Electronic Supplementary Information

Significantly Enhanced Photocatalytic Performance of In2O3 Hollow Spheres via

Coating Effect of N,S-Codoped Carbon Layer

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1. Experimental details

1.1 Characterizations

The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Panalytical X-pert diffractometer with CuK α radiation. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (SEM, SU8100), and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai-F20) with an acceleration voltage of 200 kV. All TEM samples were prepared from depositing a drop of diluted suspension in ethanol on a carbon film coated copper grid. PHI QUANTUM2000 photoelectron spectrometer (XPS) was used to characterize the surface composition of products. The surface areas of these samples were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system.

1.2 Photoelectric measurements

Photoelectrochemical measurements were performed in a homemade three electrode quartz cell with a PAR VMP3 Multi Potentiostat apparatus. A Pt plate was used as the counter electrode, and Hg/HgCl₂ electrode was used as the reference electrode. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass that was cleaned by ultrasonication in a mixture of ethanol and acetone for 10 min and dried at 60 °C. Typically, the sample powder (10 mg) was ultrasonicated in ethanol (0.2 mL) to disperse it evenly to get a slurry. The slurry was spread onto

FTO glass, whose side part was previously protected using Scotch tape. After air drying, the Scotch tape was unstuck. Then, the working electrode was further dried at 300 °C for 3 h to improve the adhesion. The exposed area of the working electrode was 2.5 cm^2 . The electrochemical impedance spectroscopy (EIS) measurement was carried out using a CHI-760E workstation at the open circuit potential in the frequency range of $0.01 \text{ Hz}-10^5 \text{ Hz}$. In the three-electrode cell, the electrolytes were $0.025M \text{ KH}_2\text{PO}_4$ and $0.025M \text{ Na}_2\text{HPO}_4$ standard buffer solution (25 °C, pH = 6.864) without any additive under open circuit potential conditions. The visible light irradiation source was a 300 W Xe arc lamp system. The cathodic polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of $100 \text{ mV} \text{ s}^{-1}$.

1.3 Photocatalysis for hydroxylation of arylboronic acid to phenol

The photocatalyst (5 mg), phenylboronic acid (0.1 mmol, 1 equiv.), and N,N-diisopropylethylamine (DIPEA, 0.3 mmol) were added to ethanol (2 mL). The mixture was stirred and irradiated by using blue LED (450 nm, 3 W) in air at room temperature for 10 h. ¹H NMR spectroscopy was employed to determine the yield. To carry out the recycling experiments, the photocatalyst was recovered by centrifuging at 10000 rpm for 10 min, and washed with fresh dichloromethane for three times. Finally, the recycled catalyst was dried in a vacuum at 60 °C overnight.

1.4 Density functional calculations

All of the density functional calculations were performed using plane-wave pseudopotential method, as implemented in the Cambridge Sequential Total Energy Package (CASTEP) code.¹ The local density approximation (LDA)² and ultrasoft pseudopotential³ were used to describe the exchange-correlation effects and electron-ion interactions, respectively. A Morkhost-Pack mesh⁴ of k-points, Γ and 2×2×1 points was used to sample the two-dimensional Brillouin zone for the geometry optimization and for calculating the electronic properties of graphite/In₂O₃. The self-consistent convergence accuracy was set at 2×10⁻⁶ eV/atom, the convergence criterion for the force between atoms was 5.5×10⁻² eV/Å, and the maximum displacement was 2×10⁻³ Å. The graphite (001), In₂O₃ (001), In₂O₃ (110) and In₂O₃ (111) surfaces were simulated using a slab model with 14.62 Å × 14.62 Å, 10.04 Å × 9.38 Å, 10.04 Å × 15.76 Å, and 14.62 Å × 143.62 Å, respectively. All four slab models were separated by the vacuum spacing of 12 Å to wipe out the interactions between periodic images.

The adsorption energy for arylboronic acid was calculated by:

 $E_{ad} = E_{(AA + surface)} - E_{(AA)} - E_{surface}$

where $E_{(AA + surface)}$ was the total energy of the surface containing the adsorbed arylboronic acid, $E_{(AA)}$ was the total energy of arylboronic acid, and $E_{surface}$ denoted the total energy of pure surface without the adsorbed arylboronic acid.

2. Experimental results



Figure S1. Side view of the optimized stable configurations for arylboronic acid adsorbed on (a) graphite (001), (b) In_2O_3 (100), (c) In_2O_3 (110) and (d) In_2O_3 (111) surfaces.



Figure S2. Powder XRD pattern of In(OH)(2,5-PDC) precursor.



Figure S3. FT-IR spectrum in the 4000-500 cm⁻¹ spectral range for In(OH)(2,5-PDC) precursor.



Figure S4. (a) SEM image and (b-g) element mapping of In(OH)(2,5-PDC) precursor.



Figure S5. Size distributions of (a) In(OH)(2,5-PDC) precursor and (b) N,S-C/In₂O₃ HS.



Figure S6. TGA curve of In(OH)(2,5-PDC) precursor.



Figure S7. Powder XRD pattern of N,S-C/In₂O₃ HS.



Figure S8. Magnified SEM image of N,S-C/In₂O₃ HS.



Figure S9. (a,b) Elemental profiles of N,S-C/In₂O₃ HS.



Figure S10. (a) Powder XRD pattern, (b) SEM image, and (c-h) corresponding elemental mapping of In_2O_3 HS.



Figure S11. (a) Powder XRD pattern and (b) SEM image of commercial In₂O₃.



Figure S12. Photoluminescence spectra of N,S-C/In₂O₃ HS, In₂O₃ HS and commercial In₂O₃.



Figure S13. Projected density of states (PDOS) for N,S-codoped graphite $(001)/In_2O_3$ (100) interface.



Figure S14. UPS for (a,b) In_2O_3 and (c) graphite. (d) Energy band diagrams of In_2O_3 and graphite contact.

The work function (Φ) and band positions of In₂O₃ were measured by using UPS. The valance band spectra were measured with a monochromatic He 1 light source (21.2 eV) and a VG Scienta R4000 analyzer. A sample bias of -5 V was applied to observe the secondary electron cutoff (SEC). The work function could be determined by the difference between the photon energy and the binding energy of the secondary cutoff edge. As shown from Figure S14a,b, the work function of In₂O₃ was 3.49 eV, and the valence band position was at -0.219 eV. As the bandgap of In₂O₃ was 2.8 eV, the conduction band was located at 2.581 eV. It can be found from Figure S14c that the work function of graphite was 3.47 eV. On account of smaller work function of graphite, the electrons would flow from graphite to In₂O₃ until the Fermi levels of graphite and In₂O₃ are aligned. Under the equilibrium, graphite is positively charged and In₂O₃ is negatively charged near its surface because of the electrostatic induction. The band alignment between graphite and In₂O₃ was 0.02 eV (Figure S14d). The energy bands of In₂O₃ bend downward toward the interface. Benefiting from the build-in electric field and band bending at the interface, the photogenerated electrons could migrate from the conduction band of In₂O₃ to the coated carbon layers, which is consistent with the results of PDOS.



Figure S15. Apparent quantum efficiency (AQE) of the yield for oxidative hydroxylation of arylboronic acids using three different samples as the photocatalysts.

The apparent quantum efficiency (AQE) of the yield for oxidative hydroxylation of arylboronic acids in producing phenols by N,S-C/In₂O₃ HS with the incident light wavelength (λ) as a function was measured. By taking $\lambda = 450$ nm as an example, the catalyst solution was irradiated under blue light emitting diodes (LED, $\lambda = 450$ nm, 3W) for 10h. The average light density is ca. 3.85 mW·cm⁻² and the irradiation area is 4.71 cm². Thus, the number of the incident photons (N) is 1.47 × 10²¹ estimated by equation (1). Meanwhile, corresponding amounts of the yield for oxidative hydroxylation of arylboronic acids in producing phenols from photocatalytic dehydrogenation of benzyl alcohols are shown in Table 1. Therefore, the AQE calculated by equation (1) is 4.09%.

$$N = \frac{E\lambda}{hc} = \frac{3.85 \times 10^{-3} \times 4.71 \times 3600 \times 10 \times 450 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 1.47 \times 10^{21}$$
(1)

$$AQE = \frac{number \ of \ electrons \ involved \ in \ the \ reaction}{number \ of \ incident \ photons} = \frac{6.02 \times 10^{23} \times 0.1 \times 10^{-3}}{1.47 \times 10^{21}} =$$

0



Figure S16. Yield for photocatalyzed oxidative hydroxylation of arylboronic acids at AM 1.5G simulated sunlight for 4h.



Figure S17. (a) Powder XRD pattern, (b) SEM image, and (c-h) corresponding elemental mapping of N,S-C/In₂O₃ HS after five catalytic cycles.



Figure S18. ¹H NMR spectra for oxidative hydroxylation of arylboronic acid with (a) *t*-BuOH, (b) TEA, and (c) TEMPO.

MeO B(OH) ₂ Catalyst, DIEA Blue LED, in air MeO				
<i>hv</i> (450nm,	Catalyst (N,S-	DIEA	Reaction time	Conversion
LED)	C/In ₂ O ₃ HS)			(%)
No	Yes	Yes	10 h	3%
Yes	No	Yes	15 h	1.8%
Yes	Yes	No	15 h	0%

Table S1. Photocatalyzed oxidative hydroxylation of arylboronic acids in different reaction conditions.

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