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# Preparation of Cu(II) porphyrin–TiO<sub>2</sub> composite in one-pot method and research on photocatalytic property†

Xin Zhao,‡ Ying Wang,‡ Wenhua Feng, Hengtao Lei and Jun Li \*

A promising fabrication strategy used for designing TiO<sub>2</sub> photocatalysts, which enhanced the photocatalytic activity by combining TiO<sub>2</sub> with a new carboxyl-group-containing Cu(II) porphyrin (CuPp) in a sol–gel processing TiO<sub>2</sub> and a one-pot solvothermal condition, has been proposed. Both porphyrins and composite photocatalyst CuPp–TiO<sub>2</sub> have been characterized by spectroscopic techniques. Their photocatalytic performances were investigated by testing the photodegradation of 4-nitrophenol (4-NP) in aqueous solution under UV-vis light irradiation. The results reveal that the methodology for the anatase TiO<sub>2</sub> photocatalyst is easy to achieve, and the photocatalytic activity measurements illustrate that the Cu(II) porphyrin-based TiO<sub>2</sub> photocatalyst we synthesized displays superior photocatalytic activity and good chemical stability for organic pollutant photodegradation due to the strong interactions between Cu(II) porphyrins and TiO<sub>2</sub>.

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## 1. Introduction

TiO<sub>2</sub>-based photocatalytic processes can be used in various applications such as waste water treatment, gas purification and environmental protection<sup>1–3</sup> due to its nontoxicity, good chemical stability, high photocatalytic activity and versatile properties.<sup>4–7</sup> In addition, it has shown a great potential as an inexpensive, environmentally friendly and sustainable treatment technology to remove pollutants from sewage to overcome the shortcomings of the conventional technologies.<sup>8,9</sup> However, the utilization for solar energy is limited by the narrow band gap of light absorption region in TiO<sub>2</sub>,<sup>10,11</sup> which impedes its commercialization. To improve the photocatalytic efficiency of TiO<sub>2</sub>, many techniques<sup>12,13</sup> have been carried out with the aim of eliminating the inefficient exploitation of visible light for TiO<sub>2</sub>. The synthesis of excellent photocatalytic TiO<sub>2</sub> materials with heterogeneous structure, which is extensively considered to possess higher photocatalytic activity,<sup>14</sup> may have profound implications for organic dye pollutant photodegradation.

Porphyrins, as the most promising components, have been widely used in the field of gas sorption, molecular separation,

storage, and catalysis.<sup>15–17</sup> Their photophysical properties can be easily tuned by metal ion insertion, since porphyrins are able to coordinate with metal ions readily in the central cavity causing stronger and broader photoresponse in the visible region. It is for this reason, that porphyrins are considered to be efficient sensitizers to harvest light on the surface of TiO<sub>2</sub>.<sup>18,19</sup> In particular, ideally designed Cu(II) porphyrins–TiO<sub>2</sub> composites were found to be more effective sensitizers in the photodegradation of organics,<sup>20,21</sup> which could not only extend the absorption range in the solar spectrum, but also enhance the separation of photogenerated electron–hole pairs, thus increasing activity and stability in the photocatalytic processes of the porphyrin–TiO<sub>2</sub> system.

Studies have shown that metal complexes of porphyrins are highly photostable when adsorbed on the surface of TiO<sub>2</sub>.<sup>18,22</sup> The sol–gel process allows the direct introduction of visible light sensitive species like porphyrins inside the TiO<sub>2</sub> matrix with ease during the synthesis.<sup>23,24</sup> The heterogeneous structure formation is advantageous to environmental applications. Herein, we report a route for the synthesis of a novel Cu(II) carboxyl porphyrin (Fig. 1) *via* a sol–gel process and in solvothermal conditions (Fig. 2), which helps in the easy realization of the efficient porphyrin–TiO<sub>2</sub> photocatalyst. The CuPp–TiO<sub>2</sub> composite has been characterized with spectroscopic techniques, N<sub>2</sub> sorption and 4-nitrophenol (4-NP) degradation, which reveals that the heterogeneous CuPp–TiO<sub>2</sub> composite exhibits potential visible photocatalytic activity and higher recyclability than P25, thus, making our synthetic route a prospective method for the preparation of highly efficient and stable porphyrin–TiO<sub>2</sub> photocatalysts.

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an, Shaanxi 710069, P. R. China. E-mail: junli@nwnu.edu.cn

† Electronic supplementary information (ESI) available: Integral TEM images of (a) TiO<sub>2</sub>, (b) CuPp–TiO<sub>2</sub> photocatalyst (Fig. S1). Corresponding EDX element mapping of CuPp–TiO<sub>2</sub> composite photocatalyst (j) for carbon, (k) for oxygen, (l) for titanium, (d) for nitrogen, (e) for copper (Fig. S2). The degradation efficiency of 4-NP in the presence of CuPp–TiO<sub>2</sub> composite photocatalyst with scavengers (Fig. S3). See DOI: 10.1039/c7ra09585f

‡ These authors contributed equally to this work.



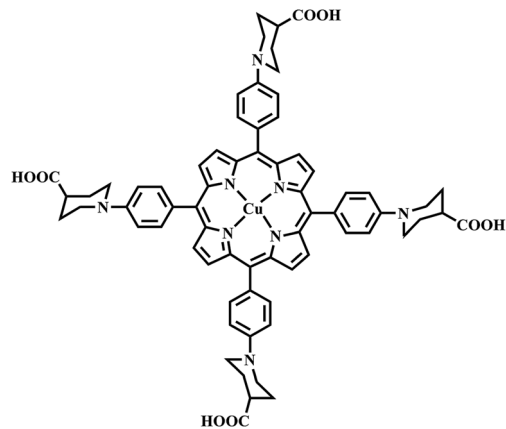


Fig. 1 Chemical structure of CuPp.

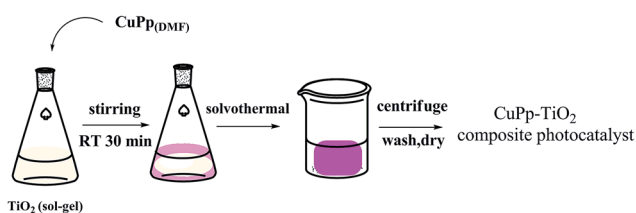


Fig. 2 The preparation of CuPp-TiO<sub>2</sub> composite photocatalyst with sol-gel procedure and solvothermal conditions.

## 2. Experimental

### 2.1 Materials, reagents and equipment

All reagents and solvents used were purchased from commercial sources and used without further purification except pyrrole, which was distilled before use.

UV-vis diffuse reflectance spectra (UV-vis-DRS) were recorded on a Shimadzu UV-3100 system using BaSO<sub>4</sub> as a reference. Mass spectrometry (MS) analyses were carried out on a matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS, Krato Analytical Company of Shimadzu Biotech, Manchester, Britain). Elemental analyses (C, H and N) were performed by Vario EL-III CHNOS instrument. The Powder X-ray diffraction (XRD) was examined with a Bruker D8 diffractometer using graphite monochromatic copper radiation (Cu-K $\alpha$ ) at 40 kV and 30 mA over the  $2\theta$  range 5–80°. FT-IR spectra were recorded on a BEQUNDX-550 spectrometer on samples embedded in KBr pellets. The surface property of the sample was determined by XPS *via* Axis Ultra, Kratos (UK) using monochromatic Al K radiation (150 W, 15 kV, 1486.6 eV). Model XPA-VII photocatalytic reactor with a halogen lamp as the light source (Xujiang Electromechanical Plant, Nanjing, China) was employed to evaluate the degradation of 4-NP.

### 2.2 Synthesis of porphyrins

**2.2.1 Synthesis of ester porphyrins H<sub>2</sub>Pp-OMe, CuPp-OMe.** The synthetic routes of 5, 10, 15, 20-tetrakis(4-(4-carboxylic)piperidyl) phenyl porphyrin are shown in Fig. 3. The

detailed procedures were as follows: 5, 10, 15, 20-tetrakis(4-(4-formatemethyl)piperidyl) phenyl porphyrin (H<sub>2</sub>Pp-OMe) was prepared *via* the well-known Adler-Longo method:<sup>25</sup> 1-(4-aldehydephenyl) piperidine-4-carboxylic acid (3.7068 g, 15 mmol) was dissolved in propionic acid (90 mL) with vigorous stirring at 140 °C, and newly distilled pyrrole (1 mL, 15 mmol) in propionic acid (10 mL) was added dropwise in 30 min. The solvent was removed after another 1 h reaction. Furthermore, 20 mL ethanol was added and cooled to room temperature. Then, the mixture was filtrated under vacuum and purified by chromatography on a silica gel column using 2% ethanol of CH<sub>2</sub>Cl<sub>2</sub> as the eluent to produce H<sub>2</sub>Pp-OMe as a purple solid.

Yield: 11%. Mp: >250 °C. Anal. calcd (found) for C<sub>72</sub>H<sub>74</sub>N<sub>8</sub>O<sub>8</sub> (mol. wt: 1179.41), %: C 73.63 (73.32); H 6.91 (6.32); N 8.97 (9.50); O 10.49 (10.86). MS:  $m/z$ : 1180.57 (M + H<sup>+</sup>) amu. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{\text{max}}$ /nm, 431 (Soret band), 523, 568, 656 (Q bands). <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.88 (m, 8H,  $\beta$ -H), 8.09 (d, 4H, Ar), 7.29 (d, 4H, Ar), 3.98–3.08 (t, 16H,  $\alpha$ -H), 3.78 (s, 12H, –COOCH<sub>3</sub>), 2.67–2.58 (m, 4H, –CHC=O–), 2.24–2.01 (m, 16H,  $\beta$ -H), –2.68 (s, 2H, N-H). FT-IR (KBr):  $\nu$ , cm<sup>–1</sup>, 3379, 2937, 2803, 1730, 1607, 1515, 1311, 1192, 1042, 922, 804.

An excess of ten times of Cu(OAc)<sub>2</sub> (0.2 g) and H<sub>2</sub>Pp-OMe (0.1785 g) was dissolved separately in ethanol (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) with stirring at room temperature for 12 h. TLC was checked at the conclusion of the reaction. After removing the unreacted solid salt and solvent, the crude product was chromatographed on a silica column with dichloromethane as the eluent, a purple solid of CuPp-OMe was obtained.

Yield: 86%. Mp: >250 °C. C<sub>72</sub>H<sub>72</sub>CuN<sub>8</sub>O<sub>8</sub> (mol. wt: 1240.94), %: C 70.27 (69.69); H 6.01 (5.85); N 9.02 (9.03); O 9.97 (10.31); Cu 4.73 (5.12). MS:  $m/z$  1241.48 (M + H<sup>+</sup>) amu. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$ /nm, 430 (Soret band), 545 (Q band). FT-IR (KBr):  $\nu$ , cm<sup>–1</sup>, 2951, 1728, 1600, 1503, 1304, 1187, 1045, 920, 802.

**2.2.2 Synthesis of CuPp.** The synthesis of CuPp is similar to the method previously reported in the literature:<sup>26</sup> CuPp-OMe was mixed with 1 mol L<sup>–1</sup> aqueous KOH (20 mL) using THF as the solvent heated to reflux at 66 °C for 48 h. Additional water was added to the resulting water phase until the solid was completely dissolved, and then the solution was acidified with HCl (1 mol L<sup>–1</sup>) until no further precipitate appeared (pH = 3). The precipitated solid was filtered and washed with distilled water. Finally, the compound CuPp was obtained after vacuum drying at 80 °C for 6 h.

Yield: 86%. Mp: >250 °C. C<sub>68</sub>H<sub>64</sub>CuN<sub>8</sub>O<sub>8</sub> (mol. wt: 1184.83), %: C 69.33 (68.93); H 5.36 (5.44); N 9.25 (9.46); O 10.27 (10.80); Cu 5.79 (5.37). MS:  $m/z$  1185.41 (M + H<sup>+</sup>) amu. UV-vis (DMF)  $\lambda_{\text{max}}$ /nm, 432 (Soret band), 547, 591 (Q bands). FT-IR (KBr):  $\nu$ , cm<sup>–1</sup>: 3413, 1704, 1602, 1505, 1102, 938, 802.

### 2.3 Preparation of TiO<sub>2</sub> nanometer photocatalyst

The preparation procedure of TiO<sub>2</sub> sol nanometer photocatalyst is given below: in the first step, anhydrous ethanol (30 mL) tetrabutyltitanate (10 mL, 29.4 mmol) and acetic acid (2 mL) were mixed together at room temperature under continuous stirring. Then, nitric acid (0.5 mL), H<sub>2</sub>O (1 mL) and anhydrous



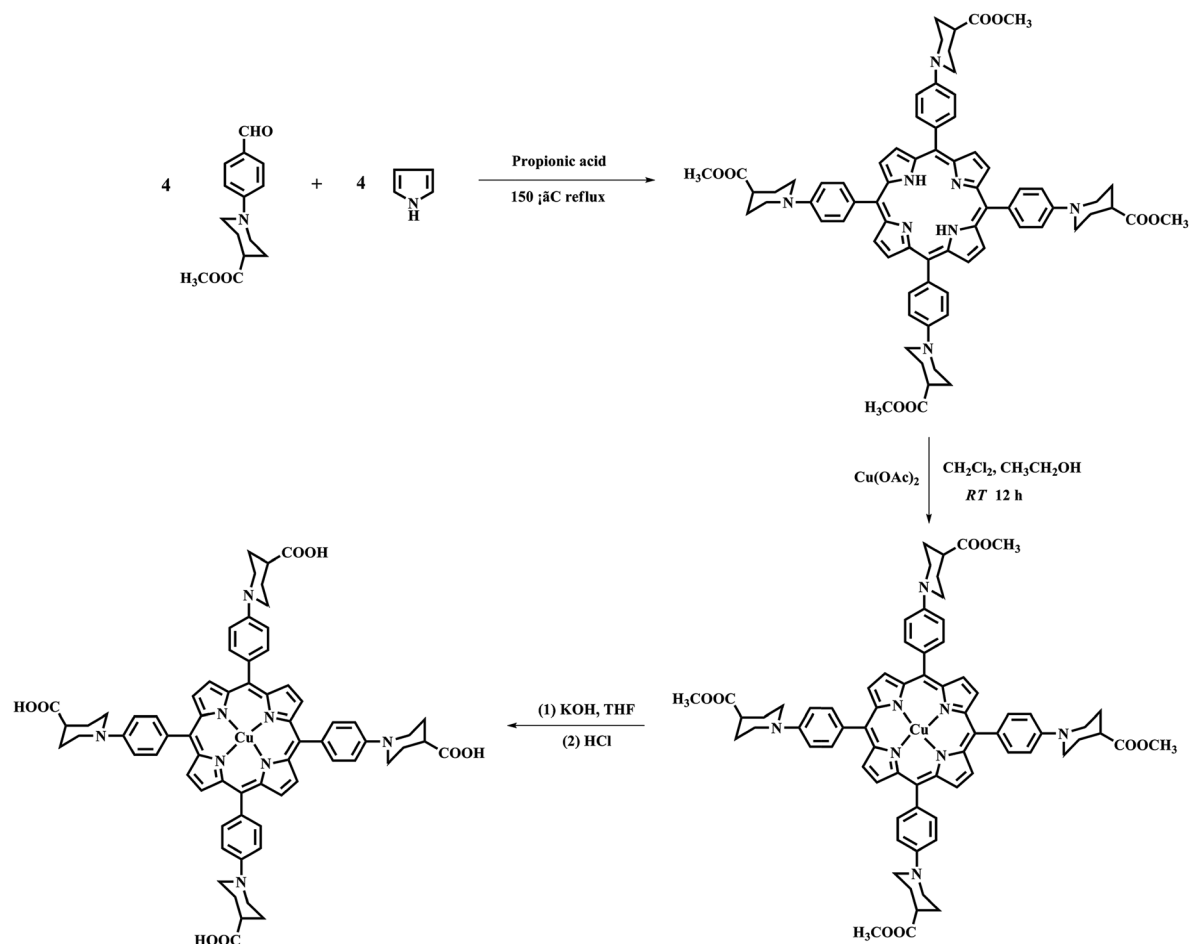


Fig. 3 Synthesis of the H<sub>2</sub>Pp-OMe, CuPp-OMe and CuPp.

ethanol (10 mL) was added dropwise to the above solution for 1.5 h. After that, a translucent TiO<sub>2</sub> sol was obtained.

Second, 6 drops of water were added to 5 mL of TiO<sub>2</sub> sol, and the mixture was stirred for 30 min. Then, the mixture was transferred into a 25 mL Teflon-lined autoclave casing at 90 °C and heated to 150 °C for 24 h. A gel like photocatalyst was obtained after cooling to room temperature. The sample was washed with anhydrous ethanol several times and soaked for 24 h. Finally, TiO<sub>2</sub> nanoparticles were fabricated after being dried and ground.

#### 2.4 The synthesis of CuPp-TiO<sub>2</sub> photocatalyst

The preparation procedure of mesoporous CuPp-TiO<sub>2</sub> was similar to that of TiO<sub>2</sub> nanometer photocatalyst synthesis, except that the CuPp load was increased: 0.0175 g amount of as-prepared CuPp was dissolved in 6 mL DMF. TiO<sub>2</sub> (5 mL) was added dropwise to the solution of CuPp-DMF (2 mL), and distilled water (0.3 mL) was added to the mixed solution severally. Then, the solvothermal condition was analogous to that mentioned above.

#### 2.5 Photocatalytic activity tests

The photoreactivity experiments were carried out using a Model XPA-VII photocatalytic reaction instrument according to the

previous report:<sup>27</sup> 10 mg photocatalysts were added into 50 mL 4-NP ( $1 \times 10^{-4}$  mol L<sup>-1</sup>) solution. The suspension was stirred vigorously with air bubbled when irradiating by 400 W of the central light source. The photocatalysis lasted for 60 min, and every 6 min we took out 3 mL sample of the suspension. The photocatalysts were separated from the solution by centrifugation, and the quantity of 4-NP was measured by its absorption at 317 nm with a Shimadzu UV-1800 UV-vis-NIR system.

#### 2.6 Stability of the photocatalyst

The stability test for CuPp-TiO<sub>2</sub> photocatalyst was carried out following a procedure similar to that used for the photodegradation of 4-NP. The experimental procedure and test conditions were the same as those mentioned above; the experiments were repeated six times. Catalysts for each test were collected by centrifugation, washed with distilled water, and dried in a vacuum oven after every photocatalytic cycle experiment.

#### 2.7 Photocatalytic mechanism investigation

Active species trapping experiment was employed to detect reactive species in photocatalysis process, which was carried out with the same procedure as that for the photodegradation test, except for the addition of selected scavengers. Benzoquinone (BQ, 0.2 mM), ammonium oxalate (AO, 10 mM), and isopropyl



alcohol (IPA, 10 mM) were selected as scavengers of superoxide anionic radicals ( $\cdot\text{O}_2^-$ ), photoinduced holes ( $\text{h}^+$ ) and hydroxyl radicals ( $\cdot\text{OH}^-$ ), respectively.

### 3. Results and discussions

#### 3.1 Morphology analysis

The surface morphology of the  $\text{TiO}_2$  and  $\text{CuPp-TiO}_2$  photocatalyst can be seen in Fig. 4a and c from the SEM images. It can be observed that the microsphere of  $\text{CuPp-TiO}_2$  possesses a similar appearance as the  $\text{TiO}_2$  we prepared previously. Integral TEM images shown in Fig. S1† show that the composite has a microsphere structure, which indicates that the  $\text{CuPp}$  molecules on the surface of  $\text{TiO}_2$  particles have no effect on the size and shape of the  $\text{TiO}_2$  powders.

The high resolution transmission electron microscopy (HRTEM) images of  $\text{TiO}_2$ , which was synthesized with a sol-gel procedure under solvothermal conditions, are shown in Fig. 4b to exhibit the crystal lattice indices of  $\{001\}$  and  $\{101\}$ , which is typical of anatase  $\text{TiO}_2$ .<sup>28–31</sup> Therefore, it can be concluded that the crystallization processes, as further confirmed by XRD measurements, occur uniformly *via* the strategy.  $\text{CuPp-TiO}_2$  photocatalyst illustrated in Fig. 4d shows a heterojunction structure, which exists as two different types of lattice fringes in the  $\text{CuPp-TiO}_2$  composite: the narrow fringe spacing (about 0.36 nm) could be assigned to the  $\{101\}$  planes of anatase  $\text{TiO}_2$ . Moreover, a wider lattice spacing of about 0.71 nm is also observed, which may come from the crystal plane of  $\text{CuPp}$ .<sup>32,33</sup> This verified that  $\text{CuPp}$  deposited well onto the surface of  $\text{TiO}_2$

nanoparticles and permeated readily into the spaces among the nanoparticles.<sup>34</sup> This may be ascribed to the infiltration of  $\text{CuPp}$  in the process of high-temperature solvothermal synthesis. These observations show that the preservation of  $\text{CuPp}$  crystals significantly modified the crystal structure of the  $\text{TiO}_2$ . Furthermore, we created massively intrinsic channels for photoproduced holes and electrons. Thereby,  $\text{CuPp-TiO}_2$  composite photocatalyst with a heterojunction structure is capable of displaying superior photocatalytic activity, which is in a good agreement with the photocatalytic experimental results.

#### 3.2 XRD analysis

X-ray diffraction (XRD) measurements were conducted to investigate the crystal phase of  $\text{CuPp-TiO}_2$  particles and the effect of  $\text{CuPp}$  on the crystal structure of  $\text{TiO}_2$ . As shown in Fig. 5, there is almost no difference between  $\text{CuPp-TiO}_2$  and  $\text{TiO}_2$ . XRD spectra taken in  $2\theta$  configuration have exhibited peaks at  $25.3^\circ$ ,  $38.3^\circ$ ,  $48.0^\circ$ ,  $54.2^\circ$ ,  $63.4^\circ$ ,  $69.1^\circ$  and  $75.5^\circ$ , and they can be indexed to the  $(1\ 0\ 1)$ ,  $(0\ 0\ 4)$ ,  $(2\ 0\ 0)$ ,  $(1\ 0\ 5)$ ,  $(2\ 1\ 1)$ ,  $(2\ 0\ 4)$ , and  $(2\ 1\ 5)$  lattice planes reflection of anatase  $\text{TiO}_2$  (JCPDS card 21-1272),<sup>35</sup> which gives higher photocatalytic activity than rutile and brookite.<sup>36,37</sup> The  $\text{CuPp}$  diffraction fringe fails to display owing to the infinitesimal amount of  $\text{CuPp}$  on the surface of  $\text{TiO}_2$ , indicating that the  $\text{CuPp}$  loaded on the surface of  $\text{TiO}_2$  microsphere could scarcely transform the intrinsic crystal of  $\text{TiO}_2$ .

#### 3.3 UV-vis-DRS analysis

The UV-visible diffuse-reflectance (UV-vis-DRS) spectra were measured in the range of 200–800 nm in order to explore the

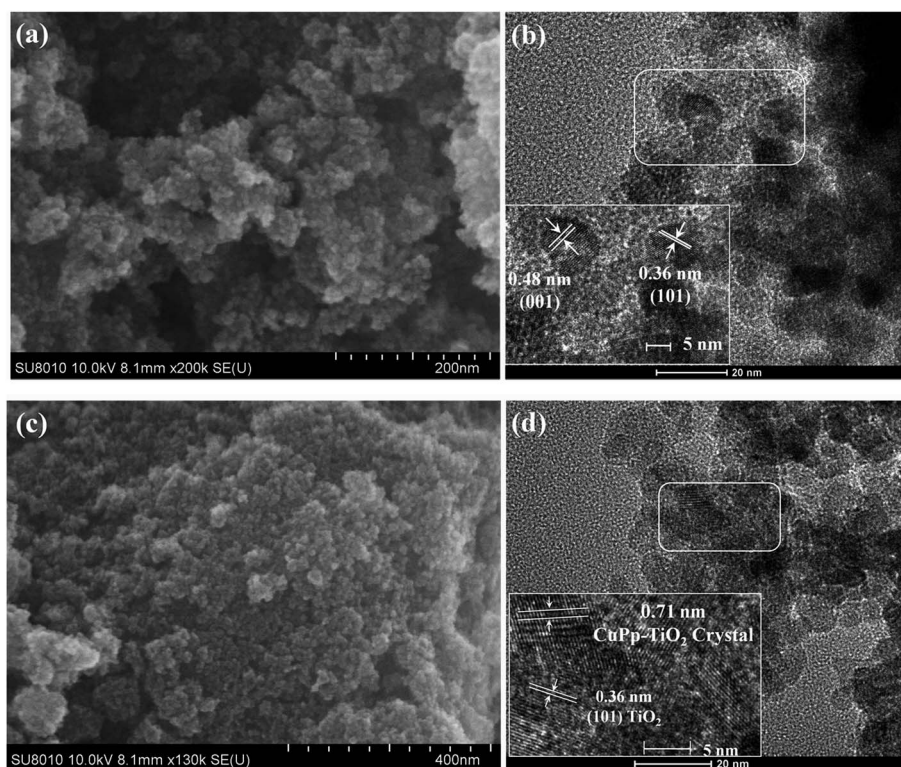


Fig. 4 SEM and TEM images of  $\text{TiO}_2$  (a), (b);  $\text{CuPp-TiO}_2$  composite (c), (d).





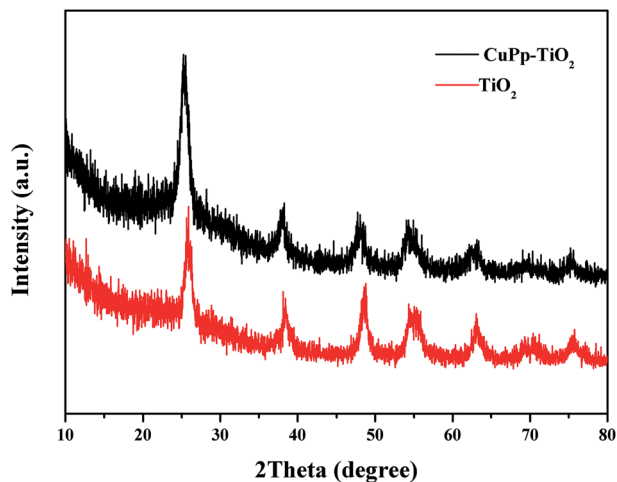


Fig. 5 XRD patterns of  $\text{TiO}_2$  and  $\text{CuPp-TiO}_2$  composite.

optical response of  $\text{TiO}_2$  and  $\text{CuPp-TiO}_2$ . As shown in Fig. 6, no obvious absorption peaks were observed above 400 nm for  $\text{TiO}_2$ . However,  $\text{CuPp-TiO}_2$  photocatalyst, which exhibited peaks typical of  $\text{CuPp}$ , demonstrated that the  $\text{CuPp}$  might influence the band width of  $\text{TiO}_2$ . This proves that the  $\text{CuPp}$  unit was perfectly impregnated onto the surface of  $\text{TiO}_2$ . As a result, the  $\text{CuPp-TiO}_2$  photocatalyst expanded the absorption range for the solar spectrum in comparison with  $\text{TiO}_2$ . It is noticed that the Soret and Q bands of the  $\text{CuPp-TiO}_2$  are slightly blue-shifted and broadened relative to  $\text{CuPp}$  in a DMF solution, implying that  $\text{CuPp}$  in  $\text{CuPp-TiO}_2$  photocatalyst had adopted a type H stack mode.<sup>38</sup> The band gap energies can be determined by extrapolating the absorption edge onto the energy axis (shown in Fig. 6 insertion), wherein the conversion of the reflectance to absorbance data was obtained by the Kubelka-Munk function ( $K-M$ ).<sup>39,40</sup> The band gap energies of  $\text{TiO}_2$  and  $\text{CuPp-TiO}_2$  samples are 3.23 and 3.18 eV, respectively.

### 3.4 FT-IR spectra analysis

The FT-IR spectra were used to verify the interaction between  $\text{CuPp}$  and  $\text{TiO}_2$ . As shown in Fig. 7, there exists a broad

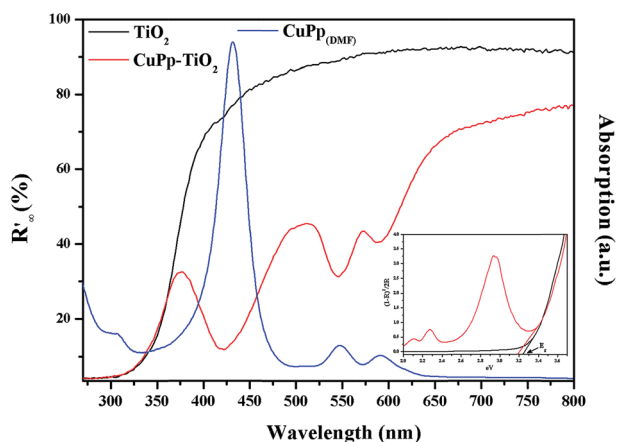


Fig. 6 UV-vis-DRS spectra of  $\text{TiO}_2$  (black line),  $\text{CuPp-TiO}_2$  (red line) composite and UV-vis spectrum of  $\text{CuPp}$  (blue line), the insertion is the Kubelka-Munk function.

characteristic vibration band of  $\text{Ti-O}$  around  $707\text{ cm}^{-1}$ . The disappearance of the  $\text{C=O}$  stretching vibration of the carboxyl group in  $\text{CuPp}$  molecules around  $1705\text{ cm}^{-1}$  and the new band at around  $1650\text{ cm}^{-1}$  and the weak absorptions at around  $1406\text{ cm}^{-1}$  in  $\text{CuPp-TiO}_2$  might be ascribed to the emergence of asymmetric and symmetric stretch of  $\text{-COO}^-$ . Therefore, this serves as sufficient evidence that  $\text{CuPp}$  is able to be chemisorbed on the surface of  $\text{TiO}_2$ . Moreover, enhancement of electron transferring between  $\text{CuPp}$  and  $\text{Ti}$  orbital manifold of  $\text{TiO}_2$  can be tuned by  $\text{O=C-O-Ti}$  bonds.<sup>41,42</sup> The appearance of  $\text{C-O-Ti}$  and  $\text{C=O}$  groups in  $\text{CuPp-TiO}_2$ , which were provided with polarity, resulted in asymmetric electronic structures, contributing to the improvement of photocatalytic activity further.

### 3.5 XPS analysis

X-ray Photoelectron Spectroscopy (XPS) analyses were used to investigate the surface chemical states and composition change of  $\text{TiO}_2$  and  $\text{CuPp-TiO}_2$ . Fig. 8 showed the XPS spectra of both  $\text{TiO}_2$  and  $\text{CuPp-TiO}_2$ . The survey spectra (Fig. 8a) show that the  $\text{CuPp-TiO}_2$  composite contains the  $\text{Cu}$ ,  $\text{Ti}$ ,  $\text{O}$  and  $\text{C}$ , while  $\text{TiO}_2$  consists of  $\text{Ti}$  and  $\text{O}$ , which was consistent with the corresponding EDX-measured elemental maps (Fig. S2†). The element of  $\text{C}$  for  $\text{TiO}_2$  mainly comes from adventitious carbon-based contaminants. There is an enhancement of the  $\text{C 1s}$  peak intensity in  $\text{CuPp-TiO}_2$ , which may attributed to the massive amounts of adsorbed  $\text{CuPp}$  molecules. As for  $\text{Ti 2p}$  spectra (Fig. 8b), the  $\text{Ti 2p}_{3/2}$  binding energy of the  $\text{CuPp-TiO}_2$  (465.0 eV) is higher than that of the  $\text{TiO}_2$  sample (464.7 eV); this suggested that the  $\text{Ti}$  atom of the  $\text{TiO}_2$ , as the acceptor, coordinates with the  $\text{O}$  atom of  $\text{CuPp}$  as the donor, *i.e.*  $\text{Ti}$  atom of the  $\text{TiO}_2$  adopted the electrons of the  $\text{O}$  atom in the carbonyl group ( $\text{O=C=O}$ ) from  $\text{CuPp}$  molecules,<sup>43,44</sup> which is in agreement with the FT-IR results. As a result, the electron cloud density of  $\text{O}$  atom in  $\text{CuPp}$  decreased and is accompanied with an increased valence for the  $\text{O}$  atom, and consequently an increased binding energy of  $\text{O 1s}$  (530.8 eV) (Fig. 8c) compared to that of  $\text{TiO}_2$  (530.2 eV).<sup>45</sup> Moreover, the peaks located at 934.1 and 954.1 eV (ref. 46) also

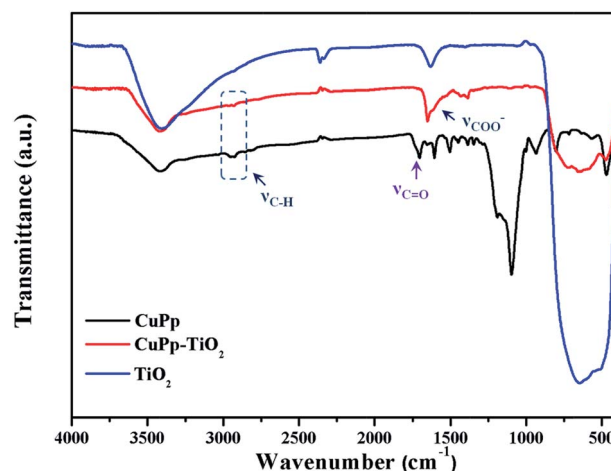


Fig. 7 The FT-IR spectra of  $\text{CuPp}$ ,  $\text{CuPp-TiO}_2$ ,  $\text{TiO}_2$  composite.



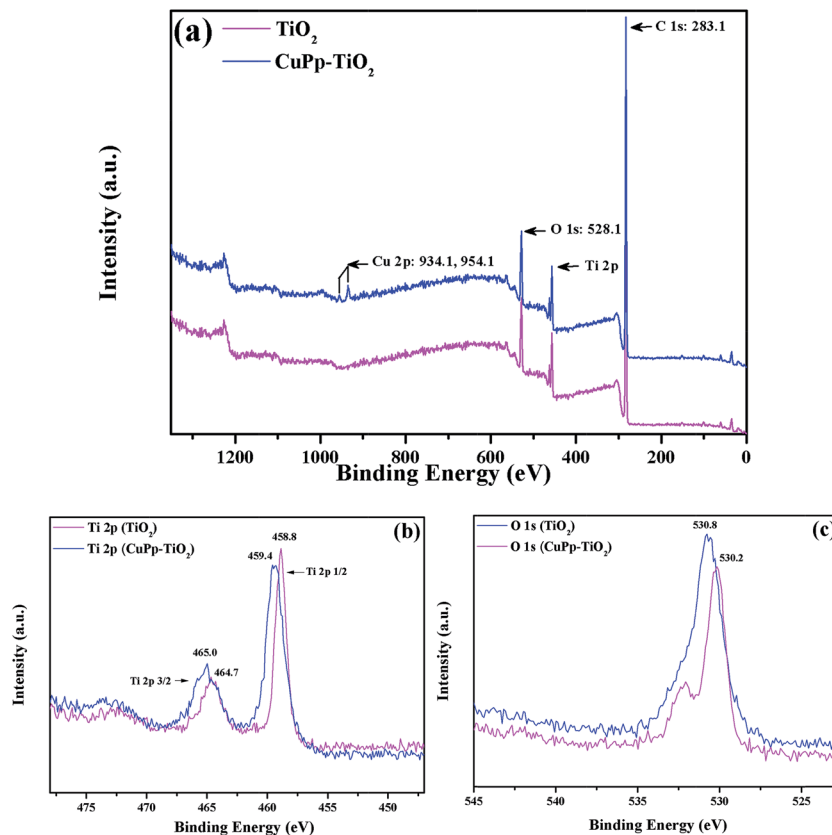


Fig. 8 XPS spectra of the TiO<sub>2</sub> and CuPp-TiO<sub>2</sub> composite photocatalyst, (a) survey spectra, (b) Ti 2p spectra, (c) O 1s spectra.

imply the presence of CuPp in CuPp-TiO<sub>2</sub> composite, indicating CuPp molecules adsorbed on the TiO<sub>2</sub> nanoparticle surface.

### 3.6 BET analysis

N<sub>2</sub> adsorption analyses were used to evaluate the porous properties of the samples. Fig. 9 demonstrated the nitrogen adsorption-desorption isotherm and pore size distribution curve of TiO<sub>2</sub> and CuPp-TiO<sub>2</sub> composite. The pore size distribution is calculated from the desorption branch of a nitrogen isotherm by the Barrett-Joyner-Halenda (BJH) method.<sup>47</sup> The samples exhibit a type IV adsorption isotherm with a hysteresis loop according to IUPAC classifications, whose adsorption branch of the isotherm is not consistent with the desorption branch, indicating that both of them are typical characteristics of a mesoporous structure.<sup>48</sup> The detailed tested data are summarized in Table 1. The as-prepared TiO<sub>2</sub> and CuPp-TiO<sub>2</sub> possessed high BET specific surface area of 127.89–140.57 m<sup>2</sup> g<sup>-1</sup>, which are far higher than those of commercial TiO<sub>2</sub> (anatase, BET specific surface area 8 m<sup>2</sup> g<sup>-1</sup>).

### 3.7 Photocatalytic activity analysis

The photocatalytic activities were assessed by the degradation of organic dyes 4-nitrophenol (4-NP) in aqueous solution under white light illumination. P25, the mixture of CuPp and TiO<sub>2</sub> serve as references for investigating photocatalytic activities. Fig. 10 shows the photocatalytic efficiency of all samples

compared to the blank test, which contained 4-NP(aq) only. As expected, all samples exhibit relatively effective photocatalytic ability in comparison with the blank test. P25 exhibits a favorable performance in photocatalytic activity, whereas the CuPp-TiO<sub>2</sub> composite photocatalyst displays a higher removal rate in 4-NP photocatalytic degradation. As such, the CuPp-TiO<sub>2</sub> composite photocatalyst manifests inherent superior catalytic

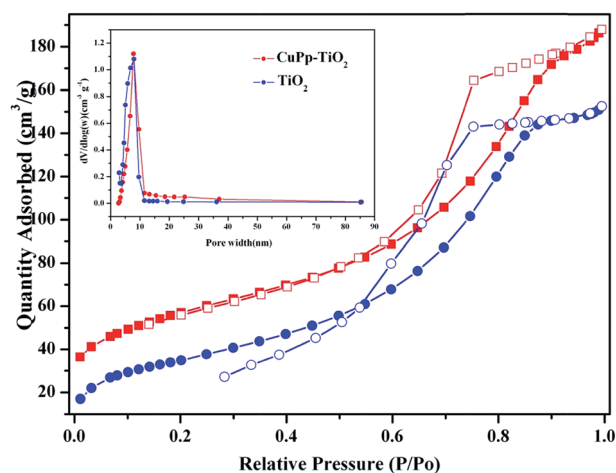


Fig. 9 N<sub>2</sub> adsorption (solid symbols)–desorption (open symbols) isotherms of TiO<sub>2</sub> and CuPp-TiO<sub>2</sub> composite. The inset picture was pore size distribution.



**Table 1** The detailed pore information of mesoporous TiO<sub>2</sub> and CuPp-TiO<sub>2</sub>

Samples	BET (m <sup>2</sup> g <sup>-1</sup> )	Pore width (nm)	V <sub>BJH</sub> (cm <sup>3</sup> g <sup>-1</sup> )
TiO <sub>2</sub>	127.89	7.21	0.32
CuPp-TiO <sub>2</sub>	140.57	7.15	0.29

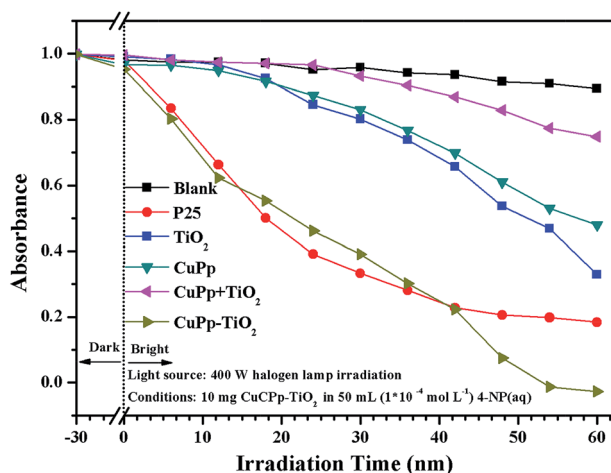
activity to the mixture of CuPp and TiO<sub>2</sub>, which confirmed that it is the heterojunction structures formed by sol-gel progress and solvothermal conditions that improve the efficiency of the photoreactivity process.

### 3.8 The repeatability test

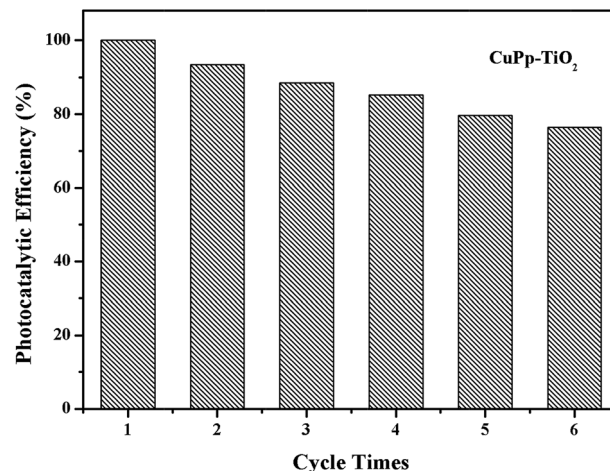
The photostability and reusability are important indicators to measure the practical performance of the catalyst. The study of CuPp-TiO<sub>2</sub> reproducibility in photocatalytic degradation of 4-NP was carried out to evaluate stability of CuPp-TiO<sub>2</sub> composite. As can be seen in Fig. 11, 100% 4-NP was removed in the first run, and the degradation efficiency decreased gradually with increasing cycle times. The catalytic efficiency of CuPp-TiO<sub>2</sub> composite for the next five cycles was reduced to 93.3%, 88.5%, 85.6%, 81.5% and 78.1% respectively, indicating the photocatalytic activity did not obviously decrease within six cycles of reutilization, which exhibited relatively high stability in photodegradation. The stability test confirmed that the CuPp dispersed on the surface of TiO<sub>2</sub> exhibited remarkable stability under irradiation, because of the interactions between Cu(II) porphyrin and TiO<sub>2</sub> in CuPp-TiO<sub>2</sub> composite photocatalyst.

### 3.9 Mechanism explanation

Active species trapping experiment has been carried out to detect the active species in accordance with previous reports.<sup>49,50</sup> It has been widely known that the hydroxyl radicals (<sup>•</sup>OH), superoxide anion radicals (<sup>•</sup>O<sup>2-</sup>) and photogenerated holes (h<sup>+</sup>) are the main active species in the photocatalysis process,<sup>51,52</sup> which can be detected through the trapping experiment with



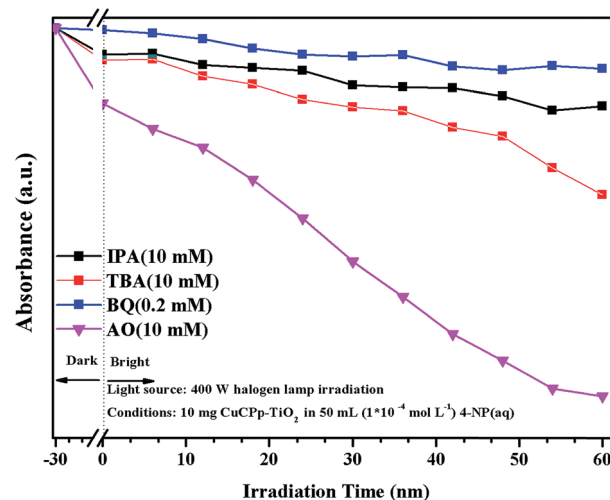
**Fig. 10** Photodegradation of 4-NP vs. irradiation time with samples.



**Fig. 11** Photocatalytic efficiency of the mesoporous CuPp-TiO<sub>2</sub> for 4-NP degradation in six cycles.

scavengers isopropyl alcohol (IPA), benzoquinone (BQ) and ammonium oxalate (AO) respectively.<sup>53-55</sup> As shown in Fig. 12, the degradation efficiency of 4-NP is changed slightly with the addition of AO as a h<sup>+</sup> scavenger, indicating that h<sup>+</sup> does not dominate the photodegradation progress. On the contrary, the degradation percentage reduced to a certain extent with the participation of IPA and TBA, which served as <sup>•</sup>OH scavengers. The degradation activity is dramatically inhibited after the addition of BQ, which inferred that <sup>•</sup>O<sup>2-</sup> is the main active species in 4-NP photocatalytic degradation (Fig. S3†). It can therefore be concluded that 4-NP degradation was inhibited to some degree by the addition of each of the three scavengers, which suggested that <sup>•</sup>OH, h<sup>+</sup>, and <sup>•</sup>O<sup>2-</sup> were all involved in the photodegradation process.

The photocatalytic mechanism of CuPp-TiO<sub>2</sub> is explicated in the following description based on the above results. The valence band (VB) and conduction band (CB) energies for CuPp



**Fig. 12** Effects of some selected scavengers on the photocatalytic degradation of 4-NP over CuPp-TiO<sub>2</sub> composite photocatalyst under visible light irradiation.



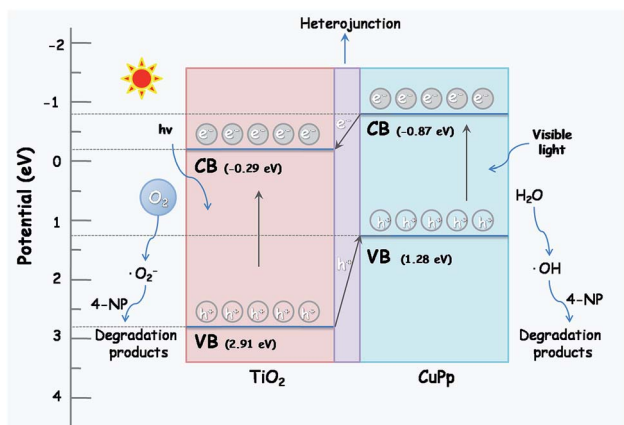


Fig. 13 The possible photocatalytic mechanism of CuPp–TiO<sub>2</sub> composite photocatalyst under halogen lamp irradiation.

are 1.28 and  $-0.87$  eV respectively,<sup>56</sup> which is lower than that of TiO<sub>2</sub> (2.91,  $-0.29$  eV). Therefore, the energy level of the excited CuPp and the CB position of TiO<sub>2</sub> overlap well. The electrons in VB of TiO<sub>2</sub> can be excited and injected into the CB of TiO<sub>2</sub> when the light irradiates on the surface of the photocatalyst CuPp–TiO<sub>2</sub>. Photocatalytic activity is greatly enhanced due to the heterojunction structure in the CuPp–TiO<sub>2</sub> composite photocatalyst.<sup>51,57</sup> As shown in Fig. 13, the photogenerated electrons generated by the absorption of visible light in the CB of the CuPp migrate to the CB of the TiO<sub>2</sub> through the heterojunction structure forming reduction sites. The excited electrons were captured by O<sub>2</sub> to produce peroxy radicals ( $\cdot\text{O}_2^-$ ), which were capable of oxidizing 4-NP molecules. Furthermore, the photo-induced holes in the VB of TiO<sub>2</sub> flow to the VB of CuPp forming oxidation sites, thus resulting in the reaction with H<sub>2</sub>O to produce  $\cdot\text{OH}$  and the degradation of 4-NP in the final step. Consequently, photogenerated electrons and holes are spatially isolated with high efficiency, which greatly inhibits their undesirable recombination.<sup>38,58,59</sup> Moreover, the mesoporous structure of CuPp–TiO<sub>2</sub> with large BET surface area is beneficial to pollutant adsorption and leads to more active interaction with TiO<sub>2</sub> and 4-NP.

## 4. Conclusion

A feasible route for the generation of Cu(II) porphyrin based TiO<sub>2</sub> composite photocatalyst with a heterogeneous structure has been comprehensively expounded in this study. Spectral techniques and gas sorption experiments have been used to characterize its spectroscopic properties and porous structures. The TiO<sub>2</sub> and CuPp–TiO<sub>2</sub> obtained by sol–gel process and solvothermal method exhibit anatase phase, as confirmed by XRD, contributing to a high efficiency of the photodegradation of 4-NP in the photocatalytic tests. CuPp–TiO<sub>2</sub> composite photocatalyst retained remarkable stability in photocatalysis experiments even after six cycles. It is hoped that this methodology for the porphyrin–TiO<sub>2</sub> photocatalyst preparation could serve as a foundation for future applications in photocatalytic degradation.

## Conflicts of interest

There are no conflicts declare.

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## References

- 1 A. Fujishima, *J. Photochem. Photobiol., C*, 2012, **13**(3), 169–189.
- 2 R. Vasilic, S. Stojadinovic, N. Radic, *et al.*, *Mater. Chem. Phys.*, 2015, **151**, 337–344.
- 3 S. G. Kumar and L. G. Devi, *J. Phys. Chem. A*, 2011, **115**(46), 13211–13241.
- 4 Y. And and R. Joseph, *J. Phys. Chem. B*, 2003, **107**(43), 11970–11978.
- 5 A. L. Linsebigler, G. Lu and J. T. Yates, *Chem. Rev.*, 1995, **95**(3), 735–758.
- 6 T. H. Tran, A. Y. Nosaka and Y. Nosaka, *J. Phys. Chem. B*, 2006, **110**(50), 25525–25531.
- 7 Y. Kakuma, A. Y. Nosaka and Y. Nosaka, *Phys. Chem. Chem. Phys.*, 2015, **17**(28), 18691–18698.
- 8 S. S. Lee, H. Bai, Z. Liu and D. D. Sun, *Environ. Sci. Technol.*, 2015, **49**, 2541–2548.
- 9 S. Xu, H. Lu, L. Chen and X. Wang, *RSC Adv.*, 2014, **4**(85), 45266–45274.
- 10 D. Yu, J. Bai, H. Liang, T. Ma and C. Li, *Dyes Pigm.*, 2016, **133**, 51–59.
- 11 M. M. Yu, J. Li, W. J. Sun, *et al.*, *J. Mater. Sci.*, 2014, **49**(16), 5519–5528.
- 12 S. Bingham and W. A. Daoud, *J. Mater. Chem.*, 2011, **21**, 2041–2050.
- 13 J. Yu, X. Zhao and Q. Zhao, *Thin Solid Films*, 2000, **379**(1–2), 7–14.
- 14 Z. Xiong, L. Zhang and X. S. Zhao, *Chem.–Eur. J.*, 2014, **20**(45), 14715–14720.
- 15 S. Motoyama, R. Makiura, O. Sakata, *et al.*, *J. Am. Chem. Soc.*, 2011, **133**(15), 5640–5643.
- 16 S. Kumar, M. Y. Wani, C. Audia, C. T. Arranja, *et al.*, *J. Mater. Chem. A*, 2015, **3**(39), 19615–19637.
- 17 Z. Zhang, W. Y. Gao, L. Wojtas, *et al.*, *Angew. Chem.*, 2012, **51**(37), 9330–9334.
- 18 S. Afzal, W. A. Daoud and S. J. Langford, *ACS Appl. Mater. Interfaces*, 2013, **5**(11), 4753–4759.
- 19 J. Roales, J. M. Pedrosa, M. Cano, *et al.*, *RSC Adv.*, 2013, **4**(4), 1974–1981.
- 20 C. Wang, J. Li, G. Mele, *et al.*, *Dyes Pigm.*, 2010, **84**(2), 183–189.
- 21 G. Mele, E. Garcialópez, L. Palmisano, *et al.*, *Appl. Catal., B*, 2007, **38**(4), 309–319.
- 22 Y. Luo, J. Li, G. P. Yao, *et al.*, *Catal. Sci. Technol.*, 2012, **2**, 841–846.





- 23 L. Tasseroul, S. Lambert, M. C. Páez, *et al.*, *Dev. Brain Res.*, 2011, **44**(2), 314–318.
- 24 C. Wang, J. Li, G. Mele, *et al.*, Efficient degradation of 4-nitrophenol by using functionalized porphyrin-TiO<sub>2</sub>, photocatalysts under visible irradiation, *Appl. Catal., B*, 2007, **76**(3–4), 218–226.
- 25 G. Mele, S. R. Del, G. Vasapollo, *et al.*, *J. Phys. Chem. B*, 2005, **109**(25), 12347–12352.
- 26 S. Sun, M. Pan, X. Hu, *et al.*, *Catal. Lett.*, 2016, **146**(6), 1087–1098.
- 27 G. P. Yao, J. Li, Y. Luo, *et al.*, *J. Mol. Catal. A: Chem.*, 2012, **361–362**(9), 29–35.
- 28 H. G. Yang, C. H. Sun, S. Z. Qiao, *et al.*, *Nature*, 2008, **453**, 638–641.
- 29 R. Wang, K. Hashimoto, A. Fujishima, *et al.*, *Adv. Mater.*, 2010, **10**(2), 135–138.
- 30 M. H. Yang, P. C. Chen, M. C. Tsai, *et al.*, *CrystEngComm*, 2013, **15**(15), 2966–2971.
- 31 L. Wang, L. Zang, J. Zhao, *et al.*, *Chem. Commun.*, 2012, **48**(96), 11736–11738.
- 32 M. M. Yu, C. Wang, J. Li, *et al.*, *Appl. Surf. Sci.*, 2015, **342**, 47–54.
- 33 X. Zhao, X. Liu, M. M. Yu, *et al.*, *Dyes Pigm.*, 2017, **136**, 648–656.
- 34 C. Liu, D. Yang, J. Yang, *et al.*, *ACS Appl. Mater. Interfaces*, 2013, **5**(9), 3824–3832.
- 35 H. Wang, X. Gao, G. Duan, *et al.*, *J. Environ. Chem. Eng.*, 2015, **3**(2), 603–608.
- 36 T. A. Kandiel, L. Robben, A. Alkaim, *et al.*, *Photochem. Photobiol. Sci.*, 2013, **12**(4), 602–609.
- 37 J. Zhang, P. Zhou, J. Liu, *et al.*, *Phys. Chem. Chem. Phys.*, 2014, **16**(38), 20377–20381.
- 38 A. D'Urso, M. E. Fragala and R. Purrello, *Chem. Commun.*, 2012, **43**(49), 8165.
- 39 H. Lin, C. P. Huang, W. Li, *et al.*, *Appl. Catal., B*, 2006, **68**(1–2), 1–11.
- 40 B. K. Das, S. J. Bora, M. Chakraborty, L. Kalita, R. Chakraborty and R. Barman, *J. Chem. Sci.*, 2006, **118**, 487–494.
- 41 D. Chen, D. Yang, J. Geng, J. Zhu and Z. Jiang, *Appl. Surf. Sci.*, 2008, **255**(5), 2879–2884.
- 42 P. Zhou, J. Yu and M. Jaroniec, *Adv. Mater.*, 2014, **26**(29), 4920–4935.
- 43 S. J. Zhang, *Ultrason. Sonochem.*, 2012, **19**(4), 767–771.
- 44 J. Yu, G. Dai, Q. Xiang, *et al.*, *J. Mater. Chem.*, 2011, **21**(4), 1049–1057.
- 45 D. A. H. Hanaor and C. C. Sorrell, *J. Mater. Sci.*, 2011, **46**(4), 855–874.
- 46 H. Wang, D. Zhou, S. Shen, *et al.*, *RSC Adv.*, 2014, **4**, 28978–28986.
- 47 A. I. Carrillo, E. Serrano, J. C. Serrano-Ruiz, *et al.*, *Appl. Catal., A*, 2012, **435–436**(17), 1–9.
- 48 W. Xuan, C. Zhu, Y. Liu, *et al.*, *Chem. Soc. Rev.*, 2012, **41**(5), 1677–1695.
- 49 L. L. He, Z. F. Tong and Z. H. Wang, *J. Colloid Interface Sci.*, 2018, **509**, 448–456.
- 50 H. Huang, N. Huang and Z. H. Wang, *J. Colloid Interface Sci.*, 2017, **502**, 77–88.
- 51 J. Shu, Z. Wang, G. Xia, Y. Zheng, *et al.*, *Chem. Eng. J.*, 2014, **252**, 374–381.
- 52 N. Serpone, *Sol. Energy Mater. Sol. Cells*, 1995, **38**, 369–379.
- 53 Y. N. Wang, K. J. Deng and L. Z. Zhang, *J. Phys. Chem. C*, 2011, **115**, 14300–14308.
- 54 L. Q. Ye, K. J. Deng, F. Xu, L. H. Tian, T. Y. Peng and L. Zan, *Phys. Chem. Chem. Phys.*, 2012, **14**, 82–85.
- 55 X. P. Song, Q. Yang, X. H. Jiang, M. Y. Yin and L. M. Zhou, *Appl. Catal., B*, 2017, **217**, 322–330.
- 56 W. J. Sun, J. Li, G. Mele, *et al.*, *J. Mol. Catal. A: Chem.*, 2013, **366**(1), 84–91.
- 57 H. Wang, L. Zhang, Z. Chen, *et al.*, *Chem. Soc. Rev.*, 2014, **43**(15), 5234–5244.
- 58 J. Low, J. Yu, M. Jaroniec, *et al.*, *Adv. Mater.*, 2017, **29**(20), 1601694–1601714.
- 59 J. Yu, J. Low, W. Xiao, P. Zhou and M. Jaroniec, *J. Am. Chem. Soc.*, 2014, **136**, 8839–8842.

