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## Rationally Designed a Double-Shell Dodecahedral Microreactor with Efficient Photo-electron Transfer: N-doped C Encapsulated Ultrafine In<sub>2</sub>O<sub>3</sub> Nanoparticles

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Abstract: It is desirable but challenging to design efficient micro-/nanoreactors for chemical reactions. In this study, we fabricated mesoporous double-shelled hollow microreactor composed of Ndoped C coated ultiafine  $In_2O_3$  nanoparticles (N-C/In<sub>2</sub>O<sub>3</sub> HD) by the thermolysis of dodecahedral In-based framworks in Ar atmosphere. The obtained N-C/In<sub>2</sub>O<sub>3</sub> HD exhibited excellent photocatalytic activity toward photocatalytic oxidative hydroxylation of a series of arylboronic acids substrates, due to its enhanced optical absorption and efficient separation of photo-generated electron-hole pairs endowed by the unique structure and uniformly coated N-doped C layers. Furthermore, we found that  $O_2{}^{\scriptscriptstyle \sim}$  was the critical active species in the process of photocatalytic oxidative hydroxylation of arylboronic acids, and the formation mechanism of this radical was also proposed. The theoretical calculation further confirmed the N-doped C layer acted as electron acceptor and revealed the microscopic charge carrier migration path via the  $In_2O_3/N$ -doped graphite interfaces i.e., the photo-generated electrons from hybrid states of In<sub>2</sub>O<sub>3</sub>, composed of In 5s and 2p orbitals, transferred into the hybrid states of N-doped graphite, composed of C 2p and N 2p orbitals. The present study may be helpful for understanding and designing carbon-based micro-/nanoreactors for photocatalytic reactions and can be useful for investigating other relevant micro-/nanoractors as well.

#### Introduction

In comparison with the solid catalysts, the hollow structures, which have naturally existed or synthesized void space inside the shell, could provide a confined reaction "microenvironment" for chemical reactions. Thus hollow structures treated as micro-/nanoreactors have attracted considerable attention.<sup>[1-6]</sup> When hollow micro-/nanoreactors used as photocatalysts, the multiple reflection of light inside the hollow interior could reduce the loss of light, providing more chances for light absorption.<sup>[7-11]</sup> As a result, the number of photogenerated charge carriers, as a key

factor to the photocatalytic efficiency of the photocatalysts, was significantly increased with hollow morphology.<sup>[12-13]</sup> This character provided the possibility to design and fabricate highlyefficient hollow micro-/nanoreactors for photocatalytic reactions. It was widely accepted that the migration and separation of the electron-hole pairs were another key factors to the photocatalytic efficiency.<sup>[14,15]</sup> The faster separation and diffusion led to the better photocatalytic performance. The hollow structures with mesoporous shell were composed of nanoparticles with small grain size, which gave rise to better charge separation, because the small grain size could shorten the diffusion pathways of the photo-generated electron-hole pairs. Moreover, the mesoporous shell was preferred due to the advantages of the mesoporous pores in diffusion for photocatalysis.<sup>[16,17]</sup> However, limited by the complicated multi-step synthesis and poor repeatability, the of hollow micro-/nanoreactors with fabrication reaular mesoporous shells and composed of ultrafine nanoparticles was still a difficult task.

Combining carbon materials with photocatalysts had been considered as one of the effective approach to improve the separation of photo-generated electron-hole pairs, due to the low price and the high electrical conductivity of carbon.<sup>[16-23]</sup> Recent studies found that partial substitution of carbon atoms with nitrogen atoms having lone electron pairs could enhance the separation efficiency of electron-hole pairs significantly by supplying additional negative charges in the carbon networks.<sup>[24]</sup> How to uniformly coat N-doped C layers on hollow micro-/nanoreactors to enhance their photocatalytic performance was a challenging issue. Therefore, it was urgent to find a simple and effective approach to synthesize regular mesoporous hollow microreactors, composed of N-doped C layers coated ultrafine nanoparticles.

Herein, using the dodecahedral In-based frameworks as a sacrificial template, we fabricated the mesoporous doubleshelled hollow dodecahedral microreactors composed of Ndoped C coated ultrafine In<sub>2</sub>O<sub>3</sub> nanoparticles (N-C/In<sub>2</sub>O<sub>3</sub> HD) by in-situ thermally converted method in Ar atmosphere. In theory, the structure of metal organic frameworks (MOFs) could be rationally modified at the molecular level through selection or design of modulator, and then different heteroatoms could be introduced to carbon via thermal decomposition under different atmospheres.<sup>[26-30]</sup> Thus, the obtained N-C/In<sub>2</sub>O<sub>3</sub> HD contained the following three characters. (1) The shells, with regular mesoporous distribution, were constructed by ultrafine In2O3 nanoparticles (~10 nm) coated with N-doped carbon layers, which was beneficial for shortening the diffusion pathways of the photo-generated electron-hole pairs. (2) N-doped carbon layers uniformly distributed on the surface of In2O3 to produce intimate contacted interfaces, which guaranteed the highly efficient

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Supporting information for this article is given via a link at the end of the document. Experiment details, XRD, SEM, EDX and TGA of precursor (Fig. S1-S4). XRD, BET, Elemental line profiles, XPS of annealed product (Fig. S5-S10). XRD, SEM and EDX of ln2O<sub>3</sub> HD, ln2O<sub>3</sub> SD and ln2O<sub>3</sub> NP (Fig. S11-S13). SEM and XRD of product after five recycling experiments (Fig. S14). Contrast experiment of photocatalytic oxidative hydroxylation of arylboronic acids (Table S1).

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electron transfer for photocatalytic reactions. (3) The double shells of the obtained microreactors could provide more reactive sites to improve the photocatalytic activity. As expected, the obtained N-C/ln<sub>2</sub>O<sub>3</sub> HD exhibited excellent photocatalytic activity toward oxidative hydroxylation of a series of arylboronic acids substrates. The present work provided a general approach for the fabrication of efficient micro-/nanoreactors for photocatalytic reactions.

#### **Results and Discussion**



Scheme 1. Schematic showing the synthetic process of monodisperse mesoporous double-shelled hollow dodecahedron composed of N-doped C coated  $In_2O_3$  ultrafine nanoparticles (N-C/In\_2O\_3 HD).

Scheme 1 illustrated the detail synthetic process of mesoporous double-shelled hollow dodecahedron composed of N-doped C coated ultrafine  $In_2O_3$  nanoparticles (N-C/In\_2O\_3 HD). The formation of monodisperse In-rho-ZMOFs with a unique dodecahedral structure was achieved via a simple solvothermal reaction of using Indium(III) nitrate hydrate (In(NO\_3)\_3·4H\_2O) as In salt, 2-aminoterephthalic acid as organic ligand and benzimidazole as modulator. Experimental details could be referred to ESI†. After postannealing treatment in Ar atmosphere, N-C/In\_2O\_3 HD could be readily obtained.

In-rho-ZMOFs precursors were first examined by X-ray power diffraction (XRD) (Figure S1). The precursors exhibited sharp diffraction peaks and all peaks matched well with simulated and previous report <sup>[31]</sup> confirming the product as pure phase In-MOFs with good crystallinity. The morphology of the In-MOFs was characterized by field-emission scanning electron microscopy (FESEM), and the representative image of In-rho-ZMOFs precursors was shown in Figure 1a and Figure S2a. It indicated that these precursor particles showed highly uniform dodecahedral shape with a smooth surface and an average apex-to-apex diameter of 1.3-1.6  $\mu$ m (Figure S3). To better visualize the dodecahedral structure, we investigated the In-rho-ZMOFs precursor particles from different viewing angles under SEM observation. The corresponding dodecahedral model with {110} facets matched well with the SEM images (Figure S2b-d).



**Figure 1.** (a) FE-SEM images of In-rho-ZMOFs precursor, (b) SEM image of N-C/In<sub>2</sub>O<sub>3</sub> DY, Inset: High-magnification SEM images of In-rho-ZMOFs precursor in (a) and N-C/In<sub>2</sub>O<sub>3</sub> DY in (b), (c) and (d) TEM image of multiple N-C/In<sub>2</sub>O<sub>3</sub> HD particle and a single N-C/In<sub>2</sub>O<sub>3</sub> HD particles, (e) a magnified view of part of (d) with an inset of a size distribution histogram of In<sub>2</sub>O<sub>3</sub> nanoparticles, (f) HRTEM image of N-C/In<sub>2</sub>O<sub>3</sub> HD particle, (g) the corresponding SAED pattern; (h-I) STEM image and EDX elemental mapping of In, O, C, N.

As for the composition of In-rho-ZMOFs precursor, elemental mapping by energy-dispersive X-ray spectroscopy (EDX) showed that the elements In, O, C, N were uniformly distributed throughout the whole dodecahedral particle (Figure S2e-i). The existence of N was attributed to the amino groups of imidazole ring of ligand (2-aminoterephthalic acid) and imidazole rings of modulator (benzimidazole). Based on the above analysis, the nitrogen containing In-rho-ZMOFs dodecahedrons with {110} facets were successfully synthesized. According to the thermogravimetric analysis (TGA) result (Figure S4), the annealing condition for the carbonization of In-MOFs was set to 500 °C for 60 min in Ar atmosphere with a ramping rate of 2 °C·min<sup>-1</sup> to convert the resulting In-rho-ZMOFs phase into the cubic In<sub>2</sub>O<sub>3</sub> phase. The crystallographic structure and phase of the annealed products were characterized by XRD. As revealed by XRD analysis (Figure S5), the In-rho-ZMOFs precursors were completely transformed to pure cubic In<sub>2</sub>O<sub>3</sub> phase (PDF No. 00-006-0416) after the annealing process. The detailed morphological and structural features of the obtained N-C/In<sub>2</sub>O<sub>3</sub> HD were further characterized by FESEM and transmission electron microscopy (TEM). The FESEM image (Figure 1b) indicated the overall dodecahedral morphology of the In-rho-MOFs precursors was well preserved. However, the sizes of the N-C/In<sub>2</sub>O<sub>3</sub> HD became smaller than In-rho-ZMOFs precursors due to the shrinkage effect during carbonization process (Figure S6). Moreover, each facets of the N-C/In<sub>2</sub>O<sub>3</sub> HD became concave and the surface was very rough and composed of closely packed small nanoparticles.

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#### The inside structural information of N-C/In<sub>2</sub>O<sub>3</sub> HD was confirmed by TEM analysis. From Figure 1c, the double-shelled hollow structure could be clearly observed with the welldeveloped inner cavity, and the inner shell still possessed dodecahedral structure features. A magnified TEM image (Figure 1d) distinctly indicated that the mesoporous distributed throughout the shell and the highly symmetric dodecahedral shell framework was constructed by small subunits with size of around 10 nm (Figure 1e). The high-resolution TEM (HRTEM) image (Figure 1f) indicated that these small In<sub>2</sub>O<sub>3</sub> nanoparticles were well coated by the external carbon layer. The porosity of N-C/In<sub>2</sub>O<sub>3</sub> HD was further revealed by the nitrogen adsorptiondesorption isotherms (Figure S7). The N-C/In<sub>2</sub>O<sub>3</sub> HD gave rise to a high Brunauer Emmett Teller (BET) surface area of about 35.6 m<sup>2</sup>/g (Figure S7a), and the Barrett-Joyner-Halenda (BJH) pore sizes distributions were about 2 nm and 11 nm (Figure S7b). Figure 1f gave very clear lattice fringes with a d-spacing 0.292 nm, which corresponded well with the (222) plane of cubic $\ln_2O_3$ . The corresponding selected-area electron diffraction pattern (Figure 1g) showed a set of concentric rings, which matched well with cubic In<sub>2</sub>O<sub>3</sub>. A typical HAADF-STEM image and the corresponding element mapping profiles showed the homogeneous dispersion of In, O, C, N elements in the N-C/In<sub>2</sub>O<sub>3</sub> HD (Figure 1h-I). The presence of these elements could be further confirmed by the elemental line profiles (Figure S8).



Figure 2. High-resolution (a) In 3d, (b) O 1s, (c) C 1s, (d) N 1s XPS spectra of N-C/In<sub>2</sub>O<sub>3</sub> DY nanoparticles.

Moreover, surface chemical compositions and chemical state of elementals were investigated by the X-ray photoelectron spectroscopy (XPS). The survey spectrum indicated that the In, O, C, and N element existed in the N-C/In<sub>2</sub>O<sub>3</sub> HD (Figure S9). Figure 2a showed the XPS spectrum of In 3d double peaks, which were centred at 444.3 and 451.8 eV, corresponding to typical spin-orbit split In  $2d_{5/2}$  and In  $2d_{3/2}$ , respectively.<sup>[32]</sup> The result indicated that the In (III) was the predominate state in the sample. The high-resolution spectra of O 1s displayed a broad asymmetric curve, which was composed by three deconvoluted peaks centred at 529.7, 530.3 and 531.7 eV corresponding to the lattice oxygen (O<sub>L</sub>), oxygen-deficient regions (O<sub>V</sub>), and chemisorption oxygen species (O<sub>C</sub>), respectively (Figure 2b).<sup>[33]</sup> The C 1s spectrum (Figure 2c) could be deconvoluted into three major peaks. The peak at 284.7 eV was assigned to the C-C bonds of sp<sup>3</sup>-carbon. The peak at 285.2 eV corresponded to the sp<sup>2</sup>-carbon containing nitrogen atoms (C=N bond), which confirmed the nitrogen-doping in the carbon layer. The carbon atoms bonded to carbonyl group (C=O) was represented by the peak at 289.0 eV.<sup>[34]</sup> The convolution of N 1s peak was shown in the Figure 2d. Two component peaks at the binding energy of 399.5 and 400.6 eV were ascribed to the existence of N-In-O and N-C bonds,<sup>[35]</sup> which further confirmed the existence of Ndoped carbon layer. Therefore, the N-C/ln<sub>2</sub>O<sub>3</sub> HD was comprised of In<sub>2</sub>O<sub>3</sub> nanoparticles coated by N-doped C layer. The formation mechanism could be inferred as follows: during the annealing process, the indium ion in the In-rho-ZMOFs dodecahedral structure had been transformed to In2O3 nanoparticles, while both the organic ligand (2-aminoterephthalic acid) and modulator (benzimidazole), which possessed both nitrogen and carbon elements, could easily in situ carbonized to form the N-doped porous carbon laver. Moreover, the organic ligands were linked by Indium metal nodes, which were uniformly distributed in the In-rho-ZMOFs, then a uniform dispersion of In<sub>2</sub>O<sub>3</sub> nanoparticles coated by N-doped carbon layer was obtained after the thermal annealing the In-rho-ZMOFs.



Figure 3. (a) Illustration of the formation process of the mesoporous double-shelled hollow dodecahedral structure. (b-f, b<sub>1</sub>-f<sub>1</sub>) SEM images of the products obtained at 500 °C under Ar atmosphere for different time. (b<sub>2</sub>-f<sub>2</sub>) TEM images of the products obtained at 500 °C under Ar atmosphere for different time.

In order to better comprehend the growth mechanism of the double-shelled hollow dodecahedral structure of N-C/In<sub>2</sub>O<sub>3</sub> HD, the time-dependent evolution of shape and structure were elucidated by XRD, SEM, and TEM. The formation process of N-C/In<sub>2</sub>O<sub>3</sub> HD was reasonable illustrated in Figure 3a. After calcined at 500 °C in Ar atmosphere for 5 min, the product retained well the size and solid dodecahedral morphology of the In-rho-ZMOFs precursor (Figure 3b). But, the surface of this product became rough and was decorated with a number of small particles (Figure 3c), which mainly attributed to the incomplete pyrolysis of In-roh-ZMOFs and partially

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transformation into the cubic In<sub>2</sub>O<sub>3</sub> phase. The obtained In<sub>2</sub>O<sub>3</sub> phase was confirmed by the XRD pattern (Figure S10). With the increase of calcined time to 10 min (Figure 3d), more complete pyrolysis allowed the formation of a higher density of In<sub>2</sub>O<sub>3</sub> nanoparticles, resulting in the mesoporous structure on the surface of solid dodecahedron. When the outer shell of In-roh-ZMOFs was completely converted to In<sub>2</sub>O<sub>3</sub> coated by C layer (calcined for 20 min), the internal In-roh-ZMOFs components were also gradually pyrolyzed to form the void space (Figure S10), leading to the yolk-shell structure. Meanwhile, the outer shell of dodecahedral had shrunk, as shown in Figure 3e. After calcined for 60 min, the internal In-roh-ZMOFs were completely converted to In<sub>2</sub>O<sub>3</sub> coated by C layer (Figure S10), and formed the double-shell hollow structure (Figure 3f). Finally, the mesoporous double-shelled hollow dodecahedral microreactor composed by N-doped C coated In<sub>2</sub>O<sub>3</sub> ultrafine nanoparticles was achieved.



**Figure 4.** (a) Photocatalytic equation and condition of oxidative hydroxylation of aryboronic acids. (b) Kinetic profiles of oxidative hydroxylation of arylboronic acids using N-C/In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP photocatalysts under blue light irradiation. (c) Recyclability of N-C/In<sub>2</sub>O<sub>3</sub> HD in oxidative hydroxylation of arylboronic acids, (d) the oxidation hydroxylation reaction of various arylboronic acids with and without N-C/In<sub>2</sub>O<sub>3</sub> HD catalysts.

Photocatalytic activity of the obtained N-C/In<sub>2</sub>O<sub>3</sub> HD was evaluated by oxidative hydroxylation of arylboronic acids in an ethanol solvent. In order to determine the conditions for this photocatalytic reaction, the comparative experiments had been performed in the absence of light, DIEA and catalyst (Table S1). The result indicated that only a trace of the product was obtained without any one of them (light, DIEA and catalyst). Therefore, this photocatalytic reaction was carried out under blue light emitting diodes (LED,  $\lambda$ =450nm, 3W) irradiation using DIEA as co-catalyst in a Schlenk tube (Figure 4a). To investigate the synergistic effects of N-doped C layers and mesoporous double-shelled hollow dodecahedron constructed by ultrafine subunits on the photocatalytic activity, the photocatalytic activity of N-C/In<sub>2</sub>O<sub>3</sub> HD was compared with In<sub>2</sub>O<sub>3</sub> HD (obtained by calcining N-C/In<sub>2</sub>O<sub>3</sub> HD under pure oxygen atmosphere), which maintained the mesoporous double-shelled hollow structure of N-C/In<sub>2</sub>O<sub>3</sub> HD (Figure S11), In<sub>2</sub>O<sub>3</sub> SD (porous solid dodecahedron structure obtained by calcining In-MOFs precursor under pure oxygen atmosphere, Figure S12) and In<sub>2</sub>O<sub>3</sub> NP (synthetic In<sub>2</sub>O<sub>3</sub> nanoparticles, Figure S13). As shown in Figure 4b, N-C/In<sub>2</sub>O<sub>3</sub> HD exhibited a much better catalytic activity than the three other catalysts with the yield of product reaching about 99 % after 24 h. This results indicated that the Ndoped C layers and mesoporous double-shelled hollow dodecahedral structure played positive effects on photocatalytic oxidative hydroxylation of arylboronic acids. The cycle stability of the N-C/In<sub>2</sub>O<sub>3</sub> HD catalysts was checked by redoing the equal reaction process for five cycles with an intermittent evacuation every 24 h. As shown in Figure 4c, N-C/In<sub>2</sub>O<sub>3</sub> HD catalysts exhibited high performance cycle stability without any obvious loss of photocatalytic efficiency. The structure and morphology of catalysts showed no obvious change after five cycles of photocatalytic reaction (Figure S14). In order to prove the efficient catalytic activities of N-C/In<sub>2</sub>O<sub>3</sub> HD as microreactor, the oxidative hydroxylation of various arylboronic acids substrates were performed under the same photocatalytic condition. As the results shown in Figure 4d, the yields of the corresponding target products were about 85-99% in each case, indicating that the N-C/In<sub>2</sub>O<sub>3</sub> HD was an excellent microreactor and catalyst for a series of photocatalytic oxidative hydroxylation of arylboronic acids.

In order to investigate the mechanism of photocatalytic oxidative hydroxylation of arylboronic acids with N-C/In<sub>2</sub>O<sub>3</sub> HD as highly-efficient catalyst, the UV-vis absorption spectra of N-C/In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP were measured to analyse their optical adsorption properties. As shown in Figure 5a, the N-C/In<sub>2</sub>O<sub>3</sub> HD had the broadest and strongest absorption in the visible-light region among these four samples, attributing to the synergistic effect of uniformly coated N-doped C layers and multiple reflections of light caused by doubleshelled hollow structure. The enhanced optical absorption of N-C/In<sub>2</sub>O<sub>3</sub> HD could produce more photo-generated electron-hole pairs, which was the necessary element of high photocatalytic activity. The separation and transfer of photo-generated electron-hole pairs originated from N-C/In $_2O_3$  HD, In $_2O_3$  HD,  $In_2O_3$  SD and  $In_2O_3$  NP were investigated by the linear sweep voltammetry, photocurrent response, and electrochemical impedance spectroscopy, respectively. Figure 5b showed the linear sweep voltammetry (LSV) curves of these four samples, and indicated that N-C/In2O3 HD had a higher cathodic current density for reduction of water to H<sub>2</sub> than In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP. Compared with In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP, the integration of coating N-doped C layer with double-shelled hollow structure could accelerated charge transfer ability, which was responsible for its higher property in LSV.

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Figure 5. (a) Uv-vis absorption spectra of N-C/In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and  $In_2O_3$  NP samples, (b) Linear sweep voltammetry (LSV) curves of N-C/In\_2O\_3 HD,  $In_2O_3$  HD,  $In_2O_3$  SD and  $In_2O_3$  NP samples, (c) photo-current density of N-C/In\_2O\_3 HD, In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP samples measured at 1.3 V vs Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode under dark and light condition, (d) electrochemical impedance spectroscopy Nyquist plots of N-C/In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP samples.

The photocurrent density of N-C/In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP samples were measured under a 1.3 V potential to investigate the separation efficiency of photogenerated pairs. As shown in Figure 5c, the N-C/In<sub>2</sub>O<sub>3</sub> HD exhibited the highest photocurrent density, which was about 1.4, 2.5 and 6.4 times higher than that of In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP, respectively. In order to further verify the separation efficiency of photo-generated electron-hole pairs, the photoluminescence (PL) emission spectra of N-C/In<sub>2</sub>O<sub>3</sub> HD, In2O3 HD, In2O3 SD and In2O3 NP were measured and the results were shown in Figure S15. The intensities of main emission peak (centred at about 498 nm), attributed to the bandband PL phenomenon, present an obvious trend of N-C/In<sub>2</sub>O<sub>3</sub> HD<In<sub>2</sub>O<sub>3</sub> HD<In<sub>2</sub>O<sub>3</sub> SD<In<sub>2</sub>O<sub>3</sub> NP, which was consistent with the trend of photocurrent densities. This indicated that the N-C/In2O3 exhibited the highest separation efficiency of photogenerated electron-hole pairs among all the four In<sub>2</sub>O<sub>3</sub> samples. Furthermore, the electrochemical impedance spectrum of N-C/In<sub>2</sub>O<sub>3</sub> HD (Figure 5d) showed a smaller semicircular in the Nyquist plot than that of In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP, indicating a lower charge-transfer resistance in the hollow hybrid composite (coating N-doped C layer) which could warrant efficient transportation and separation of photo-generated electron-hole pairs.<sup>[36]</sup> In conclusion, the N-C/In<sub>2</sub>O<sub>3</sub> HD could generate more effectively separated electrons and holes under visible-light irradiation, attributed to the ultrafine subunits, which shortened the diffusion pathways of photo-generated electrons and holes, and the uniformly coated N-doped C layers, which provided electron storage and transfer channel.





Figure 6. (a) UV-vis adsorption spectra of the cationic radical of TMPD generated by N-C/In2O3 HD, In2O3 HD, In2O3 SD and In2O3 NP samples in the present of light, (b) The oxidative hydroxylation of arylboronic acids into phenol, where (1) represented the H atom from boronic group and (2) represented the H atom from phenolic hydroxyl group, (c) <sup>1</sup>H NMR spectra of oxidative hydroxylation of arylboronic acids without TEMPO. (d) 1H NMR spectra of oxidative hydroxylation of arylboronic acids with TEMPO.

The subsequent transfer of the separated photo-generated electrons was further investigated. It was well known that the photoactive macromolecular systems could mediate the electron transfer from N,N,N',N'-tetramethyl-phenylenediamine (TMPD) to molecular oxygen, thereby resulting in superoxide radical O2and blue-colored cationic radical species with strong absorption band at 563 nm and 612 nm.<sup>[37]</sup> As Figure 6a shown, the solution after N-C/In<sub>2</sub>O<sub>3</sub> HD reaction had the strongest characteristic adsorption peaks among all the four In<sub>2</sub>O<sub>3</sub> samples, indicating that N-C/In<sub>2</sub>O<sub>3</sub> HD could produce more O<sub>2</sub><sup>--</sup> than In<sub>2</sub>O<sub>3</sub> HD, In<sub>2</sub>O<sub>3</sub> SD and In<sub>2</sub>O<sub>3</sub> NP. In addition, 2,2,6,6-tetramethylpiperidine-1oxyl (TEMPO), which was well-known as a O2<sup>-</sup> scavenger, was added to the reaction mixture (Figure 6b) under standard conditions. Compared with the high yield (99%) of product (Figure 6c) without the addition of TEMPO, the yield of product became zero in the presence of TEMPO (Figure 6d). The TEMPO consumed all the  $O_2^{-}$ , which was the one of the active species in the photocatalytic oxidative hydroxylation of arylboronic acid. In addition, the other possible active species, such as hydroxyl radical (·OH) and photo-generated hole (h<sup>+</sup>), were also investigated by introducing tertiary butanol (t-BuOH) and trimethylamine (TEA) as sacrificial agent, respectively. The experimental results showed that, after adding t-BuOH and TEA, the conversion of arylboronic acid to phenol remained almost the same as when no scavenger was added. Thus, it could be

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concluded that  $O_2^{--}$  was the critical active species in the photocatalytic oxidative hydroxylation of arylboronic acids. In order to further prove the existence of  $O_2^{--}$ , electron spin resonance (ESR) measurements were conducted in which 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used to capture superoxide radical anion  $O_2^{--}$ . As shown in Figure. S16, a clear characteristic ESR signal for DMPO– $O_2^{--}$  was detected. The result further indicated the formation of  $O_2^{--}$  in the photocatalytic process.



Scheme 2. Schematic showing the proposed reaction mechanism for oxidative hydroxylation of arylboronic acids with N-C/ln<sub>2</sub>O<sub>3</sub> HD as the catalyst and micro-reactor.

possible photocatalytic mechanism The of oxidative hydroxylation of arylboronic acids by using N-C/In<sub>2</sub>O<sub>3</sub> HD as the catalyst and micro-reactor was proposed as following (Scheme 2). Firstly, under blue LED light irradiation, the N-C/In<sub>2</sub>O<sub>3</sub> HD was excited to generated electron-hole pairs. Owing to the uniformly coated N-doped C layers, the photo-generated electrons transferred to the N-doped C layers, leaving the photogenerated holes on the In2O3 nanoparticles. Secondly, the separated photo-generated electrons reduced the adsorbed O<sub>2</sub> molecules to produce  $O_2^{-}$ , and the separated photo-generated holes oxygenated iPr<sub>2</sub>Net molecule to form iPr<sub>2</sub>N<sup>+</sup>Et. Thirdly, the reactant (arylboronic acid) diffused through the mesoporous shell, and its conversion into the intermediate was oxygenated by O2". This intermediate diffused further into the inner shell and was converted into the final product (phenol); and this reaction was reduced by iPr<sub>2</sub>N<sup>+</sup>Et. The mechanism of radical formation in this system could be described by the following reactions (Eqs. 1-4):

$$In_2 O_3 + hv \rightarrow In_2 O_3 (h_{VB}^* + e_{CB}^-)$$
 (1).

 $h_{VB}^+ + e_{CB}^- \rightarrow heat$ 

 $e_{CB}^- + O_2 \rightarrow O_2^-$ 

$$h_{VB}^{+} + iPr_2NEt \rightarrow iPr_2N^{+}Et$$
 (4)

The above analysis indicated that the improved photocatalytic oxidative hydroxylation of arylboronic acids by  $N-C/ln_2O_3$  HD catalysts, acted as microreactors, was attributed to the synergistic effect of uniformly coated N-doped C layers and the structural characteristics (mesoporous double-shelled hollow dodecahedron composed of ultrafine nanoparticles).



Figure 7. Projected density of states (PDOS) for the  $In_2O_3$  (100)/N-doped graphite (001) (a,b), the  $In_2O_3$  (110)/N-doped graphite (001) (c,d), and the  $In_2O_3$  (111)/N-doped graphite (001) (e,f), respectively.

Based on the above analysis, it could be found that the uniformly coated N-doped C layers played a key role in improving the separation of photo-generated electron-hole pairs. In order to clearly analyse the microcosmic separation mechanism of photo-generated carriers, the projected density of states (PDOS) of the In<sub>2</sub>O<sub>3</sub> (100)/N-doped graphite (001), In<sub>2</sub>O<sub>3</sub> (110)/N-doped graphite (001), and In<sub>2</sub>O<sub>3</sub> (111)/N-doped graphite (001) interfaces were calculated and presented in Figure 7. Due to the substitutional N impurity had one more valence electron than the C in graphite, the spin-splitting of single electron levels could be found from Figure 7. From the magnified PDOS (the inset of Figure 7), it could be found that hybrid states of C 2p and N 2p orbitals pass through the highest occupied level in all these three In<sub>2</sub>O<sub>3</sub>/N-doped graphite interfaces, indicating that the N-doped graphite acted as the electron acceptor. This was consistent with the previous experimental results. The microscopic charge carrier migration path via In<sub>2</sub>O<sub>3</sub>/N-doped graphite interfaces was that the photo-generated electrons from hybrid states of In2O3, composed of In 5s and O 2p orbitals, transferred into the hybrid states of N-doped graphite, composed of C 2p and N 2p orbitals.

#### Conclusions

(2).

(3).

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summary, the mesoporous double-shelled hollow In dodecahedral microreactors composed of N-doped C coated ultrafine In<sub>2</sub>O<sub>3</sub> nanoparticles (N-C/In<sub>2</sub>O<sub>3</sub> HD) had been successfully synthesized by the thermolysis of dodencahedral In-based framworks in Ar atmosphere. The obtained N-C/In<sub>2</sub>O<sub>3</sub> HD, acted as a microreactor, exhibited excellent catalytic activity toward photocatalytic oxidative hydroxylation of a series of arylboronic acids substrates, attributed to the enhanced optical absorption and efficient separation of photo-generated electronhole pairs endowed by the unique structure and uniformly coated N-doped C layers. In the further research, we found that O2<sup>-</sup> was the critical active species in the photocatalytic oxidative hydroxylation of arylboronic acids. The microscopic charge carrier migration path via In<sub>2</sub>O<sub>3</sub>/N-doped graphite interfaces was revealed by theoretical calculation, i.e., the photo-generated electrons from hybrid states of In<sub>2</sub>O<sub>3</sub>, composed of In 5s and 2p orbitals, transferred into the hybrid states of N-doped graphite, composed of C 2p and N 2p orbitals. We believe that the method described in this paper provides a simple yet effective route to rationally design of delicate micro-/nanoreactors for applications beyond photocatalysis.

#### **Experimental Section**

#### Preparation of In-rho-ZMOFs dodecahedron:

In a typical synthesis,  $ln(NO_3)_{3}\cdot 4H_2O$  (0.015g, 0.040 mmol), 4,5-Imidazoledicarboxylic acid (0.021g, 0.135 mmol) and Benzimidazole (0.1g, 0.846 mmol) were dissolved in 6 mL of N,N-dimethylformamide (DMF). After stirring by ultrasonic concussion for 10 minutes, the mixture was transferred to a 50 mL round bottom flask and placed in an oven at 100 °C for 4 hours. After reaction, the product was collected via centrifugation and washed several times with fresh ethanol, then dried at 60 °C overnight.

## Synthesis of mesoporous double-shelled hollow dodecahedron composed of N-doped C coated $In_2O_3$ ultrafine nanoparticles (N-C/In\_2O\_3 HD):

N-C/In<sub>2</sub>O<sub>3</sub> HD was synthesized via calcination of the obtained In-rho-ZMOFs dodecahedron at 500 °C for 1h in Ar atmosphere with heating rate of 2 °C·min<sup>-1</sup>.

#### Characterization:

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 CuKα 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 suspensions in ethanol on a carbon film coated copper grid. PHI QUANTUM2000 photoelectron spectrometer (XPS) was used to characterize the surface compositions of product. 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.

#### Photocatalytic activity test:

The photocatalyst (5mg), 4-Methoxyphenylboronic acid (0.1 mmol, 1 equiv), and DIEA (N,N-Diisopropylethylamine) (0.3 mmol, 3 equiv) were added to 2 mL CH<sub>3</sub>CH<sub>2</sub>OH. The mixture was stirred and irradiated by using blue LEDs (450 nm, 3W) for 24 h under air at room temperature. 1H NMR determined the yield. To carry out the recycle reactions, the photocatalyst was recovered by centrifuging at 10000 rpm for 5 min, and

washed with fresh  $CH_2Cl_2$  three times. Finally, the recycled catalyst was dried in a vacuum at 60 °C overnight.

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Mesoporous double-shelled hollow dodecahedral microreactors composed of N-doped C coated In2O3 ultrafine nanoparticles had been synthesized by using benzimidazole decorated dodecahedral In-based frameworks as a hard template. The obtained sample exhibited excellent photocatalytic activity toward photocatalytic oxidative hydroxylation of a series of arylboronic acids substrates.



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Rationally Designed a Double-Shell Dodecahedral Microreactor with Efficient Photo-electron Transfer: N-doped C Encapsulated Ultrafine In<sub>2</sub>O<sub>3</sub> Nanoparticles