Supporting information for

A Facile Construction of Yolk-Shell Structured Metal-TiO$_2$ Nanocomposite with Potential for p-Nitrophenol Reduction

Xi-Jie Lin,$^{a,b}$ Tian-Qi Sun,$^{a,*}$ Yong-Gang Sun,$^{a,b}$ Chen Zeng,$^{d}$ Rong-Wen Lu *$^e$ and An-Min Cao*$^{a,b}$

$^a$CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, and CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, People’s Republic of China.

$^b$University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China.

$^c$State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, People’s Republic of China.

$^d$College of Food Science & Technology, Huazhong Agricultural University, Wuhan, People’s Republic of China.

E-mail: anmin_cao@iccas.ac.cn, lurw@dlut.edu.cn

Experimental section:

Chemicals: Formaldehyde solution (37%), chloroplatinic acid hexahydrate (Pt, 37%), anhydrous ethanol (A.R.) and potassium carbonate anhydrous (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. 3-Aminophenol (A.R.), ammonium tetrachloropalladate (II) (Pd, 37%), tetrabutyl titanate (A.R.), silver nitrate (A.R.), iodobenzene (A.R.) and phenylboronic acid (A.R.) were purchased from Alfa Aesar.

Synthesis of metal salt/3-aminophenol formaldehyde resin nanospheres:

Firstly, 0.55 g of 3-aminophenol was dissolved in 50 mL of deionized water. After complete dissolution, suitable amount of specific metal salt was added and continued to stir for 10 minutes. And then, 1.1 mL of formaldehyde solution was added and white precipitate formed quickly. After 3 hours polymerization, the yellow product was collected by washing and centrifuging several times. Finally, the final product dried at 80 °C overnight.

Synthesis of yolk-shell structured metal-TiO$_2$ nanocomposite:

At first, 0.1 g of above metal salt/3-aminophenol formaldehyde resin nanosphere was dispersed in solvent which mixed by 72 mL of anhydrous ethanol and suitable amount of deionized water. After ultrasound dispersing evenly, this mixture was added to 100 mL flask which contained 10 mL of anhydrous ethanol and 0.2 mL of TBOT, and continued to react for 4 hours under 80 °C. The product was collected by washing and centrifuging several times and dried at 80 °C overnight. Finally, the product was calcined in air at 550 °C to remove the phenolic resin.

Synthesis of TiO$_2$ hollow nanospheres:

Firstly, 0.55 g of 3-aminophenol was dissolved in 50 mL of deionized water. After completely dissolution, 1.1 mL of formaldehyde solution was added and white precipitate formed quickly. After 3 hours polymerization, the yellow product was collected by washing and centrifuging several times. Finally, the final product dried at 80 °C overnight. And then, 0.1 g of above3-aminophenol formaldehyde resin nanosphere was dispersed in solvent which mixed by 72 mL of anhydrous ethanol and suitable amount of deionized water. After ultrasound dispersing evenly, this mixture was added to 100 mL flask which contained 10 mL of anhydrous ethanol and 0.2 mL of TBOT, and continued to react for 4 hours under 80 °C. The product was collected by washing and centrifuging several times and dried at 80 °C overnight. Finally, the product was calcined in air at 550 °C to remove the phenolic resin.

Synthesis of Ag/TiO$_2$ nanoparticle:

Ag-hTiO$_2$ nanoparticle was prepared by impregnation method. Firstly, 0.5 g of TiO$_2$ hollow nanosphere was dispersed in ethanol, and then 25 μL of AgNO$_3$ aqueous solution (1 M) was added. After reacting overnight, ethanol was evaporated and the powder was collected and calcined in air at 550 °C. And the Ag loading amount was 0.53 % wt that analysed by ICP-AES.
Catalytic activity of yolk-shell structured Ag-TiO₂ nanocomposite in the reduction of p-nitrophenol (PNP): The reduction of p-nitrophenol into p-aminophenol in the presence of NaBH₄ was used to test the catalytic activity and recyclability of yolk-shell structured Ag-TiO₂ nanocomposite. A standard quartz cuvette was used as the reactor. At first, freshly prepared NaBH₄ aqueous solution (1 mL, 0.053 mol/L) was added to the quartz cuvette containing 0.5 wt% catalyst aqueous solution (0.75 mL, 0.25 mg/mL). After sonication, p-nitrophenol aqueous solution (2 mL, 0.15 mmol/L) was added to above mixed solution, and monitored by UV-vis with a scan range of 250 nm to 500 nm.

Characterizations
Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) was recorded with a JEOL 2100 F instrument operating at 200 kV. X-ray diffraction (XRD) patterns was performed on a Rigaku D/max 2500 type instrument using CuKα radiation with a step size of 0.01. The metal loading amount was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Shimadzu ICPE-9000. The N₂ adsorption/desorption isotherms were carried out at liquid nitrogen temperature after sample was outgassed at 120 °C, by using a Micrometrics ASAP 2010 apparatus. The specific surface area of the samples was calculated by using the Brunauer-Emmett-Teller (BET) method. Pore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) method from the adsorption branch. The reduction of p-nitrophenol was monitored by UV-vis spectrum with Shimadzu UV-2600. The X-ray photoelectron spectroscopy (XPS) datas were taken on an ESCALab220i-XL electron spectrometer from VG Scientific by using 300 W Al Kα radiations.
Fig. S1 (a) Bright field-STEM image of yolk-shell structured Ag-TiO$_2$ nanocomposite. (b-d) Elemental mappings of yolk-shell structured Ag-TiO$_2$ nanocomposite. The element was Ti, O, and Ag, respectively.

Fig. S2 (a) XPS full scan spectrum of Ag-TiO$_2$. (b) High resolution XPS spectra of Ag 3d.

Fig. S3 DF-STEM images of Ag-TiO$_2$ with different Ag loadings: (a) 0.15 wt%; (b) 0.49 wt%. 
Fig. S4 TEM images of Ag-TiO$_2$ with different shell thickness by changing the H2O addition amount: (a) 0.5 mL; (b) 1 mL.

Fig. S5 (a-b) TEM and Dark field-STEM images of yolk-shell structured Pd-TiO$_2$ nanocomposite, and insets in a and b were the HR-TEM image and the EDS spectra, respectively. (c-d) TEM and Dark field-STEM images of yolk-shell structured Pt-TiO$_2$ nanocomposite, and insets in c and d were the HR-TEM image and the EDS spectra, respectively.

Fig. S6 XRD patterns of (a) yolk-shell structured Pd-TiO$_2$ nanocomposite and (b) yolk-shell structured Pt-TiO$_2$ nanocomposite, respectively.
**Fig. S7** TEM image (a) and DF-STEM image (b) of Ag/Pt-TiO$_2$, and inset in (a) was the EDS spectra.

**Fig. S8** TEM and DF-STEM images of (a-b) yolk-shell structured Pt/Pd-TiO$_2$ nanocomposite and (c-d) yolk-shell structured Ag/Pd-TiO$_2$ nanocomposite. The inset was the EDS spectra.

**Fig. S9** TEM image of the recycled Ag-TiO$_2$ catalyst.