# **RSC Advances**

## PAPER

Cite this: RSC Adv., 2014, 4, 14281

Received 9th October 2013 Accepted 28th January 2014

DOI: 10.1039/c3ra45670f

www.rsc.org/advances

### 1. Introduction

With the development of photocatalytic technology in terms of environmental purification and solar energy conversion, TiO<sub>2</sub> has so far been found to be the most promising semiconductor photocatalyst because of its superior photocatalytic activity, chemical stability, low cost, and environmental friendliness.<sup>1,2</sup> However, a major drawback of TiO<sub>2</sub>,its lower utilization of solar energy (it is only sensitive to UV light), limits its extensive application.<sup>3,4</sup> Therefore, the exploitation of visible-light-driven photocatalysts is essential for the practical application of photocatalytic technology. Until now, two major approaches have been employed to extend the light absorption of semiconductor

photocatalysts to the larger visible spectral region. One of them is the modification of TiO<sub>2</sub>, including non-metals doping,<sup>5</sup> metals doping,<sup>6,7</sup> precious metal deposition,<sup>8</sup> semiconductor coupling,<sup>9</sup> *etc.* The other method is to exploit novel non-TiO<sub>2</sub>based semiconductor photocatalysts with strong visible light response, such as Bi<sub>2</sub>WO<sub>6</sub>,<sup>10</sup> BiOX (X = Cl, Br, I),<sup>11-13</sup> Ag/AgX (X = Cl, Br, I),<sup>14</sup> InNbO<sub>4</sub>,<sup>15</sup> Ag<sub>3</sub>VO<sub>4</sub>,<sup>16</sup> BiVO<sub>4</sub>,<sup>17</sup> *etc.* However, these methods are expected to be further developed to satisfy largescale applications under visible light radiation. Hence, the potential of visible-light-driven photocatalysts with high efficiency still needs to be fully investigated.

As a new type of non TiO<sub>2</sub>-based semiconductor photocatalyst, BiOX (X = Cl, Br, I) has attracted great attention recently due to its good photocatalytic activity under UV or visible light illumination, unique layered structure, high activity, and high photocorrosion stability.<sup>18</sup> Among them, BiOCl possesses the tetragonal matlockite structure, a layered structure composed of  $[Bi_2O_2]^{2+}$  layers interleaved with double Cl layers. Recently, BiOCl is reported to be an important photocatalyst for the degradation of organic compounds under visible light illumination. For example, Zhang *et al.*<sup>19</sup> prepared BiOCl microspheres by a general one-pot solvothermal process,

## One-pot solvothermal synthesis of Cu-modified BiOCl via a Cu-containing ionic liquid and its visible-light photocatalytic properties<sup>†</sup>

Jun Di,<sup>a</sup> Jiexiang Xia,<sup>a</sup> Sheng Yin,<sup>a</sup> Hui Xu,<sup>b</sup> Li Xu,<sup>c</sup> Yuanguo Xu,<sup>a</sup> Minqiang He<sup>a</sup> and Huaming Li<sup>\*a</sup>

Novel visible-light-driven Cu-modified BiOCl uniform sphere-like materials have been successfully synthesized through a one-pot ethylene glycol (EG)-assisted solvothermal process in the presence of 1-octyl-3-methylimidazolium copper trichloride ([Omim]CuCl<sub>3</sub>). The Cu-modified BiOCl materials were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), Raman, photoluminescence (PL) and UV-vis diffuse reflectance spectroscopy (DRS). The results of the XRD, XPS, SEM, EDS, Raman analyses indicated that metal Cu was evenly distributed on the surface of the BiOCI microspheres in the form of Cu<sup>2+</sup>. During the reaction process, the metal-based ionic liquid acted as the solvent, the template, the Cl source and the Cu source at the same time. It is possible to tune the morphology of the Cu-modified BiOCL materials by varying the amount of ionic liquid used. In addition, the electrochemical and photocatalytic properties of the Cu-modified BiOCl materials were investigated. After the introduction of Cu<sup>2+</sup>, the photocurrent of the Cu-modified BiOCl materials was higher than that of the pure BiOCl. And the Cu-modified BiOCl materials exhibited higher photocatalytic activity for the degradation of methylene blue (MB) and bisphenol A (BPA) than that of pure BiOCl. The increased photocatalytic activity of the Cu-modified BiOCI materials was attributed to its large adsorption capacity, broad light absorption band and high separation efficiency of photo-generated electrons and holes. On the basis of these findings, the Cu-modified BiOCl materials showed great promise as photocatalysts for degrading organic pollutants and other applications

View Article Online

View Journal | View Issue

<sup>&</sup>lt;sup>a</sup>School of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang, 212013, P. R. China. E-mail: lhm@ujs.edu.cn; Fax: +86-511-88791108; Tel: +86-511-88791108

<sup>&</sup>lt;sup>b</sup>School of the Environment, Jiangsu University, Zhenjiang 212013, P. R. China

<sup>&</sup>lt;sup>c</sup>School of Material Science and Engineering, Jiangsu University, Zhenjiang, 212013, P. R. China

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra45670f

and the band gap of the as-prepared BiOCl powders was estimated to about 3.22 eV. The photocatalytic activity of BiOCl on the degradation of MO is better than that of TiO<sub>2</sub> (Degussa, P25) under UV-vis light irradiation and that of C-doped TiO2 under visible light ( $\lambda > 420$  nm) irradiation. However, its photocatalytic activity has also been limited by its wide band gap and the high recombination of the photogenerated electron-hole pairs. Some strategies have been exploited to expand the visible light absorption range and improve the quantum efficiency of BiOCl, in order to enhance its photocatalytic activity. For instance, Chang et al.<sup>20</sup> used a narrow band gap material NaBiO<sub>3</sub> coupled with BiOCl to enlarge its visible-light-absorption ability. Gao et al.21 dispersed BiOCl nanoparticles on the both surfaces of graphene sheets to form a sandwich-like structure via a facile chemical-bath method. The unique 2D carbon nanostructure and the C-Bi chemical coupling in the graphene/BiOCl nanocomposite increased the separation efficiency of the electronhole, and then enhanced its ability to photodegrade methylbenzene under UV irradiation, compared with bare BiOCl. It has been proved that the metal modification can enhance the structure and morphology of photocatalysts, leading to the reduction of electron-hole recombination and an improvement of the photocatalytic activity.<sup>22-24</sup> To the best of our knowledge, the relevant information regarding the application of metal modified BiOCl in visible light photocatalytic degradation of organic pollutants has seldom been reported.

Ionic liquids (ILs) have received a great deal of attention as new types of environmentally-friendly reaction media, due to their promising properties such as negligible vapor pressure, wide electrochemical window, wide temperature range, good dissolving ability, high thermal stability, high ionic conductivity, non-flammability, etc.25,26 The application of ILs in inorganic nanomaterial preparation has received increasing attention in recent years. Many inorganic nanostructures have been fabricated through various IL-involved processes, including high-quality TiO2 nanocrystals,27 rod-like, star-like and flower-like ZnO nano structures,28 Bi2S3, Sb2S3 nanorods,<sup>29</sup> and ultrathin SmVO<sub>4</sub> nanosheets.<sup>30</sup> Among them, Lewis acidic ILs based on 1-alkyl-3-methylimidazolium metal chloride ( $[C_n mim]Cl/MCl_2$ ) (M = Zn, Fe, Cu, Mg, Ni, Co, etc.) have also been used in the synthesis of inorganic nanomaterials. These Lewis acidic metal-based ILs not only have the general advantages of the conventional ionic liquids, but also possess some unique characteristics, such as strong magnetic field response, moisture-stable, intermediate Lewis acidity, etc.<sup>31-35</sup> For example, Taubert<sup>36</sup> introduced a novel protocol for the controlled synthesis of CuCl nanoplatelets with a well-developed crystal structure and a tunable particle size and synthesized them from the Cu-containing ionic liquid. It was possible to tune the particle size, thickness, and connectivity by varying the reaction temperature. The approach provided a simple and green method to tune the properties of the CuCl nanocrystals and assemble them for applications in catalysis. However, few studies have been reported to synthesize inorganic nanomaterials via these metal-based ILs. The use of metal-based ILs in inorganic synthesis still needs to be fully exploited.

In this study, novel visible-light-driven Cu-modified BiOCl materials were solvothermally synthesized by a Cu-containing ionic liquid. A series of characterization methods were conducted to characterize the synthesized Cu-modified BiOCl materials. The Cu-containing ionic liquid acted not only as the solvent and the template, but also as the Cl source and the Cu source. The photocatalytic activity of the Cu-modified BiOCl materials was evaluated using methyl blue (MB) and bisphenol A (BPA) as target pollutants in  $H_2O_2$  system. The relationship between the photocatalytic activity and the structural properties of the Cu-modified BiOCl materials was discussed. The reasons for the enhanced photocatalytic activity of Cu/BiOCl were also carefully illustrated.

### 2. Experimental section

#### 2.1. Preparation of the photocatalysts

**2.1.1. Material and sample preparation.** All chemicals were analytical grade and used as received without purification. Commercially available 30 wt%  $H_2O_2$  was purchased from Sinopharm Chemical Reagent Co., Ltd. The ionic liquid 1-octyl-3-methylimidazolium chloride ([Omim]Cl) (99%) was purchased from Shanghai Chengjie Chemical Co. Ltd.

2.1.2. Preparation of the ionic liquid 1-octyl-3-methylimidazolium copper trichloride ([Omim]CuCl<sub>3</sub>). 0.01 mol of [Omim]Cl and 0.01 mol of  $CuCl_2$  were mixed and added into a three-necked flask with stirring. The mixture was stirred at room temperature for 24 h, and then the product [Omim]CuCl<sub>3</sub> was collected and dried under a vacuum.

**2.1.3. Preparation of BiOCl.** BiOCl powder was synthesized by a one-step solvothermal method according to ref. 13. In a typical procedure, 1 mmol of  $Bi(NO_3)_3 \cdot 5H_2O$  was dissolved into an EG solution (20 mL) containing 1 mmol of ionic liquid [Omim]Cl, and the mixture was stirred for 30 min, and then transferred into 25 mL Teflon-lined autoclave up to 80% of the total volume. The autoclave was then heated at 140 °C for 24 h and cooled down to room temperature. The final product was separated by centrifugation, washed with distilled water and absolute ethanol for four times, and dried under vacuum at 50 °C for 24 h before further characterization.

2.1.4. Preparation of Cu-modified BiOCl. Cu-modified BiOCl materials were prepared in a method similar to the previously used solvothermal method. In a typical procedure, 1 mmol of  $Bi(NO_3)_3 \cdot 5H_2O$  was dissolved in an EG solution (20 mL) containing stoichiometric amounts of ionic liquid [Omim]CuCl<sub>3</sub>, and the mixture was stirred for 30 min and then transferred into 25 mL Teflon-lined autoclave up to 80% of the total volume. The autoclave was then heated at 140 °C for 24 h and cooled down to room temperature. The final product was separated by centrifugation, washed with distilled water and absolute ethanol four times, and dried under vacuum at 50 °C for 24 h before further characterization. Cu-modified BiOCl materials with different Cu modification ratios were synthesized by adding 1/3 mmol, 1 mmol, 5 mmol and 10 mmol of [Omim]CuCl<sub>3</sub>. The final products were marked as Cu/BiOCl (1:3), Cu/BiOCl (1:1), Cu/BiOCl (5:1) and Cu/BiOCl (10:1) according to the different Cu/Bi molar ratios.

#### 2.2. Characterization

X-ray powder diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity Cu-K $\alpha$  ( $\lambda = 1.54$  Å). X-ray photoelectron spectroscopy (XPS) was measured on a PHI5300 with a monochromatic Mg Ka source to explore the elements on the surface. The field-emission scanning electron microscopy (FE-SEM) measurements were carried out with a field-mission scanning electron microscope (JEOL JSM-7001F) equipped with an energy-dispersive X-ray spectroscope (EDS) which was operated at an acceleration voltage of 10 kV. Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Renishaw Invia) in a backscattering geometry with a 532 nm laser as an excitation source. The photoluminescence (PL) spectra of the samples were obtained by a QuantaMaster & TimeMaster Spectrofluorometer with an excitation wavelength at 360 nm. UV-vis diffuse reflectance spectroscopy (DRS) was recorded on an UV-2450 spectrophotometer (Shimadzu Corporation, Japan).

#### 2.3. Photocatalytic activity

Photocatalytic activities of the Cu-modified BiOCl powders were evaluated by photocatalytic degradation of MB and BPA under visible light irradiation. Experiments were carried out in a Pyrex photocatalytic reactor under 300 W Xe lamp with a 400 nm cutoff filter. Aeration was performed by using an air pump to ensure a constant supply of oxygen and to complete mixing of the solution and the photocatalyst during photoreactions. In a typical photocatalytic experiment, 10 mg and 50 mg of Cumodified BiOCl powders were dispersed into 100 mL of MB solution (10 mg  $L^{-1}$ ) and BPA solution (10 mg  $L^{-1}$ ), respectively. The suspension was strongly and magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium of pollutant on the catalyst surface. Then, about 3 mL of the suspension was taken from the reaction cell. Visible light illumination was conducted after 3 mL of H<sub>2</sub>O<sub>2</sub> (30%) was added into the suspension. During irradiation, about 3 mL of the suspension was continually taken from the reaction cell at fixed intervals. The photocatalyst powders and the MB or BPA solution were separated by centrifuge. The MB concentration was analyzed through a UV-vis spectrophotometer (UV-2450, Shimadzu) by checking the absorbance at 663 nm. For the concentration of BPA, high performance liquid chromatography (HPLC) was used to analyze the remnant amounts.

#### 2.4. HPLC Analysis

The HPLC setup was equipped with two Varian ProStar210 pumps, an Agilent TC-C (18) column, and a Varian ProStar325 UV-Vis Detector at 230 nm. A solution of methanol and H<sub>2</sub>O in the ratio 75 : 25 (v/v) was used as the mobile phase at 1 mL min<sup>-1</sup>, and 20  $\mu$ L of the sample solution was injected.

#### 2.5. Photoelectrochemical measurement

To investigate the photoelectrochemical properties of Cumodified BiOCl powders, the modified electrodes were prepared. The photocurrent measurements were carried out with an electrochemical analyzer (CHI660B, Chen Hua Instruments, Shanghai, China) in a standard three-electrode system, which employed a platinum wire as the counter electrode, a saturated Ag/AgCl electrode as the reference electrode, and a indium tin oxide (ITO) glass as the working electrode, respectively. The ITO was cut into 3 cm  $\times$  1 cm slices and successively bathed in 1 M NaOH solution for 10 min and acetone for 30 min, and then it was washed with water and dried prior to use. 10 mg of the sample was ultrasonically dispersed in 1 mL of absolute ethanol and 1 mL EG, and 20 µL of the resulting colloidal dispersion (5 mg mL<sup>-1</sup>) was then dip-coated onto a  $0.5 \times 1 \text{ cm}^2$  ITO glass electrode. The photocurrent measurements were performed at a constant potential of 0 V. A phosphate buffer solution (PBS, 0.1 M, pH 7.4) was prepared by mixing stock standard solutions of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>, and adjusting the pH with 0.1 M NaOH or H<sub>3</sub>PO<sub>4</sub>, which was used as the supporting electrolyte throughout the photoelectrochemical measurements. A 500 W Xe arc lamp was utilized as the light source for the photoelectrochemical measurement. All the electrochemical tests were carried out at room temperature under an air atmosphere.

### 3. Results and discussion

#### 3.1. Structure and morphology characterization

The XRD pattern of the as-prepared Cu/BiOCl (5 : 1) material is shown in Fig. 1. All the peaks for the samples were readily indexed to the tetragonal phase of BiOCl (JCPDS card no. 06-0249), with lattice constants of a = 3.891 Å, c = 7.369 Å. The narrow sharp peaks suggested that the Cu/BiOCl products were highly crystalline. Interestingly, the intensity ratio of the (110) peak to the (012) peak in this result of Cu-modified BiOCl microspheres structures was larger than the data of the BiOCl JCPDS card. The result indicated that the structure of Cu/BiOCl (5 : 1) crystal had special anisotropic growth along the (110) plane. However, no typical patterns of copper species were observed in Cu-modified BiOCl, which was probably due to the ions of Cu being modified on the surface of the BiOCl.



Fig. 1 The XRD pattern of the as-prepared Cu/BiOCl (5 : 1) crystals.

Therefore, in the XRD analysis, no impurity peaks were observed, which confirmed the high purity of the Cu-modified BiOCl products.

The surface chemical composition of the Cu/BiOCl (5 : 1) nanostructures is analysed by XPS spectroscopy (Fig. 2). The binding energies obtained in the XPS analysis is corrected for specimen charging by internally referring to the adventitious carbon at a binding energy of 284.6 eV. The survey XPS spectrum (Fig. 2a) shows that the Cu-modified BiOCl microspheres are composed of elements of Bi, O, Cl and Cu. The carbon peak came from the adventitious carbon and some trace of the EG in the sample. In the high-resolution spectrum (Fig. 2b), it can be seen that two strong peaks at 159.27 eV and 164.64 eV are assigned to Bi  $4f_{7/2}$  and Bi  $4f_{5/2}$ , which is characteristic of Bi<sup>3+</sup> in the Cu-modified BiOCl material. The XPS signal of Cl 2p (Fig. 2c) at a binding energy of 198.56 eV shows the characteristic of Cl<sup>-</sup> anions. The high-resolution spectrum (Fig. 2d) shows that the peak binding energy of 530.76 eV is assigned to O



Fig. 2 XPS spectra of the as-prepared Cu/BiOCl (5:1) material: (a) survey of the sample; (b) Bi 4f; (c) Cl 2p; (d) O 1s; (e) Cu 2p.

1s, which is the characteristic of  $O^{2-}$  in the Cu-modified BiOCl materials. The above results are in good agreement with the literature.<sup>37</sup> Meanwhile, Fig. 2e showed the high-resolution Cu 2p XPS spectra of the samples. The Cu 2p XPS peaks could be resolved into two typical peaks, 933.75 eV and 954.28 eV, and they were ascribed to binding energies of Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , respectively, which was due to there being Cu<sup>2+</sup> in Cu-modified BiOCl material.<sup>38</sup> Based on the XRD and XPS analyses, the Cu element existed in the form of Cu<sup>2+</sup>, and the Cu<sup>2+</sup> was distributed on the surface of BiOCl in Cu-modified BiOCl materials.

The surface morphology of the as-prepared samples was examined by scanning electron microscopy. The pure BiOCl samples have been reported in our previous work.13 The BiOCl was made up of irregular sphere-like structures, with an average diameter of 1-3 µm. There was a rugged area assembled in a scattered manner by numerous BiOCl nanosheets on the surface of every BiOCl microsphere. Fig. 3 is the SEM images of Cu/BiOCl (5:1) materials. From the SEM picture in Fig. 3a, it can be clearly seen that uniform sphere-like Cu/BiOCl hierarchical structures were formed, and the average diameter of the microspheres was 3-5 µm. After careful examination of the high-magnification SEM images (Fig. 3b) of the sample, the entire Cu/BiOCl microsphere structures were tightly assembled by numerous Cu/BiOCl nanosheets with the diameter of several nanometers. Moreover, the surface of Cu/BiOCl microsphere was regular, without rugged areas, which was different from pure BiOCl. It can be seen that metal-based ionic liquid [Omim]-CuCl<sub>3</sub> as a soft template agent played a critical role in controlling the crystal structure and morphology of the Cu/BiOCl microspheres. In our previous work,13 we proved that the ionic liquid [C<sub>16</sub>mim]Cl acted as a soft template, a capping agent and the Cl source for the synthesis of pure BiOCl. In the synthesis of Cu-modified BiOCl, metal-based ionic liquid [Omim]CuCl<sub>3</sub> not



**Fig. 3** SEM images of the Cu/BiOCl (5 : 1) microspheres structures (a) the low magnification SEM image; (b) top view SEM image; (c) EDS of the Cu/BiOCl (5 : 1) microspheres.

Energy (keV)

#### Paper

only acts as the solvent, the template and the Cl source, but also acts as the metal Cu source. Fig. 3c is the EDS pattern of Cu/BiOCl (5 : 1) materials, and it indicates that the Cu-modified BiOCl materials contain Bi, O, Cl and Cu elements, and the Si element is attributable to the Si foil. This result further proved that the as-prepared samples were Cu-modified BiOCl materials, which was consistent with the results of the XRD and XPS analyses.

The Raman spectra of the BiOCl and Cu/BiOCl (5:1) materials are shown in Fig. 4. Four Raman peaks of the BiOCl sample were observed, and among them, the peak at 113.4  $\text{cm}^{-1}$  was featured with broad full width half maximum (FWHM), and it could not be ascribed to any ordinary Raman bands of BiOCl and silicon reasonably.<sup>39</sup> The peaks at 143.3 cm<sup>-1</sup>, 197.3 cm<sup>-1</sup> and 396 cm<sup>-1</sup> were the characteristic peaks of BiOCl, which could be ascribed to three different Raman modes of BiOCl.40 The band at 143.3  $\text{cm}^{-1}$  was attributed to  $A_{1g}$  internal Bi–Cl stretching mode and the band at 197.3 cm<sup>-1</sup> was assigned to  $E_{1g}$ internal Bi-Cl stretching mode.<sup>39</sup> In addition, there was a broad weak band at 396 cm<sup>-1</sup>, which was attributed to the  $E_g$  and  $B_{1g}$ modes involving the motion of the oxygen atoms.<sup>41</sup> For Cu-modified BiOCl materials, the peak at 113.4 cm<sup>-1</sup> disappeared, the two peaks at 199.2 cm<sup>-1</sup> and 397.9 cm<sup>-1</sup> had a little blue-shift when compared with those of pure BiOCl, which was attributed to the laser-induced compressive stress in the BiOCl film.<sup>41</sup> In general, the disappearance of the Raman peak  $(113.4 \text{ cm}^{-1})$  and the blue-shift indicated that the modified Cu<sup>2+</sup> had interacted with the BiOCl crystal, and the modification of Cu<sup>2+</sup> had changed the properties of the BiOCl nanostructure. The composition of the Cu/BiOCl materials was further examined by FT-IR spectroscopy. As shown in Fig. S1,† it could be seen that the absorption band of pure BiOCl at 528 cm<sup>-1</sup> was ascribed to the Bi-O stretching mode. For the Cu/BiOCl (5:1), it can be observed that a little shift of the 528 cm<sup>-1</sup> characteristic peak happened, which further confirms that there is an intense interaction between the Cu<sup>2+</sup> and BiOCl materials. As shown in the FT-IR that, no characteristic absorption peaks of the ionic liquid are found in the FT-IR spectra. This shows the ionic liquid could be easily removed from the surface of the material by washing with water and alcohol.

#### 3.2. Photoelectrochemical properties

As we all know, the separation efficiency of electrons and holes plays a key role in the photocatalytic reaction: the better the electron and hole separation efficiency is, the higher the photocatalytic activity would be.<sup>42,43</sup> The photocurrent is from the photo-generated electrons in the conducting bands of a semiconductor photocatalyst when the semiconductor is excited by visible light irradiation. Hence, the photocurrent test of a semiconductor can be used to evaluate the separation efficiency of electrons and holes. The transient photocurrent responses of BiOCl and Cu/BiOCl material electrodes are recorded for several on-off cycles of visible light irradiation, as is shown in Fig. 5. Upon light illumination, the photocurrent increases sharply reaching a steady state quickly. When the light is turned off, the current returns quickly to its dark current state. The Cu-modified BiOCl samples have higher currents than that of the pure BiOCl. Moreover, the photocurrent responses of Cu-modified BiOCl samples increase gradually with the amount of Cu<sup>2+</sup> from 1:3 to 5:1 (Cu/Bi molar ratios) and then the photocurrent begins to decline. The above analysis revealed that the Cumodified BiOCl materials could effectively reduce the recombination of photo-generated electrons and holes, and produce longer living photo-generated carriers. Therefore, the Cumodified BiOCl materials were expected to exhibit an improved photocatalytic activity for organic pollutant degradation.

#### 3.3. Photoluminescence spectra analysis

It is well known that the semiconductor can be excited to produce photo-generated electrons and holes when the energy of the incident photons matches or exceeds the bandgap.<sup>1,44</sup> Some electrons and holes recombine on the surface or inside of the semiconductor, dissipating the input energy in the form of heat or emitted light, and then the fluorescence is generated. So, the stronger the fluorescence emission intensity is, the



Fig. 4 Raman spectra of BiOCl and Cu/BiOCl (5 : 1) photocatalysts.



Fig. 5 Transient photocurrent responses of BiOCl and Cu/BiOCl photocatalysts.

higher the recombination rate of the photo-generated carriers will be.45,46 Fig. 6 shows the photoluminescence spectra of the pure BiOCl and Cu/BiOCl (5:1) materials excited by 360 nm irradiation. It could be found that the main emission peak was centered at about 468 nm for the pure BiOCl sample. For Cu-modified BiOCl materials, the position of the emission peak in the PL spectrum was similar to that of the pure BiOCl, but the emission intensity decreased, which indicated that the Cu/BiOCl (5:1) materials had a much lower recombination rate of photo-generated charge carriers. This demonstrated that the recombination of photo-generated charge carriers was greatly inhibited by the introduction of Cu<sup>2+</sup>, which showed the photogenerated electrons and holes in the Cu/BiOCl (5:1) materials had higher separation efficiency than those in the pure BiOCl. This result also indicated that the Cu-modified BiOCl materials were expected to exhibit an improved photocatalytic activity for organic pollutant degradation.

#### 3.4. Influence of the amount of the ionic liquid

In order to investigate the influence of the amount of the ionic liquid, the XRD and SEM analyses of the as-prepared samples with different Cu/Bi molar ratios were conducted. Fig. 7 shows the XRD patterns of Cu/BiOCl (1 : 3), Cu/BiOCl (1 : 1) and Cu/BiOCl (10 : 1) materials. It could be seen that all the peaks for the three samples were readily indexed to the tetragonal phase of BiOCl (JCPDS card no. 06-0249), with lattice constants of a = 3.891 Å, c = 7.369 Å. No impurity could be detected from these patterns of BiOCl. This indicated that well-crystallized BiOCl could be easily obtained under the current synthetic conditions. The structures of the three Cu/BiOCl crystals also had special anisotropic growth along the (110) plane like the Cu/BiOCl (5 : 1) materials. No any diffraction peaks of copper species were observed in the three Cu-modified BiOCl materials because of the Cu<sup>2+</sup> was modified on the surface of the BiOCl.

The SEM images of the Cu/BiOCl (1:1) material are shown in Fig. 8. As can be seen from Fig. 8a and b, the Cu/BiOCl (1:1)material had a uniform sphere-like architecture with diameters



Fig. 7 XRD patterns of Cu/BiOCl samples with different Cu contents.

of approximately 2-5 µm. The high-magnification SEM image (Fig. 8c) showed that the surface of the Cu/BiOCl (1:1) microspheres was smooth and there was no evidence for the presence of nanosheets, which was different from the Cu/BiOCl (5:1) material. EDS analysis shows that the sample are composed of Bi, O, Cl and Cu elements (Fig. 8d). Fig. 9 displays the SEM images of the as-synthesized Cu/BiOCl (10:1) sample. It could be seen that the morphology of the sample was that of a clusterlike structure assembled by scattered nanosheets, which could not form the sphere-like architecture. The EDS analysis on the Cu/BiOCl (10:1) microspheres (Fig. 9d) suggested that the sample only contained the elements of Bi, O, Cl and Cu. From the SEM images of different materials, it could be found that microspheres with smooth surface were formed when a small amount of the ionic liquid was added; when the amount of the ionic liquid was increased, the surface of the microspheres became a flower-like hierarchical structure; with the amount of



Fig. 6 PL spectra of the pure BiOCl and Cu/BiOCl (5 : 1) materials.



Fig. 8 SEM images of the Cu/BiOCl (1:1) microspheres structures. (a) The low magnification SEM image; (b) the high magnification SEM image; (c) top view SEM image; (d) EDS of the Cu/BiOCl (1:1) microspheres.



Fig. 9 The SEM images (a–c) and EDS (d) of the as-prepared Cu/BiOCI (10 : 1) crystals.

the ionic liquid further increased, sphere-like architecture could not be formed, and a cluster-like structure was formed. It revealed that the amount of the ionic liquid played an important role in the morphology of the products. Furthermore, it could be predicted that the Cu/BiOCl (5:1) sample may has the highest photocatalytic activity because the specific surface area of the Cu/BiOCl (5:1) material was large, which could form more active sites in photocatalytic reaction and then enhance the photocatalytic activity.

#### 3.5. UV-vis diffuse reflectance spectra

The UV-vis diffuse reflectance spectra (DRS) of the Cu/BiOCl samples with different Cu contents are shown in Fig. 10. It was apparent that the absorption edge of the pure BiOCl was about 370 nm. The  $Cu^{2+}$  modification effectively increased the absorption in the visible light region. The colour of BiOCl is white, and the colour of Cu–BiOCl is green. The light absorption



Fig. 10 UV-vis diffuse absorption spectra of Cu/BiOCl samples with different Cu contents.

in the visible light region resulted from the introduction of  $Cu^{2+}$ . Especially in the absorption with wavelengths higher than about 550 nm, the optical absorption intensity showed a large increase. This suggested that the Cu-modified BiOCl samples should have better photoactivity than the pure BiOCl. The band gap of the powders, calculated by means of Kubelka–Munk theory, has been presented (Fig. S2†). As Fig. S2† shows, the Cu-modified BiOCl samples have a smaller band gap than BiOCl. The lower band gaps facilitate the electronic transition.

#### 3.6. Photocatalytic activity

 $H_2O_2$  is a strong oxidizing agent, and it can be decomposed into H<sub>2</sub>O and O<sub>2</sub>, which will not cause secondary pollution when used in water treatment. Many metal ions, such as Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  etc., can catalyze the decomposition of  $H_2O_2$  to produce hydroxyl radicals ('OH). Hydroxyl radicals are a kind of non-selective strong oxidants, which can degrade a variety of organic pollutants to generate CO<sub>2</sub> and H<sub>2</sub>O. Therefore, to investigate the photocatalytic activity of Cu-modified BiOCl materials for degradation of methylene blue (MB), H<sub>2</sub>O<sub>2</sub> was employed in the photocatalytic experiment. Fig. 11a shows the photocatalytic activity of the BiOCl and Cu-modified BiOCl materials with different contents of Cu under visible light irradiation. Blank tests were made to eliminate interference: (a) the direct photolysis of MB with H<sub>2</sub>O<sub>2</sub> in the absence of the photocatalyst; (b) degradation of MB with the Cu/BiOCl (5:1) samples and  $H_2O_2$  in the absence of visible light. As can be seen from Fig. 11, both blank tests showed low photocatalytic activity. It indicated that light illumination was essential for photocatalytic reaction. The degradation of MB with H<sub>2</sub>O<sub>2</sub> was low. After pure BiOCl was added, the activity was slightly improved, about 44% of MB was degraded for 75 min. However, when the BiOCl samples were modified by Cu<sup>2+</sup>, the photocatalytic activity was significantly increased. After 75 min of visible light irradiation, the photocatalytic degradation efficiency of MB was about 98%, 96%, 100% and 93% for Cu/BiOCl (1:3), Cu/BiOCl (1:1), Cu/ BiOCl (5:1) and Cu/BiOCl (10:1), respectively. Among them, the Cu/BiOCl (5:1) samples displayed the highest efficient photocatalytic activity, in which all of MB was degraded under visible light irradiation within 45 min.

Fig. 11b shows the time-dependent absorption spectra of MB solution in the presence of the Cu/BiOCl (5 : 1) samples. Under visible light illumination, with the Cu/BiOCl (5 : 1) materials, the color of MB solution changed from blue to light blue and then disappeared during the reaction. The peak intensity of the UV-vis absorption related to MB decreased sharply, and the main absorption band at 663 nm almost completely disappeared after 45 min, which indicated the chromophoric structure of the MB dye was decomposed.

In order to rule out the photosensitization of the Cu/BiOCl photocatalyst in the photodegradation process, BPA was chosen as a representative colourless model organic pollutant. Fig. S3<sup>†</sup> shows the photocatalytic degradation of BPA in the presence of BiOCl and Cu/BiOCl (5:1) under visible light irradiation with or without 3 mL H<sub>2</sub>O<sub>2</sub>. When no H<sub>2</sub>O<sub>2</sub> was added, both the BiOCl and Cu/BiOCl (5:1) exhibit poor photocatalytic activity for the



Fig. 11 (a) Effects of Cu/BiOCl with different Cu contents on MB degradation efficiency; (b) temporal UV-vis absorption spectral changes during the photocatalytic degradation of MB in aqueous solution.

degradation of BPA. When the  $H_2O_2$  was added, the photocatalytic activity of photocatalysts improved. It can be seen that the Cu/BiOCl (5 : 1) sample exhibits significantly higher photocatalytic activity than pure BiOCl sample. The introduction of  $Cu^{2+}$  is beneficial to improve the photocatalytic activity.

To confirm the stability of the Cu/BiOCl sample, the XRD of the Cu/BiOCl (5 : 1) sample before and after the photoreaction has been compared. The XRD patterns were performed to determine the structural variations of the sample. The results reveal that the crystal structures of the Cu/BiOCl sample do not change after the photocatalytic reaction (Fig. S4†). These results indicate that the Cu/BiOCl sample has excellent stability for photocatalytic degradation of BPA.

#### 3.7. The proposed mechanism

In the photocatalytic activity analysis of the samples, it was confirmed that the Cu-modified BiOCl could significantly enhance the photocatalytic degradation efficiency. Generally speaking, the photocatalytic activity of catalysts depends on

many factors, such as crystallinity, surface properties, morphology, optical properties, and size.47 According to the XRD and SEM analysis, the crystal structure was not changed, which had little effect on improving the photocatalytic activity. However, the morphology of the Cu-modified BiOCl materials was regular, and more pollutant molecules could be adsorbed on the surface of the Cu-modified BiOCl microspheres. The photocatalytic reaction involves two processes: the adsorption process and photocatalytic degradation process after adsorption. Therefore, the stronger the adsorption capacity was, the better the subsequent photocatalytic degradation reaction would be. The nitrogen adsorption and desorption isotherm analysis (Fig. S5<sup>†</sup>) was carried out to characterize the specific surface areas of Cu/BiOCl (5:1) and pure BiOCl.13 The BET specific surface area of Cu/BiOCl (5:1) and BiOCl was calculated to be 36.6  $m^2\ g^{-1}$  and 16.1  $m^2\ g^{-1},^{13}$  respectively. It is known that materials with larger specific surface areas can absorb more active species and reactants on their surfaces. The results indicate that the introduction of Cu<sup>2+</sup> exaggerates the BET surface area which is beneficial to the improvement of photocatalytic activity. The DRS analysis suggested that Cu2+ modification effectively increased the absorption in the visible light region. This meant that the Cu-modified BiOCl could absorb more photons under the same light illumination conditions, and thus the photocatalytic activity could be enhanced.

Recently, many researchers suggested that the modified  $Cu^{2+}$  was the capture center of photo-generated electrons, which can reduce the recombination rate of photo-generated charge carriers.<sup>48,49</sup> For the Cu-modified BiOCl materials, the modified  $Cu^{2+}$  can improve the inner charge transfer rate, while it can effectively prevent the recombination of photo-generated electrons and holes, and then the subsequent reaction can be promoted. Moreover, the outer electron structure of  $Cu^{2+}$  is  $3d^94s^0$ , which can turn into a more stable fully charged state  $Cu^+$  with a  $3d^{10}4s^0$  structure. In this way,  $Cu^{2+}$  is combined with electrons to increase the separation efficiency of photo-generated electrons and holes. Alternately, the simultaneous redox process of trapping electrons in the  $Cu^{2+}$  states leads to  $Cu^+$  in the following reaction:

$$Cu^{2+} + e^{-} \rightarrow Cu^{+} \tag{1}$$

$$H_2O_2 + Cu^+ \to OH^- + OH^+ + Cu^{2+}$$
 (2)

During the photo-Fenton process, more and more 'OH radicals will be formed, and finally the pollutants will be directly oxidized in the aqueous solution by the active species.<sup>50,51</sup> The XPS of the Cu/BiOCl (5 : 1) after the photoreaction was shown in Fig. S6.† The peaks at 932.4 eV and 952.3 eV indicate the presence of Cu<sup>+</sup> as previously reported by others<sup>52–54</sup> whereas the existence of peaks at 934.7 eV and 954.9 eV can be attributed to the presence of Cu<sup>2+</sup>.<sup>53,55</sup> The XPS analysis further certifies the photo-Fenton process mentioned above. However, the photocatalytic activity will be reduced when the amount of modified Cu<sup>2+</sup> is excessive. This is because of the excessive Cu<sup>2+</sup> consumes a large amount of electrons, on the other hand, photo-generated electrons and holes can recombine through

the modified Cu<sup>2+</sup> on the surface of the BiOCl microspheres. At the same time, the existing literature studies show that the introduction of metal ion could cause oxygen vacancies in the BiOCl crystals and the oxygen vacancies are stable and energetically favorable within BiOCl.48,49,56-58 Therefore, it can be inferred that the introduction of Cu2+ could cause oxygen vacancies in BiOCl crystals. The occurrence of an oxygen vacancy in the BiOCl crystal significantly influences the neighboring Bi 6p states, forming a capture center of photo-excited electrons in the forbidden band, which enhances the efficient mobility of photo-generated carriers and improves the effective separation rate of electron-hole pairs.56-58 The enhanced separation rate of electron-hole pairs is beneficial to the Cu<sup>2+</sup> combines with electrons to form Cu<sup>+</sup>, which accelerates the photo-Fenton process. As is shown in (Fig. S3 and S8<sup>†</sup>), the Cu/BiOCl have a little higher photocatalytic activity than BiOCl when no H<sub>2</sub>O<sub>2</sub> was added, which indicates the generated oxygen vacancy improves the separation rate of electron-hole pairs and further enhances the photocatalytic activity. However, the photocatalytic activity of the Cu/BiOCl had a significant improvement than pure BiOCl when H2O2 was added, which indicates the synergetic effect of generated oxygen vacancy and photo-Fenton process during the photodegradation. Based on the above analysis, it can be concluded that the enhanced photocatalytic activity of Cu-modified BiOCl microspheres can be due to synergetic effects, including a large adsorption capacity, a broad light absorption band and a high separation efficiency of photo-generated electrons and holes.

### 4. Conclusions

Visible-light-driven Cu-modified BiOCl materials were synthesized by using a Cu-based ionic liquid as the solvent, the template, the Cl source and the Cu source. The metal copper was evenly distributed on the surface of the BiOCl microspheres in the form of  $Cu^{2+}$ . It was possible to tune the morphology of Cu-modified BiOCl materials by varying the amount of the ionic liquid. The high photocurrent and low PL intensity indicated that the Cu-modified BiOCl materials could effectively reduce the recombination of photo-generated electrons and holes. Cu<sup>2+</sup> modification effectively increased the absorption in the visible light region. The as-prepared Cu-modified BiOCl materials displayed an enhancement of photocatalytic activity, which was greatly improved in comparison with the pure BiOCl. In summary, the high photocatalytic activity of the Cu-modified BiOCl materials could be attributed to the large adsorption capacity, broad light absorption band and high separation efficiency of photo-generated electrons and holes.

## Acknowledgements

This work was financially supported by the National Nature Science Foundation of China (no. 21206060, 21007021 and 21177050), Jiangsu Province (1102118C), and the Special Financial Grant from the China Postdoctoral Science Foundation (2013T60506).

## References

- 1 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
- 2 R. M. Alberici and W. F. Jardim, Appl. Catal., B, 1997, 14, 55.
- 3 M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis,B. J. Marinas and A. M. Mayes, *Nature*, 2008, 452, 301.
- 4 L. F. Zhang, T. Kanki, N. Sano and A. Toyoda, *Sep. Purif. Technol.*, 2003, **31**, 105.
- 5 F. Spadavecchia, G. Cappelletti, S. Ardizzone, C. L. Bianchi,
  S. Cappelli, C. Oliva, P. Scardi, M. Leoni and P. Fermo, *Appl. Catal.*, B, 2010, 96, 314.
- 6 J. H. Chen, M. S. Yao and X. L. Wang, *J. Nanopart. Res.*, 2008, **10**, 163.
- 7 L. Pan, J. J. Zou, X. W. Zhang and L. Wang, *Ind. Eng. Chem. Res.*, 2010, **49**, 8526.
- 8 D. V. Bavykin, A. A. Lapkin, P. K. Plucinski, L. Torrente-Murciano, J. M. Friedrich and F. C. Walsh, *Top. Catal.*, 2006, **39**, 151.
- 9 W. T. Sun, Y. Yu, H. Y. Pan, X. F. Gao, Q. Chen and L. M. Peng, J. Am. Chem. Soc., 2008, 130, 1124.
- 10 L. W. Zhang, Y. J. Wang, H. Y. Cheng, W. Q. Yao and Y. F. Zhu, *Adv. Mater.*, 2009, 2, 1286.
- 11 J. X. Xia, S. Yin, H. M. Li, H. Xu, Y. S. Yan and Q. Zhang, *Langmuir*, 2011, 27, 1200.
- 12 J. X. Xia, S. Yin, H. M. Li, H. Xu, L. Xu and Y. G. Xu, *Dalton Trans.*, 2011, **40**, 5249.
- 13 J. X. Xia, J. Zhang, S. Yin, H. M. Li, H. Xu, L. Xu and Q. Zhang, *J. Phys. Chem. Solids*, 2013, **74**, 298.
- 14 M. S. Zhu, P. L. Chen and M. H. Liu, *Prog. Chem.*, 2013, 25, 209.
- 15 J. Lv, T. Kako, Z. G. Zou and J. H. Ye, J. Mater. Res., 2010, 25, 159.
- 16 X. X. Hu and C. Hu, J. Solid State Chem., 2007, 180, 725.
- 17 S. S. Dunkle, R. J. Helmich and K. S. Suslick, *J. Phys. Chem. C*, 2009, **113**, 11980.
- 18 J. Henle, P. Simon, A. Frenzel, S. Scholz and S. Kaskel, *Chem. Mater.*, 2007, **19**, 366.
- 19 X. Zhang, Z. H. Ai, F. L. Jia and L. Z. Zhang, *J. Phys. Chem. C*, 2008, **112**, 747.
- 20 X. F. Chang, G. Yu, J. Huang, Z. Li, S. F. Zhu, P. F. Yu, C. Cheng, S. B. Deng and G. B. Ji, *Catal. Today*, 2010, 153, 193.
- 21 F. D. Gao, D. W. Zeng, Q. W. Huang, S. Q. Tian and C. S. Xie, *Phys. Chem. Chem. Phys.*, 2012, **14**, 10572.
- 22 S. Sun, J. J. Ding, J. Bao, C. Gao, Z. M. Qi, X. Y. Yang, B. He and C. X. Li, *Appl. Surf. Sci.*, 2012, **258**, 5031.
- 23 J. Choi, H. Park and M. R. Hoffmann, *J. Phys. Chem. C*, 2010, **114**, 783.
- 24 X. X. Yang, C. D. Cao, L. Erickson, K. Hohn, R. Maghirang and K. Klabunde, *Appl. Catal., B*, 2009, **91**, 657.
- 25 J. A. Dahl, B. L. S. Maddux and J. E. Hutchison, *Chem. Rev.*, 2007, **107**, 2228.
- 26 Z. Ma, J. H. Yu and S. Dai, Adv. Mater., 2010, 22, 261.
- 27 K. L. Ding, Z. J. Miao, Z. M. Liu, Z. F. Zhang, B. X. Han, G. M. An, S. D. Miao and Y. Xie, *J. Am. Chem. Soc.*, 2007, 129, 6362.

- 28 I. Yavari, A. R. Mahjoub, E. Kowsari and M. Movahedi, J. Nanopart. Res., 2009, 11, 861.
- 29 Y. Jiang and Y. J. Zhu, J. Phys. Chem. B, 2005, 109, 4361.
- 30 Y. Sun and W. J. Zheng, Dalton Trans., 2010, 39, 7098.
- 31 J. Y. Kim, J. T. Kim, E. A. Song, Y. K. Min and H. Hamaguchi, *Macromolecules*, 2008, **41**, 2886.
- 32 H. Wang, R. Y. Yan, Z. X. Li, X. P. Zhang and S. J. Zhang, *Catal. Commun.*, 2010, **11**, 763.
- 33 K. Bica and P. Gaertner, Org. Lett., 2006, 8, 733.
- 34 D. H. Yin, C. Z. Li, L. Tao, N. Y. Yu, S. Hu and D. L. Yin, *J. Mol. Catal. A: Chem.*, 2006, **245**, 260.
- 35 J. G. Li, Y. F. Hu, S. F. Sun, S. Ling and J. Z. Zhang, *J. Phys. Chem. B*, 2012, **116**, 6461.
- 36 A. Taubert, Angew. Chem., Int. Ed., 2004, 43, 5380.
- 37 J. Zhang, J. X. Xia, S. Yin, H. M. Li, H. Xu, M. Q. He, L. Y. Huang and Q. Zhang, *Colloids Surf.*, *A*, 2013, **420**, 89.
- 38 W. D. Shi, J. Q. Shi, S. Yu and P. Liu, *Appl. Catal., B*, 2013, **138**, 184.
- 39 Y. Tian, C. F. Guo, Y. J. Guo, Q. Wang and Q. Liu, *Appl. Surf. Sci.*, 2012, **258**, 1949.
- 40 W. G. Fateley, N. T. Mcdecitt and F. F. Bentley, *Appl. Spectrosc.*, 1971, 25, 155.
- 41 S. H. Cao, C. F. Guo, Y. Lv, Y. J. Guo and Q. Liu, *Nanotechnology*, 2009, 20, 275702.
- 42 J. Di, J. X. Xia, S. Yin, H. Xu, L. Xu, Y. G. Xu, M. Q. He and H. M. Li, *J. Mater. Chem. A*, 2014, DOI: 10.1039/c3ta14617k.
- 43 Q. J. Xiang, J. G. Yu and M. Jaroniec, *J. Phys. Chem. C*, 2011, 115, 7355.
- 44 M. A. Fox and M. T. Dulay, Chem. Rev., 1993, 93, 341.

- 45 J. Di, J. X. Xia, S. Yin, H. Xu, M. Q. He, H. M. Li, L. Xu and Y. P. Jiang, *RSC Adv.*, 2013, **3**, 19624.
- 46 H. Xu, J. Yan, Y. G. Xu, Y. H. Song, H. M. Li, J. X. Xia, C. J. Huang and H. L. Wan, *Appl. Catal.*, B, 2013, **129**, 182.
- 47 I. S. Cho, S. Lee, J. H. Noh, G. K. Choi, H. S. Jung, D. W. Kim and K. S. Hong, *J. Phys. Chem. C*, 2008, **112**, 18393.
- 48 H. W. P. Carvalho, M. V. J. Rocha, P. Hammer and T. C. Ramalho, *J. Mater. Sci.*, 2013, **48**, 3904.
- 49 B. F. Xin, P. Wang, D. D. Ding, J. Liu, Z. Y. Ren and H. G. Fu, *Appl. Surf. Sci.*, 2008, **254**, 2569.
- 50 H. W. P. Carvalho, A. P. L. Batista, P. Hammer and T. C. Ramalho, *J. Hazard. Mater.*, 2010, **184**, 273.
- 51 A. N. Pham, G. W. Xing, C. J. Miller and T. D. Waite, *J. Catal.*, 2013, **301**, 54.
- 52 S. W. Zou, C. W. How and J. P. Chen, *Ind. Eng. Chem. Res.*, 2007, **46**, 6566.
- 53 D. Spasiano, L. D. P. Rodriguez, J. C. Olleros, S. Malato, R. Marotta and R. Andreozzi, *Appl. Catal.*, B, 2013, 136– 137, 56.
- 54 C. C. Chusuei, M. A. Brookshier and D. W. Goodman, *Langmuir*, 1999, **15**, 2806.
- 55 S. P. Xu, J. W. Ng, A. J. Du, J. C. Liu and D. D. Sun, *Int. J. Hydrogen Energy*, 2011, **36**, 6538.
- 56 X. C. Zhang, C. M. Fan, Y. W. Wang, Y. F. Wang, Z. H. Liang and P. D. Han, *Comput. Mater. Sci.*, 2013, 71, 135.
- 57 J. Jiang, L. Z. Zhang, H. Li, W. W. He and J. J. Yin, *Nanoscale*, 2013, 5, 10573.
- 58 H. J. Zhang, L. Liu and Z. Zhou, *Phys. Chem. Chem. Phys.*, 2012, 14, 1286.