Facile strategy for controllable synthesis of stable mesoporous black TiO$_2$ hollow spheres with efficient solar-driven photocatalytic hydrogen evolution

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Hydrogenated black TiO$_2$ has been proven to tune the bandgap and utilize solar energy effectively. Herein, we report a facile strategy for controllably synthesizing stable mesoporous black TiO$_2$ hollow spheres (MBTHSs) with a narrow bandgap via a template-free solvothermal approach combined with a small amine molecule reflux-encircling process and subsequent high-temperature hydrogenation, which are composed of highly crystalline pore-walls, Ti$^{3+}$ in frameworks and surface disorders. The encircled protectors especially ethylenediamine result in high thermostability of the TiO$_2$ hollow structures, which not only facilitate hydrogenation (600 °C), but also inhibit grain growth and anatase-to-rutile phase transformation as well as retain a high structural integrity. The MBTHSs with a diameter of ~700 nm possess a relatively high surface area of ~80 m$^2$/g, large pore size and pore volume of ~12 nm and ~0.20 cm$^3$/g, respectively. The diameters and wall thicknesses are controllable from ~500 nm to 1 µm and ~35 to 115 nm, respectively. The high crystallinity, integrated hollow structure, Ti$^{3+}$ in frameworks and surface disorders of the MBTHSs give rise to an extending photoresponse from the ultraviolet to the visible light region and significant improvement in the solar-driven photocatalytic hydrogen evolution rate (241 μmol h$^{-1}$/0.1 g$^{-1}$), which is two times as high as that of black TiO$_2$ nanoparticles (118 μmol h$^{-1}$/0.1 g$^{-1}$) and almost three times that of pristine mesoporous TiO$_2$ hollow spheres (81 μmol h$^{-1}$/0.1 g$^{-1}$), respectively.

Introduction

Mesoporous TiO$_2$ hollow spheres have recently attracted increasing research interest because of their specific features, such as low density, high surface-to-volume ratio, the effect of void space, high shell permeability, excellent electronic and optical properties, and widespread applications in the fields of photocatalysis, solar cells, photoelectrochemical water splitting, drug delivery, sensors and energy storage.1–4 Significant efforts have been made to fabricate various mesoporous TiO$_2$ hollow spheres as photocatalysts, and their performance indeed enhanced obviously.5–9 Usually, the synthesis approach includes template-based and template-free methods.10–12 The template-based synthesis offers great versatility for various hollow structures, but creating uniform coatings on the corresponding templates and removing them are quite complicated.13,14 What’s worse, the hollow structures could easily collapse during the removal of templates. Although the template-free approach avoids the complex multi-step synthesis procedures, it is difficult to controllably synthesize uniform mesoporous TiO$_2$ hollow spheres, with a tunable diameter, wall thickness, pore size, etc. Moreover, the large bandgap of anatase TiO$_2$ (~3.2 eV) greatly limits the efficiency of solar-driven photocatalysis, because light absorption is confined only to the ultraviolet (UV) region, which represents a small fraction of solar energy.15,16

The recent discovery of black TiO$_2$ nanoparticles by Mao and coworkers via hydrogenation has triggered a huge splash and opened a new epoch for utilizing long-wavelength light.17 Some proposals including both theoretical computations and experiments are employed to study black TiO$_2$ materials, such as the surface disorder-engineered layer, Ti$^{3+}$ (oxygen vacancy), and hydrogen plasma, which could rationally explain these phenomena and represent a big breakthrough in photocatalysis.18–22 Santo and coworkers found that the synergistic effect of oxygen vacancies and surface disorder resulted in narrowing the bandgap of black TiO$_2$ nanoparticles.26 Scrosati...
and coworkers showed that the presence of trivalent Ti reduced the bandgap energy to as low as 1.8 eV.27 Very recently, Yang and coworkers have revealed the physical origin of the Ti3+ related photoabsorption and visible light photocatalytic activity in TiO2 via two-photon photoemission spectroscopy and density functional theory calculation, which led to a better understanding of the mechanism of enhanced long-wavelength light absorption.28 Although the solar-driven photocatalytic performance of the current black TiO2 materials has been indeed state-of-the-art until now, it is still far from desirable. Mesoporous black TiO2 hollow spheres would be ideal candidates for further improving the solar-driven photocatalytic performance because the unique hollow structures are beneficial for efficient light utilization and offering more surface active sites. However, the conventional mesoporous TiO2 hollow spheres easily collapse during the high-temperature treatment process due to the low thermal stability,29,30 which is a major obstacle for effective surface hydrogenation, because the frameworks can collapse easily due to the capture of oxygen by hydrogen during the high-temperature hydrogenation process. Therefore, it is still a great challenge to controllably fabricate stable mesoporous black TiO2 hollow spheres. Herein, we demonstrate a facile route to synthesize stable mesoporous black TiO2 hollow spheres (MBTHSs) with controllable diameters and wall thicknesses through a template-free solvothermal approach combined with a small amine molecules encircling strategy and atmospheric hydrogenation (Scheme 1). Our synthesis system is suitable for efficient encircling of these small amine molecules on the surface of the mesoporous TiO2 hollow spheres (MTHSs), in which the hollow structures and anatase phase can be maintained up to 900 °C. The highly thermostable MTHSs are a good candidate for subsequent high-temperature hydrogenation. The obtained MBTHSs possess a relatively high surface area of ~80 m2 g−1 and a large pore size of ~12 nm. The diameters and wall thicknesses are controlled from ~500 nm to 1 μm and ~35 to 115 nm, respectively. Moreover, the MBTHSs extend the photosresponse from the UV to the visible light region and exhibit a high solar-driven photocatalytic hydrogen evolution rate (241 μmol h−1 g−1), which is almost three times as high as that of pristine MTHSs (81 μmol h−1 g−1). The MBTHSs will be an excellent host material to form novel heterojunction composites through the development of a variety of narrow band-gap semiconductors, noble metals with surface plasmon resonance, and the assembly of functional heterogeneous components in the mesoporous channels or cavities, and will have widespread applications in the fields of energy and environment.

**Experimental section**

**Chemicals**

Tetrabutyl titanate (TBOT), N,N-dimethylformamide (DMF), ethanol (EtOH), ethylenediamine, hexamethylenetetramine, n-butylamine, isopropylamine, trimethylamine, ammonium hydroxide, methanol and KOH were of analytical grade and purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Anhydrous oxalic acid and anatase TiO2 nanoparticles (25 nm) were purchased from Aladdin Industrial Inc. All chemicals were used as received without further purification. Deionized water was used for all experiments.

**Synthesis of the stable mesoporous black TiO2 hollow spheres**

In a typical synthesis, 0.1 g of tetrabutyl titanate (TBOT) and 7.25 g of anhydrous oxalic acid were dissolved in 65 mL of N,N-dimethylformamide. Then, the solution was transferred to a 100 mL autoclave and heated to 170 °C for 10 h. The as-synthesized samples were washed with ethanol and dried at 60 °C for 6 h. Subsequently, the products were refluxed with ethylenediamine aqueous solution (pH 11–12) for 48 h at 80–90 °C. The obtained powders were washed with deionized water several times and dried at 60 °C overnight. Finally, the resulting samples were calcined at 600 °C for 3 h in air to remove the organic species and improve the crystallinity, with a temperature ramping rate of 5 °C min−1. White mesoporous TiO2 hollow spheres were obtained (denoted as MTHSs). Before being calcined in a H2 flow at 600 °C for 3 h under normal pressure conditions, with a constant heating rate of 10 °C min−1, the hollow spheres were deaerated under an inert gas flow (N2) for 0.5 h. Finally, stable mesoporous black TiO2 hollow spheres were obtained (denoted as MBTHSs). In order to confirm the encircling strategy, several other small amine molecules, including trimethylamine, isopropylamine, n-butylamine and hexamethylenetetramine, and ammonium hydroxide were chosen for proving the effect of high thermostability. As a comparative test, commercial anatase TiO2 nanoparticles were also calcined in a H2 flow under the same conditions, and finally black TiO2 nanoparticles were obtained. The MBTHSs with different diameters were synthesized via adjusting the amount of TBOT (0.06, 0.08, 0.10, 0.12, 0.14 and 0.16 g, respectively), keeping other synthesis parameters constant. The MBTHSs with various wall thicknesses were also prepared through tuning the solvothermal reaction time (8, 9, 10, 11 and 12 h).

![Scheme 1](image-url)  
**Scheme 1** Schematic illustration of the controllable synthesis of the stable mesoporous black TiO2 hollow spheres.
Characterization

X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance diffractometer by using Cu Kα radiation (λ = 1.5406 Å, 40 kV, 40 mA). The scan rate and step size were 6° min⁻¹ and 0.02°, respectively. Raman measurements were performed with a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. The laser beam was focused with a 50× objective lens to a ca. 1 µm spot on the surface of the sample. Scanning electron microscopy (SEM) micrographs were obtained with a Philips XL-30-ESEM-FEG instrument operating at 20 kV. All binding energies were calibrated by referencing to the C 1s peak at 284.6 eV. Diffuse reflectance spectroscopy (DRS) was conducted on a UV/vis spectrophotometer (Shimadzu UV-2550) in the range of 200–800 nm. The bandgaps were estimated by extrapolating a linear part of the plots to (αhν)² = 0. Nitrogen adsorption–desorption isotherms at 77 K were collected on an AUTOSORB-1 (Quantachrome Instruments) nitrogen adsorption apparatus. All of the samples were degassed under vacuum at 180 °C for at least 8 h prior to the measurement. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area. Pore size distributions were obtained using the Barrett–Joyner–Halenda (BJH) method from the adsorption branch of the isotherms. Surface photovoltage spectroscopy (SPS) measurements were carried out with a home-built apparatus equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). The powders were sandwiched between two indium tin oxide (ITO)-coated glass electrodes, and monochromatic light was passed from a 500 W xenon lamp through a double prism monochromator (SBP300). Scanning Kelvin Probe (SKP) measurements (SKP5050 system, Scotland) were performed under normal laboratory conditions (in an ambient atmosphere). A gold electrode was used as the reference electrode. The electron paramagnetic resonance (EPR) spectra were measured at room temperature with an EPR spectrometer (JES-FA 300, 9.4 GHz, 1 mW).

Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution experiments were conducted in an online photocatalytic hydrogen generation system (AuLight, Beijing, CEL-SHP2N) at an ambient temperature (20 °C). The photocatalyst (100 mg) loaded with Pt (1 wt%) was suspended in a mixture of 80 mL of water and 20 mL of methanol in a closed-gas circulation reaction cell by using a magnetic stirrer. Prior to the reaction, the mixture was deaerated by evacuation to remove O₂ and CO₂ dissolved in water. An AM 1.5 solar power system (solar simulator (Oriel, USA) equipped with an AM 1.5G filter (Oriel, USA)) was used as the light irradiation source. Gas evolution was observed only under photoirradiation with a power density of 100 mW cm⁻², which was analyzed by an on-line gas chromatograph (SP7800, TCD, molecular sieves 5 Å, N₂ carrier, Beijing Keruida Limited). The determination of the apparent quantum efficiency for hydrogen generation was performed using the same closed circulating system under illumination of a 300 W Xe lamp with a bandpass filter (365, 420 and 520 nm) system. Once the photocatalytic reaction of a testing cycle in 3 h was complete, the reactor was replenished with 1 mL of methanol and degassed in vacuum before starting the subsequent cycle.

Photoelectrochemical properties

Photoelectrochemical properties were investigated using a Princeton Versa STAT 3 in a standard three electrode configuration with MBTHSs and MTHSs materials used as photoanodes, Pt foil as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The photoanodes were prepared by a traditional spray coating method, using a glass rod to roll a paste containing 0.2 g of powders and 0.5 mL of EtOH on a transparent conducting glass (TCO, fluorine doped SnO₂ layer, 20 Ω per square, Nippon sheet glass, Japan), and pressed at 1000 kg cm⁻² between stainless-steel plates in a hydraulic press using aluminum foil to prevent adhesion to form a film (2 × 1 cm), followed by calcination at 350 °C under a N₂ atmosphere with a constant heating rate of 10 °C min⁻¹. 1 M KOH purged with N₂ was used as the electrolyte. An AM 1.5 solar power system (Oriel, USA) was used as the light irradiation source.

Results and discussion

After surface hydrogeneration at 600 °C, the X-ray diffraction (XRD) patterns of both MBTHSs and MTHSs (Fig. 1A) show five obvious crystal peaks at 2θ = 25.2–55.2°, which could be indexed as the 101, 004, 200, 105, and 211 reflections for the original symmetry of the TiO₂ lattice is destroyed and those bands for MBTHSs demonstrate that they have been transformed to a stable mesoporous black TiO₂ hollow spheres after hydrogen gas annealing at 600 °C for 3 h (a) and stable mesoporous TiO₂ hollow spheres after being calcined in air at 600 °C for 3 h (b).

![Fig. 1 Typical XRD patterns (A) and Raman spectra (B) of the stable mesoporous black TiO₂ hollow spheres after hydrogen gas annealing at 600 °C for 3 h (a) and stable mesoporous TiO₂ hollow spheres after being calcined in air at 600 °C for 3 h (b).](image-url)
states, which would form a continuum with the conduction band edge and lead to band tail states merging with the valence band, and thus narrowing the bandgap.\textsuperscript{33,34}

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images both show mesoporous TiO\textsubscript{2} hollow spheres with diameters of \(\approx 700\) nm after H\textsubscript{2} annealing treatment (Fig. 2a and b). The mesopores can be observed obviously (inset of Fig. 2b). The high-resolution TEM image (Fig. 2c) clearly shows that the pore walls consist of highly crystalline TiO\textsubscript{2} nanoparticles. Lattice fringes with a spacing of 0.35 nm are clearly observed (Fig. 2c), which correspond well to the (101) crystallographic planes of anatase. Well-resolved diffraction rings of the selected-area electron diffraction (SAED) pattern (Fig. S1\textsuperscript{†}) further confirm the high crystallinity of the stable mesoporous black TiO\textsubscript{2} hollow spheres. By comparison with the stable mesoporous TiO\textsubscript{2} hollow spheres (Fig. 2d and e), the hollow structures are mostly retained after high-temperature hydrogenation. Furthermore, compared to MTHSs with high crystallinity (Fig. 2f), a thin disordered surface layer encircling the crystalline core could be observed clearly (Fig. 2c), indicating that the surface hydrogenation is efficient. N\textsubscript{2} adsorption/desorption isotherms of MTHSs and MBTHSs both show typical type IV curves (Fig. S2\textsuperscript{†}), indicating mesoporous materials.\textsuperscript{35} The specific Brunauer–Emmett–Teller surface area and pore size slightly vary after hydrogenation, in which the surface area, pore size and pore volume for MBTHSs are \(\approx 80\) \(\text{m}^2\) \(\text{g}^{-1}\), \(\approx 12\) nm and \(\approx 0.20\) \(\text{cm}^3\) \(\text{g}^{-1}\), respectively, indicating that the hollow structure is retained well during the high-temperature H\textsubscript{2} annealing treatment, which is in good agreement with SEM and TEM observation. Diffuse reflectance measurements reveal that the bandgap is reduced after hydrogenation, because an obvious shift in the onset of absorption from the UV to visible light region can be observed (Fig. 2g), along with color change from white to black (inset of Fig. S3\textsuperscript{†}). The bandgap for MBTHSs is about 2.59 eV (Fig. S3\textsuperscript{†}), smaller than that of MTHSs (\(\approx 3.17\) eV), which may substantially enhance the solar-driven photocatalytic activity.

The wall thickness of MBTHSs, which plays a vital role in photocatalysis, is controllable from \(\approx 35\) to 115 nm via adjusting the reaction time (Fig. 3). With increasing the reaction time, the wall thickness gradually becomes thinner due to further Ostwald ripening. The wall thickness is only \(\approx 35\) nm up to a reaction time of 12 h. On prolonging the reaction time, the hollow spheres begin to collapse. Moreover, the diameter of MBTHSs is also controllable through tuning the amounts of Ti precursors. The diameters of black TiO\textsubscript{2} hollow spheres are controlled easily from \(\approx 500\) nm to 1 \(\mu\)m with increasing the amount of Ti precursors (Fig. S4\textsuperscript{†}). The hydrolysis-condensation of Ti precursors can produce Ti(\textit{iv}) nanoclusters, and the different spatial configurations derived from their dimensions and linearity can modulate the hybrid interface, and thus lead to hollow structures with different diameters during the Ostwald ripening process. The different sizes of the hollow spheres are closely related to the photocatalytic performance because of the different surface areas and active sites. The surface areas decrease remarkably with increasing the diameters. So, controllable diameters of MBTHSs are important for photocatalysis.

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the surface states of MBTHSs and MTHSs. The Ti 2p spectra are almost identical for both (Fig. S5A\textsuperscript{†}). These features are identical with Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} centered at 458.3 and 464.2 eV, which are all assigned to Ti\textsuperscript{4+} and indicate that no Ti\textsuperscript{3+} species exist on the surface.\textsuperscript{36,37} Usually, the surface Ti\textsuperscript{3+} is unstable in air as it is easily oxidized by air or dissolved oxygen.

![Fig. 2](image-url) **Fig. 2** SEM and TEM images of the stable mesoporous black TiO\textsubscript{2} hollow spheres (a–c) after hydrogen gas annealing at 600 °C for 3 h and the stable mesoporous TiO\textsubscript{2} hollow spheres (d–f) after being calcined in air at 600 °C for 3 h. The ultraviolet-visible absorption spectra (g), electron paramagnetic resonance spectroscopy (h) and scanning Kelvin probe maps (i) of the stable mesoporous black TiO\textsubscript{2} hollow spheres (I) and stable mesoporous TiO\textsubscript{2} hollow spheres (II). The white arrows in the inset of (b) point to mesopores.

![Fig. 3](image-url) **Fig. 3** Wall thickness (WT) evolution of the stable mesoporous black TiO\textsubscript{2} hollow spheres with different solvothermal reaction times ((a) 8 h; (b) 9 h; (c) 10 h; (d) 11 h; (e) 12 h).
in water. The XPS technique could characterize only the top several nanometers surface layer of the nanomaterials, and could not provide information on the bulk. The O 1s spectrum of MBTHSs is different from that of MTHSs obviously. The former exhibits a broad O 1s peak with a strong shoulder at a high binding energy, which can be deconvoluted into two peaks centered at 529.5 and 531.3 eV. The broader peak at 531.3 eV could be attributed to Ti–OH species, implying the formation of more hydroxyl groups on the TiO2 surface after hydrogenation (Fig. S5B†). The valence band XPS for MTHSs displays typical valence band characteristics of anatase TiO2, with the edge of the maximum energy at ~2.41 eV (Fig. S5C†), while the valence band maximum (VBM) energy for MBTHSs blue-shifts toward the vacuum level at ~1.72 eV, further illustrating the efficient surface hydrogenation. Combined with the TEM analyses, the surface lattice disorder (e.g. Ti–H, O–H) can blue-shift the VBM of TiO2 through introducing midgap states which would be introduced via the formation of Ti3+ or oxygen vacancy, meanwhile, the conduction band minimum is almost unchanged.46,47 Therefore, the bandgap of anatase TiO2 is reduced after hydrogenation, which is in good agreement with the diffuse reflectance measurements. Electron paramagnetic resonance (EPR) spectra were recorded at room temperature to determine the presence of Ti3+ in the bulk. An obvious EPR signal for MBTHSs could be observed at g ≈ 1.98 (Fig. 2h), which should be assigned to Ti3+ resulting from the reduction of H2 and confirmed the presence of Ti3+ in MBTHSs.42–46 Combined with the XPS results, Ti3+ species are not present on the surface but mainly located in the bulk, which is crucial for the stability of MBTHSs and responsible for the narrow bandgap. The scanning Kelvin probe (SKP) is sensitive to discern subtle molecular interactions via vibrating electromagnetic and acoustic fields, which shows a relatively flat potential change according to the work function.48–49 The SKP images present direct evidence for potential change. The workfunction of MBTHSs (~5.19 eV) is lower than that of MTHSs (~5.34 eV), which ensures easier escape of electrons from the former and then to the cocatalysts for photocatalytic hydrogen evolution (Fig. 2l). According to SKP results, the approximate Fermi level of MBTHSs is higher than that of MTHSs, which changes the built-in electric field and surface band bending.50,51 It could accelerate the photogenerated electron transfer to the surface and then to the cocatalysts, thus greatly reducing the electron–hole recombination and improve the photocatalytic performance.

To validate the effective strategy for controllable fabrication of MBTHSs, a series of control experiments were conducted. Highly thermostable MTHSs are firstly fabricated via a solvothermal approach combined with a small amine molecules encircling strategy (Scheme 1), which are chosen as the candidate for the subsequent high-temperature hydrogenation (600 °C). Then, the stable hollow structure frameworks can withstand the subsequent high-temperature calcination (600 °C) and hydrogenation without collapse. Ethylenediamine, which is a representation of small amine molecules for this encircling strategy, plays a vital role in the formation of the highly thermostable mesoporous TiO2 hollow spheres. The highly thermostable hollow frameworks facilitate H2 gas diffusion into TiO2 and interaction with the frameworks as well as maintain the integrated hollow structures. Ordered mesoporous black TiO2 had been successfully synthesized via an ethylenediamine encircling strategy previously, which offers ideas for preparing stable mesoporous black TiO2 hollow spheres.23 Without the pre-treatment, the hollow structure can collapse after high-temperature calcination (Scheme 1). Furthermore, the diameters and wall thicknesses are also tunable via adjusting the experimental parameters. The specific structural parameters of the stable MTHSs after being calcined at different temperatures are shown in Fig. S6–S10 and Tables S1 and S2.† It is well-known that the crystal phase and crystallization of anatase TiO2 are intimately associated with the calcination temperature. The XRD patterns of the thermostable MTHSs after being calcined at different temperatures are shown in Fig. S6.† Five high-intensity peaks for the anatase phase (JCPDS no. 21-1272) can be observed. Up to a calcination temperature of 900 °C, rutile is present in trace amounts. However, without ethylenediamine encircling treatment, the rutile phase is present at 700 °C, suggesting that ethylenediamine indeed improves the crystallinity of anatase and retards the phase transformation from anatase to rutile. These results are consistent with the Raman characteristic (Fig. S7†). N2 adsorption/desorption isotherms of MTHSs with different calcination temperatures (Fig. S8†) all show typical type IV isotherms, and the main pore size distributions are relatively narrow (~10 nm). It is interesting to note that the specific BET surface area decreases slightly with increasing the calcination temperature after ethylenediamine encircling treatment (Table S1†). Conversely, without the encircling treatment, it decreases sharply, further indicating the efficient encircling effect. From the SEM images, we can clearly see that the integrated hollow structure could be retained up to 900 °C after the ethylenediamine encircling treatment, but very large TiO2 nanoparticles can be observed without the treatment (Fig. S9†). The above results all confirm that the ethylenediamine encircling strategy inhibits the grain growth and anatase-to-rutile phase transformation as well as maintains the high structural integrity of hollow spheres. The highly thermostable MTHSs could facilitate subsequent surface hydrogenation. After surface hydrogenation at 600 °C, MBTHSs could be obtained successfully and the hollow structure was retained well, which favors utilizing solar energy efficiently and thus improving the photocatalytic performance. Furthermore, a series of small amine molecules, such as trimethylamine, isopropylamine, n-butylamine, etc., and ammonium hydroxide, were selected as encircled protectors and similar effects could be obtained, in which the surface bonded N-containing species and textural properties (Fig. S10 and Table S2†) could be observed clearly, indicating the efficient protection of these small amine molecules or ammonium hydroxide. It also confirms that the encircling strategy is a universal approach for preparing highly thermostable mesoporous TiO2 hollow spheres. After surface hydrogenation, the anatase phase and integrated hollow structures are well retained (Fig. S11†).
The MBTHSs were evaluated as a catalyst for photocatalytic hydrogen evolution and exhibited higher photocatalytic activity, with a reaction rate of 241 \( \mu \text{mol h}^{-1} \text{ g}^{-1} \), than MTHSs (81 \( \mu \text{mol h}^{-1} \text{ g}^{-1} \)) under AM 1.5 (Fig. 4A). After testing for six cycles, both still exhibit nearly constant hydrogen evolution capability, indicating the high stability of the hollow structures. Obviously, the photocatalytic hydrogen evolution rate at 365 nm for MBTHSs is much higher than that at 420 and 520 nm (Fig. 4B), indicating that the main contributor to the high photocatalytic performance is still the UV light. To testify the solar energy conversion efficiency, the apparent quantum efficiency (QE) for different single wavelengths is measured, and found to be 72 and 51% for MBTHSs and MTHSs at 365 nm (Fig. 5B), respectively, implying the higher utilization ratio of photogenerated charges for the former. In the visible light region, MBTHS still exhibits photocatalytic activity, and the QE is up to \(~4\) and 3% at 420 and 520 nm, respectively (Fig. 4B). The results clearly indicate that MBTHSs exhibit high photocatalytic hydrogen evolution both under AM 1.5 and visible light, suggesting that hydrogenation narrows the bandgap and favors the separation of photogenerated electron–hole pairs, which is demonstrated by the surface photovoltage spectroscopy (SPS) analysis (Fig. S12†), a well-established noncontact technique for the photophysical processes of semiconductors.\(^{22}\) A strong SPS peak at around 350 nm for both can be observed clearly, which is attributed to the electron transitions from the valence to the conduction band (band-to-band transitions, \( \text{O}_2p - \text{Ti}_{3d} \)).\(^{22}\) The strong photovoltage intensity for MBTHSs illustrates their high efficiency of separation of photogenerated electron–hole pairs and long excitation lifetimes. What’s more, the onset of MBTHSs is red-shifted obviously, suggesting the visible light photoactivity. Furthermore, compared to MBTHSs, the crushed ones (106 \( \mu \text{mol h}^{-1} \text{ g}^{-1} \)) and black \( \text{TiO}_2 \) nanoparticles (118 \( \mu \text{mol h}^{-1} \text{ g}^{-1} \)) exhibit poorer photocatalytic activity under AM 1.5 (Fig. S13†), indicating that the hollow structures indeed increase the solar light utilization due to several times refraction of light within the hollow structures. Furthermore, the photocatalytic hydrogen evolution of MBTHSs with different pre-treatments exhibits better photocatalytic performance than the untreated one (Fig. S14†). Moreover, without Pt as a cocatalyst or methanol as a sacrificial agent, the MBTHS materials still show superior photocatalytic performance to MTHSs, even both the hydrogen production rates are ultralow (Fig. S15†). Obviously, ethylenediamine, as a representation of small amine molecules for this encircling strategy, is the most ideal candidate for preparing MBTHSs due to the highest photocatalytic activity. In addition, the photocatalytic activity for various wall thicknesses and diameters of MBTHSs is also different (Table S3 and S4†). Apparently, the MBTHSs with a wall thickness of \(~75\) nm and a diameter of \(~700\) nm show the best photocatalytic activity.

The photoelectrochemical properties of MBTHS photoanodes were studied. The linear sweep voltammmogram shows much higher photocurrent density for MBTHSs (about twice) under AM 1.5 than MTHSs (Fig. 5A), illustrating the more efficient separation of photogenerated charges. The chronoamperometry responses at 0.6 V are nearly constant for both and indicate the high stability (Fig. 5B), but the photocurrent density is higher for MBTHSs obviously, which is an indication of more efficient charge separation and transport in the sample. The electrochemical impedance measurements show the smaller interfacial resistance for MBTHSs (Fig. 5C), indicating the efficient charge separation by reducing the recombination of electron–hole pairs for MBTHSs. A positive slope in the Mott–Schottky (M–S) plots (Fig. 5D) is direct evidence of n-type semiconductor behavior for both MTHSs and MBTHSs.\(^{23}\) Furthermore, a shallower slope for MBTHSs could be obtained compared to MTHSs, suggesting an increase of donor density after hydrogenation.\(^{24}\) Carrier density can be calculated from the corresponding slope according to eqn (1):\(^{25}\)

\[
N_d = \frac{2e \epsilon_0 \epsilon_r}{(1/C^2)/dV} \tag{1}
\]

We take \( \epsilon = 55 \) for anatase \( \text{TiO}_2. \)\(^{26}\) The electron densities of MBTHSs and MTHSs are \(~5.2 \times 10^{18}\) and \(2.9 \times 10^{18}\) cm\(^{-3}\),

![Image]

Fig. 4 Photocatalytic hydrogen evolution of the mesoporous black \( \text{TiO}_2 \) hollow spheres (a) and mesoporous \( \text{TiO}_2 \) hollow spheres (b). (A) Cycling tests of photocatalytic hydrogen evolution under AM 1.5. (B) The photocatalytic hydrogen evolution rates under single-wavelength light and the corresponding apparent quantum efficiency (QE). The inset of (B) enlarges the QE of single-wavelength light at 420 and 520 nm (0.1 g catalysts).

![Image]

Fig. 5 Photoelectrochemical properties of the stable mesoporous black \( \text{TiO}_2 \) hollow spheres (a) and stable mesoporous \( \text{TiO}_2 \) hollow spheres (b). (A) Linear sweep voltammograms in the dark and under AM 1.5. (B) Chronoamperometry results under AM 1.5. (C) Nyquist plots of electrochemical impedance in the dark and under AM 1.5, and (D) Mott–Schottky plots.
respectively. The increased carrier density for MBTHSs, which is ascribed to the presence of Ti$^{3+}$ and surface disordered layer, gives rise to better electron–hole pair separation and transport, and would be responsible for the high photocatalytic hydrogen evolution.

### Conclusions

In summary, we have demonstrated a solvothermal approach combined with a small amine molecules encircling strategy for the controllable fabrication of stable MBTHSs with highly crystalline pore-walls and surface disorders. The highly thermostable hollow frameworks could withstand the subsequent high-temperature hydrogenation (600 °C) without collapse because of the stabilizing effect of the small amine molecules encircling strategy. High-temperature hydrogenation introduced a disordered shell on the outside of the crystalline TiO$_2$ core, while Ti$^{3+}$ dispersed in hollow structure frameworks. They were responsible for the long-wavelength light absorption of MBTHSs and the efficient separation of photogenerated electron–hole pairs. The solar-driven hydrogen evolution rate of MBTHSs (241 μmol h$^{-1}$ 0.1 g$^{-1}$) is several times higher than that of MTHSs (81 μmol h$^{-1}$ 0.1 g$^{-1}$) and black TiO$_2$ nanoparticles (118 μmol h$^{-1}$ 0.1 g$^{-1}$). The newly developed MBTHSs are excellent host materials for the formation of novel heterojunction composites to further improve the photocatalytic performance. The simple and effective approach also provides a promising strategy for improving the photocatalytic performance of other existing semiconductor oxides.

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### Notes and references