Supporting Information for:

Targeted deposition of ZnO₂ on brookite TiO₂ nanorods

towards high photocatalytic activity

Experimental Section

Anhydrous titanium tetrachloride, sodium lactate, zinc nitrate hexahydrate and urea of analytical grade were purchased from Alfa Aesar Company and used without further purification. Nanostructures ZnO₂ particles were prepared by homogeneous precipitation using a procedure adapted from literature.¹

Synthesize of brookite TiO₂ nanoparticles

In a typical experiment, 1.65mL of TiCl₄ was added with drop by drop to a Teflon autoclave with 40mL de-ionized water in the case of be cooled by an ice-water bath. After sufficient stirring, an acidic transparent solution that contained a hydro-soluble titanium complex was formed. Then, urea was mixed and dissolved in this solution with agitation. (*Caution! Input amount of urea has a significant impact on the final morphology: 5g of urea produces nanosheets, while 15g of urea gives rise to nanorods.*) The 5mL of sodium lactate liquor (60%) was dropped in the mixed solution while stirring for a period of time. The clarified liquid obtained was then subjected to hydrothermal treatment in an autoclave at 200°C for 20 h. After the autoclave was cooled to room temperature, the white product was then separated by centrifuge, washed with ethanol and de-ionized water for 3 times, and dried at 80°C in air for overnight, the obtained powder was titanium dioxide.

Synthesize of ZnO₂/brookite-PD nanostructures

To prepare the ZnO_2 /brookite by photo-deposition method, $1.17g Zn(NO_3)_2 \cdot 6H_2O$ was added to 0.5g of the prepared TiO₂ powders and completed with 150ml of de-ionized water, and white colloidal solution would be formed. Subsequently, the solution was irradiated by the 300W Xenon lamp for 12h and 24h with continuous stirring to get the homogeneous white ZnO_2 /TiO₂ solution, respectively. Finally, the solution was separated by filtration, washed with de-ionized water and dried overnight at 80°C.

Synthesize of ZnO₂/brookite-PRE nanostructures

To synthesize the ZnO_2 /brookite by precipitation method, 30 ml of 0.1M $ZnSO_4 \cdot 7H_2O$ aqueous solution, 30 ml of 0.1M NH_4OH aqueous solution and 0.5g of the obtained TiO_2 powders were mixed to obtain a white precipitate. After being washed with excessive de-ionized water, the precipitate was introduced into a 1M H_2O_2 aqueous solution. The dispersion solution was then heated at 75 °C for 2 h to result in ZnO_2/TiO_2 powder, which was subsequently washed with excessive

de-ionized water and finally dried at 65 °C in air.

Photocatalytic Reactions

In all catalytic activity of experiments, the samples (0.1g) were put into the solution of MO dyes or phenol (100ml, 10ppm) under UV-light irradiation, which was irradiated with a 300W Xe lamp equipped with a 300nm cutoff filter to provide ultraviolet light with $\lambda \leq 300$ nm. The MO solution or phenol containing the catalyst was magnetically stirred in the dark for 5h to reach an adsorption and desorption equilibrium to eliminate other effects. The degradation of MO solution or phenol solution was monitored by a PerKin-Elmer UV lambda 35 spectrophotometer to acquire its UV-vis adsorption spectra. Before the spectroscopy measurement, these catalyst powders were removed by centrifuge at a rate of 8000rpm.

Characterizations

The XRD spectra were examined in the 20 range of 20-85 with a Rigaku MiniFlex II diffractometer (Cu Kα radiation source, scan rate of 2°min⁻¹, target voltage of 30kV, and target current of 15mA). TEM micrographs were taken on a Tecnai G2 F20 field emission transmission electron microscope. Prior to TEM measurements, samples were sonically dispersed in an ethanol solution before a drop of this solution was deposited on a carbon film coated copper grid. EDX measurements were carried out on a field emission scanning electron microscopy (FESEM) on a JEOL JSM-6700 apparatus to obtain the chemical compositions of the samples. Brunauer-Emmett-Teller (BET) specific surface areas were measured on a Micromeritics ASAP 2020 system. The sample was pretreated in N₂ at 120°C for 1h before N₂-sorption analysis. UV-vis diffuse reflectance spectra of the samples were collected using a Varian Cary 500 UV-vis-NIR spectrometer at room temperature. ICP measurements were examined by Inductively Coupled Plasma OES spectrometer to obtained molar ratio of Zn to Ti, weight proportion of Zn in ZnO₂/brookite-PD and ZnO₂/brookite-PRE. An X-ray photoelectron spectroscopy (XPS) measurement was carried out using a monochromatic Al Ka X-ray source operating at 150 W. High-resolution spectra were collected at fixed analyzer pass energy at 20 eV. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination which was set at 284.6 eV. The accuracy of measurement of the binding energy is ± 0.1 eV and uncertainty is ≤0.2 eV.

Measurements of hydroxyl radical (•OH)

In theory, hydroxyl •OH radicals can swiftly react with terephthalic acid (TA) to become 2-hydroxy terephthalic acid (TAOH) which has a specific fluorescence emission around 425 nm, and the quantity of •OH existed in water is proportional to intensity of the fluorescence signal at 425 nm. So we use the TA as a trapping agent to detect hydroxyl •OH radicals in catalyst surfaces. In a typical synthesis, 0.01g of the photocatalysts was added in base solution ($5x10^{-4}$ M TA, $2x10^{-3}$ M NaOH) with agitation. Afterwards, the solution containing the photocatalyst was magnetically stirred in the dark for 5h to reach an adsorption and desorption equilibrium to eliminate other effects before test. UV-light irradiation was obtained by a 300W Xe lamp equipped with a 300nm cutoff filter to provide ultraviolet light with $\lambda \ge 300$ nm. Finally, the solution was sampled and centrifuged to remove the photocatalysts in every 3 minutes. Fluorescence spectra of the supernatant were detected by a Cary Eclipse fluorescence spectrophotometer, which was used an excitation light of 315 nm.²

Supporting figures and results



Fig. S1 A schematic mechanism for the construction of brookite TiO_2 nanorods with well defined facets.

The schematic formation of aggrandized length-diameter ratio of nanorod through modified hydrothermal process was exhibited in Fig.S1. Compared to our anterior work, which utilized $[Ti^{-}(C_3H_4O_3)_3]^{2-}$ complex to produce high-grade brookite nanosheets exposed with {210}, {101}, and {201} facets, increased urea usages were adopted for the fabrication of rod-shaped brookite TiO₂. The surrounded facets were preserved with brookite nanorods except the prolonged length in [001] direction. On the ground that organic amines could coordinate with Ti⁴⁺ ions to arouse the anisotropic development of nanocrystals, we proposed that the inclined adsorption of excess urea on {210} facets of brookite to stabilize the surfaces during the crystal growth was the crucial factor that guiding the preferential growth of nanorods along [001] orientation.



Fig. S2 HRTEM images and FFT (insets) of TiO₂ nanorods.

As shown in Fig. S2a, when the incident beam was parallel to the [243] direction,

the lattice fringes were terminated clearly at the (210) and (210) edges, thus these

verges formed the surface of one individual nanorod. It is also found that (210) and (210) borders shaped the facets of vertical nanorod (Fig. S2e). Therefore, four equivalent $\{210\}$ boundaries shaped the side facets of each nanorod. For the nanorod with [232] orientation presented in Fig. S2b, the stripes ended distinctly at the (101) and (101) verges. It appears that two $\{101\}$ borders formed the facets of the nanorod surface. Moreover, the angle between the adjacent side facets of the vertical nanorods is about 100° (Fig. S2f), in good agreement with that of 99.82° theoretically calculated.



Fig. S3 XRD patterns of the synthesized samples (a) ZnO_2 /brookite-PD, (b)TiO₂ nanorods, (c) ZnO_2 and (d) ZnO_2 /brookite-PRE. For comparison, the standard diffraction data for bulk brookite TiO₂ and ZnO₂ are also given.

X-ray powder diffraction (XRD) patterns of the as-obtained products were given in Fig.S3. All the diffraction lines in Fig.S3b and c can be indexed to the pure phase of TiO₂ and ZnO₂ contrasted to the standard diffraction data, respectively. Moreover, it can be concluded that TiO₂ showed peaks corresponding to brookite phase. Furthermore, the pattern of as-prepared ZnO₂/brookite-PRE demonstrated the characteristic peaks of brookite TiO₂ phase and ZnO₂ phase shown in Fig.S3d. The existence of ZnO₂ in the sample can be readily discerned from its (111) diffraction peck locating at 31.8° (inset Fig.S3), where there was no overlapping with any other peaks from brookite TiO₂ phase. However, it can be only observed the TiO₂ brookite phase in the ZnO₂/brookite-PD (Fig.S3a), this was because of the existence of a small amount of zinc peroxide (Table S2) which cannot discernible within the detection limit of our X-ray diffractometer.



Fig. S4 TEM images of ZnO₂/brookite-PD. The particles in white circle were ZnO₂.

From the TEM images shown in Fig. S4, there was some ZnO_2 deposited on the special surface of brookite TiO₂ nanorods. The pH value of the solution before illumination was 5.



Fig. S5 HRTEM images of ZnO₂/brookite-PD.

It can be seen that the d spacing of the small particles in Fig.S5a and b were 0.218nm and 0.344nm, which were quite close to the numbers of d(221) (0.213 nm) and d(111) (0.346 nm) of brookite. According to this, ZnO_2 and brookite TiO₂ cannot be well distinguished only by the d spacing of lattice fringes. So, the fast Fourier transform (FFT) of the lattice fringes were given in Fig. 2b and S6b to determine the presence of ZnO_2 .



Fig. S6 TEM and HRTEM images of ZnO₂/brookite-PD.

According to the fast Fourier transform analysis of the lattice fringes in Fig.S6b (inset), the particle which was deposition on the brookite TiO_2 nanorod was ZnO_2 , and when the incident beam was parallel to [001] direction, the lattice fringes were

terminated clearly at (220) and (220) edges.



Fig. S7 TEM and HRTEM (inset) images of (a) ZnO_2 /brookite-PD, and (c) ZnO_2 /brookite-PRE. The corresponding EDS data were separately presented in (b) and (d). Cu and C elements in EDS analysis are from the sample holder.

BET	ZnO ₂				
(m^2/g)	(%)				
51.89	1.2				
42.16	—				
207.16	—				
60.15	10.2				
32.78	8.4				
	BET (m ² /g) 51.89 42.16 207.16 60.15 32.78				

Table S1 Physicochemical properties of the obtained samples.



Fig. S8 Survey XPS spectrum (a), Zn 2p XPS spectra (b) and O 1s spectra (c) of the as-prepared TiO_2 nanorods, ZnO_2 , ZnO_2 /brookite-PD sample and ZnO.

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Compound	BE of the	BE of the	Half-width of	BE of the
	maximum of	maximum of	the XPS Zn	maximum of
	the XPS Zn	the XPS Zn	2p core-level	the XPS O 1s
	2p _{3/2}	$2p_{1/2}$	spectrum	core-level
	spectrum	spectrum		spectrum
ZnO^3	1021.8	1044.9	1.6	530.7
ZnO_2	1021.2	1044.3	1.5	529.6
TiO ₂ nanorods	_		—	529.5
ZnO ₂ /brookite-PD	1021.3	1044.4	1.45	529.5

Table S2. Binding energy (BE) and half-width of XPS spectra (eV) of the as-prepared samples.

As shown in Fig. S8a, the survey spectrum of as-prepared ZnO_2 /brookite-PD was presented, and peaks at energies of 284.5, 457, 464, 528, 563, 974, 1021 and 1044 eV were attributed to C 1s, Ti 2p_{3/2}, Ti 2p_{1/2}, O 1s, Ti 2s, O(A), Zn 2p_{3/2}, and Zn 2p_{1/2}, respectively. The C element could be attributed to the adventitious carbon-based contaminant used as the reference for calibration. In addition, survey spectra of TiO₂ nanorods showed a sharp peak of Na 1s (1070 eV), it was demonstrated that there was residual Na⁺ existed on the surface of TiO₂. The Zn 2p_{3/2} peak of ZnO₂ located at about 1021 eV was fit as two peaks: 1021.2 and 1022.3 eV, which was due to the ZnO presented on the surface of ZnO₂. As can be seen from Table S1, the half-width of the Zn 2p_{3/2} spectra of ZnO₂/brookite-PD was closed to it of ZnO₂. Furthermore, the core-level binding energy of O 1s was nearly the same with that in ZnO₂, and there had significant differences with that in ZnO in Fig.S8c and Table S1. Those results further confirmed that the ZnO₂/brookite-PD heterostructure consisted of ZnO₂ and TiO₂.



Fig. S9 UV–visible spectroscopic changes of MO in the presence of ZnO_2 /brookite-PD under ultraviolet-light irradiation.

The characteristic absorption band of MO diminishes quickly which was shown in Fig.S9. The inset photographs showed the corresponding color changes of the dye solution with the reaction time increasing. It is obvious that the intensity of the absorption band of MO in the UV-vis region decreased significantly and monotonically as a function of the irradiation time.



Fig. S10 Five cycles of the photocatalytic degradation of MO in the presence of the ZnO_2 /brookite-PD under ultraviolet-light irradiation.

Fig.S10 was the photocatalytic efficiency of ZnO₂/brookite-PD, there was no noticeable change within the 5 cycles. This implied that the material did not undergo any degradation during the reaction. The degradation rate for the as-prepared ZnO₂/brookite-PD was relatively acceleration during the each cycle. The abnormal performance of the ZnO₂/brookite-PD could be due to the presence of superficial inorganic species and organic adsorbates on the surface of ZnO₂/brookite-PD. After each cycle, the inorganic species were desorbed from the surface and the organic adsorbates degraded, resulting in the accelerating degradation rate in the following degradation cycles.



Fig. S11 XRD patterns of ZnO₂/brookite-PD after photocatalysis.



Fig. S12 TEM images of ZnO₂/brookite-PD-12.

From Fig.S12, it can be clear seen that some small particles were slightly deposited on the surface of nanorods when the illumination time was 12h. It may be because that when the time of illumination was not enough, the $\{201\}$ facets of brookite TiO₂ nanorods cannot produce enough •OH to form H₂O₂.



Fig. S13 Photocatalytic activities of ZnO₂/brookite-PD-12 for MO degradation under visible light.



Fig. S14 Fluorescence emission spectra of TAOH generated in the presence of (a) ZnO_2 /brookite-PD, (b) TiO₂ nanorods, (c) ZnO_2 , (d) ZnO_2 /brookite-PRE under UV irradiation for given period of time.



Fig. S15 (a) Photoluminescence (PL) emissions of the samples and (b) fluorescence signals of TAOH of the suspensions illuminated for 9 min.

It can be seen that the intensity of photoluminescence emissions was inversely with the electron-hole recombination rate, the intensity of ZnO_2 /brookite-PD was the weakest in Fig.S15a, so the electron-hole recombination rate was lowest. Moreover, the •OH radicals which was the important intermediate product of photocatalytic process can be measured by the fluorescence signals of TAOH, the intensity of ZnO_2 /brookite-PD was the strongest shown in Fig. S15b, so the produce of •OH radicals was the most. Therefore, the above results clearly demonstrated that the photocatalytic actively of ZnO_2 /brookite-PD was the best.



Fig. S16 UV-vis spectra of the as-synthesized materials (a) ZnO_2 /brookite-PD, (b) TiO₂ nanorods, (c) ZnO_2 and (d) ZnO_2 /brookite-PRE.

The optical properties of the various samples prepared were investigated by UV–Visible diffuse reflectance in Fig.S16. All of the samples had a strong absorption in the UV region. It can be clearly seen that the absorption edges of the ZnO_2/TiO_2 composite were both existed between that of the pure TiO₂ nanorods and ZnO₂, which was found to be around 376nm and 316nm, respectively. These observations clearly confirmed that due to the combined contribution of each component, the absorption edge of the ZnO_2/TiO_2 composite had changed. The energy of the band gap of the pure TiO₂ nanorods and ZnO₂ were estimated to be 3.33 and 4.12 eV, respectively.



Fig. S17 Valence band XPS spectra of TiO_2 nanorods (red line) and ZnO_2 (black line). Thin black lines show the linear extrapolation of the curves used for deriving the band edge position of ZnO_2 /brookite-PD sample.

Fig.S17 showed the valence band X-ray photoelectron spectroscopy (VBXPS) to investigate the electronic structure of the TiO_2 nanorods and ZnO_2 .^{4,5} By extrapolating the leading edge of the VB to its intersection with background counts near the Fermi level, the position of the Fermi level with respect to the VB maximum (VBM) could be determined. TiO_2 displayed the characteristic VB density of states of brookite TiO_2 , with the band edge at 1.8eV below the Fermi energy. On the other hand, the VBM was located at 1.0 eV below the Fermi level for the ZnO₂. So, the conduction band of ZnO₂ was located above it of TiO₂ nanorods.



Fig. S18 Schematic energy band and photo-generated charge migration through UV-light excitation of ZnO_2 /brookite-PD heterostructure.



Fig. S19 TEM images of ZnO₂/brookite-PD prepared at pH 3 (a) and pH 1 (b) by nitric acid.

To improve the homogeneity of ZnO_2 /brookite-PD, we have adjusted the pH value of the solution before illumination by HNO₃. We found that when the pH value was 3, it can be clear seen that a small amount of ZnO_2 deposited on the {201} facets of TiO₂ nanorods in Fig.S19a, and when the pH value was 1, there was almost no ZnO_2 photo-deposited on the TiO₂ nanorods in Fig. S19b. As the acidity of the solution increased, the structure of ZnO_2 deposited on the {201} facets of TiO₂ nanorods gradually decreased. In addition, Zn^{2+} in the solution before illumination can react with OH⁻ to form precipitate when we adjusted the pH value of the solution by NaOH.



Fig. S20 TEM and HRTEM images of (a) TiO_2 nanosheets and (b) Zn^{2+} /brookite nanosheet-PD.

As shown in Fig.S20a, the as-obtained sample was relatively uniform, and the mainly characterized morphology was nanosheet. But we cannot find the formation of ZnO_2 deposited on the TiO₂ nanosheet in Fig.S20b. It may be because that aspect ratio of nanostructure had the influence on the function of specific facets for heterostructures by control the electron–hole pair recombination rate.⁶



Fig S21 XRD patterns of the as-prepared samples (a) TiO_2 nanosheets and (b) Zn^{2+} /brookite nanosheet-PD.



Fig. S22 Photocatalytic activities for MO degradation under visible light of TiO_2 nanosheets and Zn^{2+} /brookite nanosheet-PD.

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