deionized water and ethanol several times, and dried in a vacuum oven at 80 °C for 12 h. Finally, the product was calcined at 500 °C for 2 h in air to yield MgO/Pt MSHS.

Electrochemical measurements

All the electrochemical measurements were performed on the electrocatalysts using a CHI660E electrochemical workstation. A platinum wire and Hg/Hg$_2$Cl$_2$ (saturated KCl) were used as the counter and reference electrodes, respectively. A glassy carbon electrode (GCE, 3 mm diameter) was polished to a mirror finish (with 1.0, 0.3, and 0.05 mm alumina powder, respectively) and thoroughly cleaned. To prepare the working electrode, 2 μL of Nafion (0.05%)-ethanol suspensions of the catalyst sample or
commercial catalyst was dropped on the surface of a GCE, respectively. The Pt loading of the catalysts is 20 μg/cm².

Methanol oxidation reaction (MOR) measurements were carried out in alkaline media. The MOR was performed in an KOH (1.0 M) aqueous solution containing methanol (1.0 M) at a potential from -0.8 to 0.4 V. Chronoamperometry was carried out in KOH (1.0 M) and methanol (1.0 M) at 0.5 V vs. SCE. All the measurements were performed at room temperature and the CV was performed at a scan rate of 50 mV s⁻¹.

**Characterization**

The crystalline structures of the as-synthesized products were analyzed by X-ray diffraction (XRD) and recorded on a Rigaku D/max-2200 diffractometer employing Cu-Kα radiation (λ=0.154 nm) at a scanning rate of 0.05 deg s⁻¹ ranging from 20 to 90°. The morphologies were investigated by a field-emission scanning electron microscopy (FESEM, ZEISS VLTRA-55, 10 kV) and transmission electron microscopy (TEM) on a JEOL instrument (JEM-2010 HR) working at 200 kV. The composition of the as-synthesized MgO/Pt nanocomposites was characterized by energy dispersive X-ray spectroscopy (EDX). S_BET was determined using a Micromeritics Tristar 3000. High-angle annular dark-field scanning TEM (HAADF-STEM) characterisations were performed with a FEI Technai G2 F30 S-Twin transmission electron microscope operating at 200 kV. The metal contents of the catalysts were measured using ICP-OES (Optima 2100 DV; Perkin Elmer).

S2. Characterization of yolk-shell MgO spheres

Figure S1. (a) SEM images of core/shell MgO microspheres. (b), (c) Low- and high-magnification TEM images of yolk-shell MgO spheres. (d) EDS of the obtained samples.
S3. XRD pattern and nitrogen adsorption-desorption isotherm plot of the sample

**Figure S2.** (a) XRD pattern of the as-synthesized multiple-shell MgO/Pt MSHS. (b) and (c) nitrogen adsorption–desorption isotherm plot of the as-synthesized MgO core/shell microspheres and multiple-shell MgO/Pt MSHS.
S4. Reduction of Pt precursor to Pt NCs

The following is a reference experiment to demonstrate that Pt nanocrystal has been reduced at high hydrothermal temperature. Pt precursor $\text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O}$ and glucose aqueous solution was added to Teflon-lined autoclave and maintained at 160 °C for 20 mins. Then the autoclave was cooled suddenly and opened quickly, the supernatant solution was taken and casted onto a holey, carbon-coated Cu grid. It can be seen Pt nanocrystals were reduced.

![TEM images](image)

**Fig. S3** (a) TEM image of Pt NCs synthesised at 160 °C for 20 mins. (b) HRTEM image of a single Pt NC.
S5. Controlled experiment without glucose

Figure S4. Controlled experiments (a) without glucose. (b), (c) and (d) using other substances to replace glucose.
Figure S5. Controlled experiments by using water-insoluble salts replace MgCO$_3$ (a) and (b) SEM and TEM images of product of hydrothermal reaction by using BaCO$_3$. (c) and (d) SEM and TEM images of product of hydrothermal reaction by using MnC$_2$O$_4$·2H$_2$O. SEM image of product of hydrothermal reaction by using (e) MgC$_2$O$_4$·2H$_2$O and ZnC$_2$O$_4$·2H$_2$O.
S7. Solubility of MgCO$_3$

Solubility (g/100 g of solvent):

- water: 0.0139 (25°C)
- water: 0.0063 (100°C)

References:


S8. Controlled experiments by using Au and Pd precursor replace Pt precursor

When Pt precursor was replaced by H$_2$AuCl$_6$. The moment H$_2$AuCl$_6$ was added into mixture solution of MgCO$_3$ and glucose, precipitation of Au nanoparticles produced immediately because of the occurrence of silver mirror reaction (Figure S2d,e). After filtration of precipitation, the solution was taken to perform hydrothermal reaction. After calcination, the product were completely core/shell MgO microspheres (Figure S2a, b and c) and no Au was detected. When H$_2$PtCl$_6$ was replaced by K$_2$PdCl$_6$, the final products of the hydrothermal reaction were composed of microspheres and large amounts of aggregation of nanoparticles (Figure S2f). EDS showed that microspheres were MgO (Figure S2g and h) and aggregations were Pd nanoparticles (Figure S2i and j).

Figure S6. (a) SEM images of products when Pt precursor was replaced by Au precursor. (b) and (c) TEM images of core/shell MgO microspheres and corresponded EDS. (d) and (e) TEM images of aggregation of Au nanoparticles and corresponded EDS. (f) SEM images of products when Pt precursor was replaced by Pd precursor. (g), (i) SEM images of MgO and aggregation of Pd nanoparticles. (h), (j) The corresponded EDS of the obtained samples.
S9. Controlled experiments by using HCl replace chloroplatinic acid

Figure S7. when Pt precursor was replaced by HCl at different concentration (a) and (b) SEM and TEM images of products by using HCl (0.02 mmol). (c) and (d) SEM and TEM images of products by using HCl (0.05 mmol). (e) and (f) SEM and TEM images of products by using HCL (0.15 mmol). (g) SEM image of products by using HCL (0.50 mmol).
S10. Controlled experiments by using HNO$_3$ and H$_2$SO$_4$ replace chloroplatinic acid

**Figure S8.** when Pt precursor was replaced by HNO$_3$ and H$_2$SO$_4$ (a) and (b) SEM and TEM images by using HNO$_3$ (0.02 mmol). (c) and (d) SEM and TEM images by using H$_2$SO$_4$ (0.01 mmol).
**S11. Table 1.** Data for the electro-oxidation of CH$_3$OH catalysed by the catalyst samples

<table>
<thead>
<tr>
<th></th>
<th>QH [mC]</th>
<th>m(Pt) [μg]</th>
<th>ECSA [m$^2$/g]</th>
<th>Mass activity [mA/mg$_{metal}$]</th>
<th>Specific activity [mA/cm$^2$]</th>
<th>$I/I_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO/Pt</td>
<td>0.119</td>
<td>2</td>
<td>14.2</td>
<td>310.4</td>
<td>4.0</td>
<td>5.9</td>
</tr>
<tr>
<td>MgO</td>
<td>0.115</td>
<td>2</td>
<td>1.2</td>
<td>0.5</td>
<td>0.04</td>
<td>/</td>
</tr>
<tr>
<td>Pt black</td>
<td>0.223</td>
<td>2</td>
<td>26.6</td>
<td>200.5</td>
<td>0.75</td>
<td>5.4</td>
</tr>
</tbody>
</table>
S12. TEM images of the MgO/Pt MSHS composite after CA test for 3600 S.

Figure S9. TEM images of the MgO/Pt MSHS composite after long-term stability test for 3600 S in Fig. 6b.