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Targeted deposition of ZnO<sub>2</sub> on brookite TiO<sub>2</sub> nanorods towards high photocatalytic activity<sup>†</sup>

Meichen Guo,<sup>ab</sup> Liping Li,<sup>a</sup> Haifeng Lin,<sup>a</sup> Ying Zuo,<sup>a</sup> Xinsong Huang<sup>a</sup> and Guangshe Li<sup>\*a</sup>

A novel heterostructure was first synthesized by directly depositing photocatalytic inert  $ZnO_2$  onto facet {201} of brookite nanorods. The heterostructure thus obtained was found to show a superior photocatalytic activity under UV-light irradiation. The exceptional photocatalytic performance was due to the band-structure match between  $ZnO_2$  and brookite as well as synergic charge accumulation by different facets of the brookite nanorods.

Heterostructures have fascinating properties and are becoming a forefront in many technological applications, including photocatalysis, lithium-ion batteries, spintronics, and opto-electronic devices.<sup>1</sup> Up to date, many types of heterostructures based on TiO<sub>2</sub> have been reported. It is well documented that there exist three common polymorphs of TiO<sub>2</sub> in nature: anatase, rutile and brookite. When compared to its anatase and rutile counterparts,<sup>2</sup> brookite is least investigated due to its narrow stability region and complicated thermodynamic and kinetic factors in formation reactions, which make it extremely difficult to prepare phase-pure brookite with facet engineering for novel functions.<sup>3</sup> It is well known that specific facets of oxide semiconductors usually show strong oxidation and reduction abilities,<sup>4</sup> which enable the selective deposition of metals or oxides onto these specific facets to form heterostructures. Nevertheless, the utilization of specific facets of brookite to design and construct novel heterostructures is rarely demonstrated successfully.

One of the prerequisites for brookite-based heterostructures is the synthesis of brookite nanorods with tunable aspect ratios, because (i) nanorods with anisotropic nature are usually in possession of unique physicochemical performances,<sup>5</sup> (ii) brookite has shown many performances not shown by its anatase and rutile counterparts;<sup>6</sup> and (iii) tunable aspect ratios



**Fig. 1** (a) TEM image, (b) high resolution TEM images, and fast Fourier transform patterns (insets) for brookite nanorods with varied orientations, and (c) views of nanorod models in various orientations.

of nanorods enable exposure of specific facets for synthesis of novel heterostructures. Some attempts have tried to control the morphology of brookite, but the majority of these syntheses have to be conducted under extreme conditions like high temperature, strong alkalinity, or inert atmosphere protection.<sup>2,3,7</sup> Even so, synthesis of brookite nanorods with tunable aspect ratios is still challenging. Motivated by this, brookite nanorods were first synthesized in this work to show preferential exposure of facets {210}, {101}, and {201} (Fig. 1).

Further, facet engineering of brookite nanorods was attempted to form heterostructures with exceptional catalytic activities. It is known that heterostructures comprising of two or more discrete nanodomains always show catalytic performance superior to individual ones.<sup>8</sup> The ever studied heterostructures are those that contain narrow-band (or zero-bandgap) semiconductors with wide-band ones (*e.g.* Bi<sub>2</sub>S<sub>3</sub>/ZnO, CdS/ZnO, ZnO/TiO<sub>2</sub>, or TiO<sub>2</sub>/WO<sub>3</sub>).<sup>9</sup> It remains unclear if much wider band-gap semiconductors can be deposited onto specific facets of wide-band semiconductors (like brookite) to form heterostructures.

Compared to conventional semiconductors with band-gaps of 3.0-3.3 eV,  $\text{ZnO}_2$  is an indirect semiconductor that shows a much wider band-gap, 4.1-4.5 eV.<sup>10</sup> More reductive electrons

<sup>&</sup>lt;sup>a</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China. E-mail: guangshe@fjirsm.ac.cn; Fax: +86-591-83702122; Tel: +86-591-83702122

<sup>&</sup>lt;sup>b</sup> School of Chemistry and Chemical Engineering, Inner Mongolia University,

Hohhot 010021, P. R. China

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could thus be generated to yield high photoreactivity.<sup>11</sup> In this work, ZnO<sub>2</sub> was directly photo-deposited onto facet {201} of brookite nanorods. By virtue of the match of electronic levels and synergic charge trapping by different facets of the brookite nanorods, the as-prepared heterostructure, ZnO<sub>2</sub>-brookite-PD, displayed excellent photo-activity that was superior to ZnO<sub>2</sub>, brookite nanorods, or even ZnO<sub>2</sub>-brookite-PRE prepared by a precipitation method.

All samples were synthesized by a modified hydrothermal method with concentrated urea (Fig. S1, ESI<sup>†</sup>), since a high urea concentration favors growth of brookite along the [001] orientation.<sup>12</sup> This compares to a previous hydrothermal reaction, where a low concentration of urea led to the formation of nanosheets.<sup>4</sup> As indicated by the TEM and high-resolution TEM (HRTEM) images in Fig. 1 and Fig. S2 (ESI<sup>†</sup>), our samples were constructed from uniform single crystal nanorods with a length of  $\sim 80$  nm and a width of  $\sim 25$  nm. These nanorods were pure brookite phase, as confirmed by X-ray diffraction (XRD) (Fig. S3a, ESI<sup>+</sup>). According to the fast Fourier transform (FFT) analysis of the lattice fringes shown in Fig. 1 (insets), the nanorods were surrounded by facets parallel to the sharply terminated (201) and  $(\overline{2}0\overline{1})$  boundaries. Therefore, two {201} borders shaped the facets of the nanorods. It is also found that (210) and (101) borders formed the facets of the nanorod surface (see more details in Fig. S2, ESI<sup>+</sup>). One can thus conclude that each nanorod is surrounded by four {210}, two {101}, and two {201} facets. The aspect ratio of the brookite nanorods was evidently raised, which is attributed to the preferential adsorption of excess urea onto the {210} facets of the nanorods, which guides the crystal growth along the [001] direction.

Facets with different energy levels for semiconductors like  $BiVO_4$ ,<sup>13</sup> anatase-TiO<sub>2</sub>,<sup>14</sup> or rutile-TiO<sub>2</sub><sup>15</sup> can selectively serve as reductive or oxidative sites to accumulate photo-generated electrons or holes under illumination for the preferential deposition of metals or oxides. Nevertheless, there were no successful examples on brookite until now. Here, facet {201} of the brookite nanorods was used as the exclusive oxidation site to load the wider-gap semiconductor ZnO<sub>2</sub>, which would be artfully exploited for the construction of heterostructures with enhanced photocatalytic properties, based on their matched energy structures. To this purpose, photo-oxidation deposition was performed. As confirmed by EDS (Fig. S7b, ESI<sup>†</sup>) and ICP (Table S1, ESI<sup>+</sup>), Zn species exist, amounting to  $1.2 \pm 0.1\%$  of our samples. It is not easy to distinguish ZnO<sub>2</sub> from brookite by lattice fringe due to the similar *d*-spacing (Fig. S5, ESI<sup>†</sup>) when using HRTEM (Fig. 2; Fig. S5 and S6, ESI<sup>+</sup>). Here, we tried FFT of the lattice fringes to confirm the presence of ZnO<sub>2</sub>. As indicated in Fig. 2b, the lattice fringes of small particles were terminated clearly at the (210) boundaries of ZnO<sub>2</sub> when the sample holder was tilted to render the ZnO<sub>2</sub> particles to be [001] oriented. Moreover, the lattice fringes of large particles were terminated sharply at the (101) and (210) boundaries of brookite when the incident beam was parallel to the  $[1\overline{2}\overline{1}]$ direction.

To further demonstrate the presence of  $ZnO_2$ , XPS data of the samples were also studied, as indicated in Fig. S8 and



Fig. 2 (a) TEM and (b) HRTEM images of  $ZnO_2$ -brookite-PD. The insets are the corresponding FFT images. (c) The formation process for targeted deposition of  $ZnO_2$  onto the {201} facets under UV irradiation to form the heterostructure  $ZnO_2$ -brookite-PD.

Table S2 (ESI<sup>†</sup>). The survey spectra (Fig. S8a, ESI<sup>†</sup>) showed the signals of Zn2p. The half-height width of the signal for Zn2p<sub>3/2</sub> was 1.45 eV for ZnO<sub>2</sub>–brookite-PD, close to that of 1.5 eV for pure ZnO<sub>2</sub>. The core-level binding energy of O1s of ZnO<sub>2</sub>–brookite-PD was 529.5 eV, nearly the same as that of ZnO<sub>2</sub> (529.6 eV), but greatly different from that of 530.7 eV for ZnO (Fig. S8c and Table S2, ESI<sup>†</sup>). So, it can be concluded that fine ZnO<sub>2</sub> particles were merely deposited onto the {201} facets of the brookite-PD, we optimized the conditions by adjusting the illumination time, pH values, or brookite shape. It was found that the best homogeneity was achieved for brookite nanorods synthesised under the following conditions: pH = 5 and illumination time of 24 h (Fig. S12, S13 and S19–S22, ESI<sup>†</sup>).

On the contrary, when ZnO<sub>2</sub> species were precipitated and mixed with brookite nanorods, the ZnO<sub>2</sub> grains on the nanorod surfaces were disclosed to be aggregated and randomly dispersed (Fig. S7c, ESI<sup>†</sup>). A schematic process is suggested for the facet-dependent recombination course in relation to ZnO2brookite-PD. Under UV-irradiation, photo-generated holes were gathered on the {201} facets, whilst the electrons were trapped on facets {101} and {210}. Subsequently, hydroxyl groups and H<sub>2</sub>O adsorbed on facet {201} would be oxidized by the holes to form 'OH radicals, which could quickly react with each other to produce H<sub>2</sub>O<sub>2</sub> molecules<sup>16</sup> that enable deposition of ZnO<sub>2</sub> specifically on {201} through interactions with surrounding Zn<sup>2+</sup> cations in the solution.<sup>17</sup> The targeted photo-deposition of ZnO<sub>2</sub> on brookite is beneficial for the preferred accumulation of photo-induced holes by the {201} facets of the brookite nanorods under UV, which, however, cannot be achieved by ZnO<sub>2</sub>-brookite-PRE when synthesized by a precipitation method.

The photocatalytic performances of the heterostructures were evaluated using a probe reaction of methyl orange degradation. For comparison, the data corresponding to pure  $ZnO_2$ and  $TiO_2$  were also given under the same conditions (Fig. 3a). Under ultraviolet irradiation, when no catalysts were involved, the decrease of MO was negligible within 3 h.  $ZnO_2$  powders nearly had no activity, while  $TiO_2$  nanorods could completely



**Fig. 3** Photocatalytic degradation of MO over the given catalysts (a) and phenol degradation (b) under UV-light irradiation.

degrade MO in 90 min. Interestingly, when ZnO<sub>2</sub> was selectively deposited on the {201} facets of the brookite nanorods, the reactivity of ZnO2-brookite-PD was remarkably improved, as evidenced by a much shortened degradation time of 40 min, and there was no noticeable change within 5 cycles of catalytic reactions (Fig. S10, ESI<sup>+</sup>). However, in the case of ZnO<sub>2</sub> deposited brookite nanorods illuminated for 12 h, the activity enhancement was not noticeable (Fig. S13, ESI<sup>+</sup>), because ZnO<sub>2</sub> was likely slightly unevenly deposited on the brookite surface, which reduces the accumulation of electrons on these surfaces and thus feebly suppresses the useless recombination of photoinduced electron-hole pairs. If ZnO2 was randomly precipitated onto the brookite nanorod surfaces, the photocatalytic activity of ZnO<sub>2</sub>-brookite-PRE was inhibited instead. Therefore, the loading sites of co-catalysts are important for an effectual photo-reactivity boost, as documented previously.<sup>13</sup> In agreement with the photoreactivity data, the heterostructure possessed a better performance as represented by a lower electron-hole recombination rate (as indicated by weaker PL emission in Fig. S15a, ESI<sup>+</sup>) and production of more 'OH radicals (as indicated by stronger fluorescence intensity in Fig. S15b, ESI<sup>+</sup>).

To exclude the impact of parallel self-sensitized paths such as that for MO, colorless phenol was also selected to study the catalytic activity of  $ZnO_2$ -brookite-PD. It is seen that phenol was completely removed in 3 h under UV irradiation (Fig. 3b). The significant difference in activities for the samples before and after deposition by various methods should not be attributed to surface area or light absorption (Table S1 and Fig. S16, ESI<sup>†</sup>). Therefore, the special photocatalytic activity of brookite-TiO<sub>2</sub> heterostructures is highly dependent on the surface structure, and deposition of co-catalyst onto specific oxidation facets would be highly beneficial for efficient improvement of reactivities.

Under UV irradiation, photo-generated electrons of the valence bands of both  $ZnO_2$  and  $TiO_2$  were excited and transferred to the conduction band, leaving photo-excited holes in the valence band, as illustrated in Fig. S18 (ESI<sup>+</sup>). As previously mentioned,<sup>4</sup> photo-induced electrons would be trapped on the reductive {210} and {101} facets of the brookite nanorods, while the holes prefer to be accumulated on the oxidative {201} facet. Owing to the selective coupling of  $ZnO_2$  with the {201} facets of the nanorods, the holes would further migrate towards  $ZnO_2$ 

with a higher valence band (VB) potential (Fig. S17, ESI<sup>+</sup>). Meanwhile, electrons produced in the conduction band (CB) of ZnO<sub>2</sub> tend to inject into facets {210} and {101} of the nanorods with a lower CB potential, which is energetically favourable.<sup>13,18</sup> Therefore, photo-induced charge carriers could be efficiently transported and separated in the present unique heterojunction of ZnO2-brookite-PD, while the recombination process of the electron-hole pairs could be remarkably impeded, which contributes crucially to the dramatic enhancement of activity when compared to the components ZnO<sub>2</sub> or brookite. The holes accumulated on the ZnO<sub>2</sub> surfaces would subsequently participate in the oxidation of OH- and the physically adsorbed water molecules to form •OH radicals, while the electrons trapped on facets {210} and {101} of the brookite nanorods are probably consumed in the reduction of dissolved  $O_2$  for the generation of  $O^{2-}$  radicals. These radicals could eventually have a vital effect in directly oxidizing organic contaminants to produce CO2 and H2O, thus constructing excellent photo-reactivity.

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