

Supporting Information

Three-dimensionally ordered hollow sphere array Pt/In₂O₃- TiO₂ with improved photocatalytic efficiency

Xinyue Zhang^{ab}, Li Li^{*ab}, Qianlong Zhou^b, Yanzhen Cao^b, Fengyan Ma^b, Yi Li^b

a. College of Materials Science and Engineering, Qiqihar University, Qiqihar, Heilongjiang 161006

b. College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar, Heilongjiang 161006

Experimental sections

2.1 Reagents

Titanium isopropoxide ($C_{12}H_{28}O_4Ti$) was purchased from Shenzhen Meiruil Chemical Technology Co., Ltd.; Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Shanghai Jingchun Biochemical Technology Co., Ltd. Indium nitrate hydrate ($In(NO_3)_3 \cdot 4.5H_2O$) was purchased from Sinopharm Chemical Reagent Co., Ltd., and NaOH, absolute ethanol, methanol, isopropanol, lactic acid, potassium persulfate ($K_2S_2O_8$), etc. were purchased from Tianjin Kaitong Chemical Reagent Co., Ltd.; Commercial photocatalyst (Degussa P25) was purchased from Aldrich Company of the United States. Triethanolamine, p-benzoquinone, tert-butanol, styrene, etc. were purchased from Tianjin Guangfu Fine Chemical Co., Ltd. Methyl orange (MO), malachite green (MG), congo red (CR), methylene blue (MB), and salicylic acid (SA) were purchased from Beijing Chemical Plant, which are commercially available analytical grade. The experimental water was secondary deionized water.

2.2 Preparation of PS microspheres

Monodisperse and tightly packed PS microspheres were synthesized by emulsification-free polymerization from the literature¹⁻³. In a typical experiment, phenylethylene (0.235 mol), $K_2S_2O_8$ (0.33 mmol) as an initiator, and deionized water (240 mL) were taken into a 500 mL three-necked flask equipped with a mechanical stirrer, a thermometer with a temperature controller, a N_2 inlet, a condenser pipe, and a water-bath. This mixture was stirred before deoxygenation using bubbling nitrogen gas at room temperature for 0.5 h to ensure the oxygen free inert system. The mixture was heated to $70 \pm 2^\circ C$ for 7 h to complete the polymerization. Finally, the spheres were centrifuged at 1000 rpm for 24 h and subsequently dried at room temperature.

2.3 Preparation of Pt/ In_2O_3 - TiO_2 composite

0.5 g PS microspheres were pretreated with methanol, naturally dried, and then mixed with 3 mL of isopropanol and 0.5 mL of titanium isopropoxide. After stirring for 1 h, vacuum impregnation for 12 h, then the light yellow powder was obtained by curing at $100^\circ C$ for 6 hours, and then it was cooled naturally. Adding 0.06 g $In(NO_3)_3 \cdot 4.5H_2O$ and 0.01 g $H_2PtCl_6 \cdot 6H_2O$ into the mixed solution of 3 mL isopropanol and 3 mL ethanol. After mixing, all the above powder at room temperature will fall into the above mixed solution. After stirring for 1 h, the vacuum was impregnated for 12 h and calcined at $550^\circ C$ for 7 h, and the final product was

obtained, which was labeled as Pt/In₂O₃-TiO₂-H. The sample without PS microspheres under the same experimental conditions was labeled as Pt/In₂O₃-TiO₂. For the comparative analysis, hollow spheres In₂O₃-TiO₂ and hollow spheres TiO₂ were synthesized under the same experimental conditions without H₂PtCl₆•6H₂O and only titanium isopropoxide. Meanwhile, hollow spheres Pt/In₂O₃-TiO₂ with the contents of indium nitrate and platinum chlorate increased twice were prepared and labeled as Pt/In₂O₃-TiO₂-D.

2.4 Characterization

The XPS spectrum of the sample was determined by a VG-ADES 400 X-ray photoelectron spectrometer using a model in which the residual gas pressure of the Mg K-ADES source was less than 10⁻⁸ Pa. The SEM analysis of the samples was carried out using a scanning electron microscope of the model S-4700 with a working voltage of 5 kV purchased from Hitachi, Japan. The SEM-EDS analysis of the samples was carried out using a scanning electron microscope of the model S-4700 with a working voltage of 5 kV purchased from Hitachi, Japan. The HR-TEM analysis of the sample was performed by JEOL-2100F field emission transmission electron microscope of JEOL Co., Ltd., and the maximum acceleration voltage was 200 kV. The specific surface area and pore diameter of the sample were measured by a 3H-2000PS2 type physical adsorption instrument of Beijing Beishi Instrument Technology Co., Ltd., and the measurement temperature was 77 K. The diffuse reflectance absorption spectrum of the solid sample was determined by the TU-1901 dual-beam UV–visible diffuse reflectance absorption spectrum produced by Beijing General Analysis Co., Ltd. The absorbance of the sample solution was determined by a UV–visible dual-beam spectrophotometer manufactured by Beijing Puyi General Electric Co., Ltd., Model TU-1901.

2.5 Photocatalytic performance experiments

The photocatalytic reaction device is self-made and consists of a built-in light source surrounded by a cylindrical quartz outer tube and a quartz glass cover. A 125 W high-pressure mercury lamp is used as the ultraviolet light source (the main emission line is at 313.2 nm), and a 400 W xenon lamp is used as the visible light source (the main emission line is larger than 410 nm, and the inner casing is made of special glass to filter out the ultraviolet light emitted by the Xe lamp). The simulated daylight source is a 1000 W xenon lamp (external type, Shanghai Bilon Instrument Co., Ltd., the emission spectrum is close to the full spectrum). In the photocatalytic experiment, the

concentration of the reaction solution such as Congo red was 50 mg/L. The photocatalytic reaction was as follows:

The catalysts for UV, visible, and simulated sunlight were: 0.09 g, 0.3 g, and 0.15 g, respectively, and the samples were dispersed in reaction solutions of 90 mL, 220 mL, and 500 mL, sonicated for 10 min. The adsorption–desorption equilibrium was achieved by stirring for 30 minutes without light. The solutions were then placed under respective light sources for illumination. Samples were taken at regular intervals and centrifuged to remove residual catalyst, and the absorbance values were determined by TU-1901 dual-beam UV–vis spectrophotometer at λ_{max} of dyes such as Congo red.

2.6 Photocatalytic hydrogen evolution experiment

The photolysis water hydrogen production experiment was carried out in a reactor closed and connected to a vacuum circulation system. 0.1 g of Pt/In₂O₃-TiO₂-H catalyst and a certain amount of sacrificial agent were dispersed in 50 mL of deionized water, vacuumed and degassed, and the light was subjected to photohydrolysis to produce hydrogen under stirring. The reactor was irradiated with a 300 W xenon lamp (PLS-SXE300 xenon lamp as the light source (Beijing Perfectlight Technology Co., Ltd), in which the lamp power is 300 W. The total luminous power is 50 W, with a visible region of 19.6 W, an ultraviolet region of 2.6 W, and a spectral range of 320–780 nm). With high purity nitrogen as the carrier gas, the output pressure was 0.4–0.6 MPa, the working voltage was about 20 mV, and the operating current was 50 mA. During the reaction, the circulating condensate temperature throughout the system was maintained at 5 °C. After 8 h of irradiation, sampling was performed, and hydrogen production was analyzed by an on-line gas chromatograph. The column is a 5 Å molecular sieve column and the detector is TCD. The hydrogen production was calculated according to the peak area measured by different reaction times, and the catalytic activity of the catalyst was measured by the total hydrogen production of 8 h.

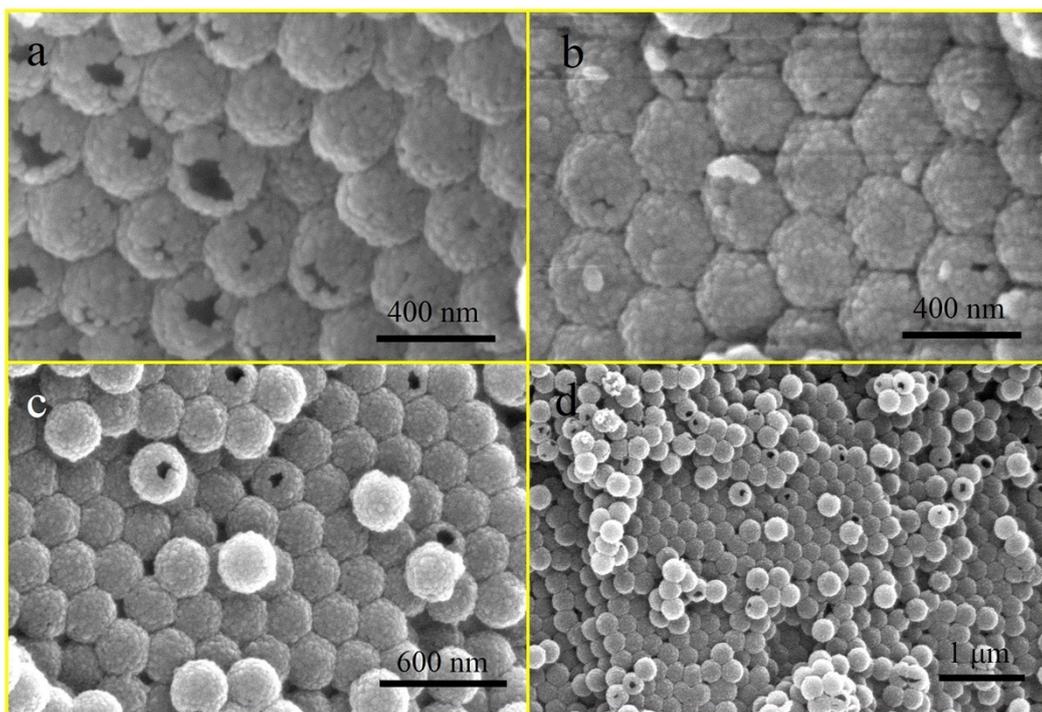


Fig.S1 SEM images of Pt/In₂O₃-TiO₂-H after photocatalytic reaction.

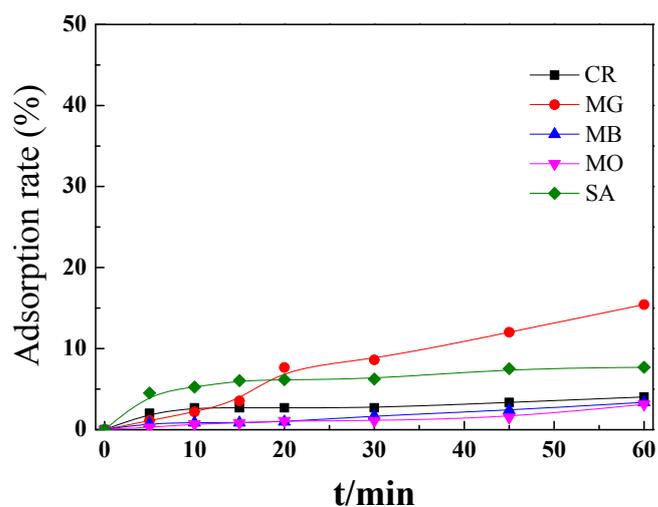


Fig.S2 Different dye adsorption experiment results of Pt/In₂O₃-TiO₂-H.

References

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