

Cite this: *RSC Adv.*, 2017, 7, 52218

A novel strategy to promote photo-oxidative and reductive abilities *via* the construction of a bipolar $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ material†

Huayu Gu,^a Guanjie Xing,^b Huimin Gu,^a Zhanli Chai^a and Xiaojing Wang^{ID} ^{*,a}

Focusing on holistically promoting both photo-oxidative and reductive abilities, we constructed a novel $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ composite, which was expected to have excellent properties for the removal of complicated contaminants from solution environments under visible light irradiation. The prepared $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ was assembled from massive N-SrTiO₃ nanoballs segmented *via* 2D interlaced nanosheets of Bi_2WO_6 . N-SrTiO₃ on its own has good reductive ability and can easily reduce Cr(VI) ions, while Bi_2WO_6 has been demonstrated to have good oxidative ability to oxidize tetracycline under visible light irradiation. Importantly, mixed contaminants (TC and Cr⁶⁺ ions) could be completely removed under visible light by the assembled $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ material. It is proposed that the holes lying at the valence band of N-SrTiO₃ are the main active species for the oxidation of tetracycline, while the electrons located at the conduction band of Bi_2WO_6 are mainly responsible for the reduction of Cr(VI) ions. The matched band structures of Bi_2WO_6 and N-SrTiO₃ were beneficial for inhibiting the recombination of electron-hole pairs and maintaining the redox capacity through a Z-type n-n heterojunction. Such a bipolar design of photo-oxidative and photo-reductive semiconductor nanomaterials is concluded to be highly effective in remediating complicated toxic residual constituents of both unfixed pharmaceuticals and heavy metals in aquatic environments.

Received 4th October 2017
Accepted 30th October 2017

DOI: 10.1039/c7ra10932f

rsc.li/rsc-advances

Introduction

Pollutants at low concentration but of high toxicity, such as antibiotic residues or heavy metal ions, have been increasingly found over recent years in aqueous environments and have been a subject of special concern.^{1–3} They are potentially dangerous to ecosystems, and especially to human health, through drinking water and the food chain.^{4,5} For example, many antibiotics can easily enter into the environment because of their poor absorption, low metabolism, abuse and overuse. The main issues lie in the large variety and quantities of both antibiotics and their intermediates present in the environment, which makes their remediation more difficult.^{6,7} Aqueous heavy metal ions, being a common component of industrial waste with notoriously toxic, mutagenic and carcinogenic properties, could also lead to the deterioration of environmental quality and pose an acute threat to human health.^{8–10} To summarize, the complexity of pollutants in water effluents means that it is imperative to develop an efficient technique that can

simultaneously remove these residual antibiotics and heavy metals, rather than any single component.^{11,12}

The semiconductor photocatalytic removal of toxic pollutants is considered to be the most promising strategy applicable, with the advantages of low cost, no secondary pollution, low energy consumption and environmental friendliness *via* the utilization of solar light.^{13,14} Most of the photocatalytic systems only focus on a single function, either oxidative degradation or reductive elimination. However, in terms of practicality, the complexity of the pollutants that need to be removed inevitably leads to high requirements for photocatalysts with both outstanding oxidation and reduction properties. Therefore, there is an urgent need to find novel materials with excellent performance to completely eliminate mixed toxic residuals. Energetics dictates that for a semiconductor to be photochemically active, the oxidative potential of the photogenerated hole in the valence band must be sufficiently positive and the reductive potential of the conduction band electron must be sufficiently negative.¹⁵ Although a single semiconductor with a big enough band gap may exhibit special redox abilities, the wide visible light response has inevitably to be sacrificed.^{16,17} Another restriction in semiconductor photocatalysis is the relatively low value of the overall quantum efficiency, mainly due to the high recombination rate of photo-excited electron-hole pairs. To address these issues, the appropriate assembly of constituent semiconductors is believed to be one of the most

^aSchool of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, Inner Mongolia, 010021, P. R. China. E-mail: wang_xiao_jing@hotmail.com

^bSchool of Chemistry, Beijing Normal University, Beijing, 100875, P. R. China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra10932f



efficient strategies.^{18,19} The electron-hole separation could be well enhanced by transferring electrons from a material with a high Fermi level to another material with a low Fermi level when they contact each other. Unfortunately, the oxidative potentials (and/or reductive potentials) are bound to increase (and/or decrease) to establish a thermodynamic equilibrium with the same Fermi level of the semiconductors at the interface.^{20,21} Thereby, at present, uniting a broad spectrum of redox capabilities, visible light response, and recycling stability for composite fabrication is a still crucial challenge.

Strontium titanate (STO) has been used as one type of highly efficient photocatalyst, due to its outstanding optical and electrical performance, good conductivity and remarkable photochemical stability.²² SrTiO₃ is a semiconductor with a wide band gap and its conductive band potential is about −0.4 eV, indicating its good reductive properties.^{23,24} Through nitrogen doping (N-SrTiO₃), its disadvantage of a narrower adsorption region of the solar light spectrum was significantly improved.²⁵ It has been well proven that N-SrTiO₃ can efficiently reduce Cr(VI) ions under visible light. However, the recombination rate of the photoinduced electron-hole pairs in N-SrTiO₃ was faster than surface reductive reactions, leading to its deactivation after a few cycles. Moreover, the performance of N-SrTiO₃ for the oxidation of organic pollutants is still far from satisfactory. On the other hand, Bi-based semiconductor materials, such as Bi₂O₃, Bi₄Ti₃O₁₂, Bi₂WO₆, and Bi₂MoO₆, as novel kinds of photocatalysts have attracted much attention because of their layer structures and excellent catalytic properties. In particular, n-type semiconductor bismuth tungstate (Bi₂WO₆), with a valence band (VB) potential of 2.94 eV and a conduction band (CB) potential of 0.24 eV, is most interesting as a visible-light-responsive photocatalyst for the oxidative degradation of organic pollutants, owing to its excellent oxidation ability.^{26–29} According to a recent report from Zhou *et al.*,³⁰ monolayer Bi₂WO₆ with a sandwich substructure serves as a layered heterojunction with holes generated on its active surface layer, leading to outstanding photocatalytic oxidative performance with good separation of electron-hole pairs. Huang *et al.*³¹ also found that under visible light irradiation, Bi₂WO₆ could exhibit obvious photo-oxidative activity in pollutant degradation. A disadvantage of this nanomaterial is its poor reductive ability, due to the small negative potential of the conduction band.

In terms of their individual characteristics, the skilful incorporation of N-SrTiO₃ and Bi₂WO₆ may produce enhanced redox ability under visible light irradiation and efficiently accelerate electron-hole pair separation due to their matched band structure. In this work, a series of n-n heterojunctions of Bi₂WO₆/N-SrTiO₃ were successfully prepared through a two-step hydrothermal method. The removal rate of tetracycline, as a model sample for photocatalytic oxidation over the samples, was tested, while Cr(VI) ions were used as a model for the reductive ability. The redox abilities were further evaluated by simultaneous tetracycline oxidation and Cr(VI) ion reduction under visible light irradiation. Finally, a possible mechanism for the removal of mixed pollutants over Bi₂WO₆/N-SrTiO₃ was proposed.

Experimental

Material preparation and characterization

Preparation of N-SrTiO₃. The reagents were all analytical grade and used without further purification. N-SrTiO₃ powder was prepared using a hydrothermal method. The detailed procedure was provided in our previous work.²⁵

Preparation of Bi₂WO₆/N-SrTiO₃. Bi₂WO₆/N-SrTiO₃ powder was prepared using a hydrothermal method. A certain amount of Bi(NO₃)₃·5H₂O was dissolved in 17 mL of deionized water, and Na₂WO₄·2H₂O was added to the above solution according to a molar ratio of 2 : 1. Then, 1 mL of HNO₃ (1 mol L^{−1}) was further added to the above mixture under magnetic stirring. Afterward, a certain amount of N-SrTiO₃ was added to the solution and stirring was continued for another 30 min. After that, the mixture was transferred into a Teflon-lined autoclave. The autoclave was sealed and maintained at 150 °C for 24 h. After cooling to room temperature in air naturally, the mixture was centrifuged and washed with distilled water and ethanol several times and then dried in air at 60 °C.³² The mass ratio of Bi₂WO₆ to N-SrTiO₃ was set as 5, 8, 10, 15, and 20%, and the obtained samples were correspondingly labelled as Bi₂WO₆/NSTO5, Bi₂WO₆/NSTO8, Bi₂WO₆/NSTO10, Bi₂WO₆/NSTO15 and Bi₂WO₆/NSTO20, respectively.

Characterization. The phase structures and particle sizes of all of the as-prepared samples were characterized by X-ray power diffraction (XRD, PANalytical Empyrean) with a copper gun. Samples morphologies were obtained using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) on a HITACHI S-4800 apparatus and a Tecnai G2F20S-TWIN apparatus with an acceleration voltage of 200 kV, respectively. A Perkin Elmer IR spectrometer was used to measure the frequencies of vibrations of surface groups of the as-prepared samples. The specific surface areas were determined from the nitrogen absorption data at liquid nitrogen temperature using the Barrett-Emmett-Teller (BET) technique on a Micromeritics ASAP 2000 Surface Area and Porosity Analyzer. Energy dispersive X-ray energy spectroscopy (EDS) was performed at an acceleration voltage of 20 kV on a HITACHI S-4800 apparatus. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo ESCALAB 250 with Al K α (1486.6 eV) line at 150 W. To compensate for surface charge effects, the binding energies were calibrated using the C 1s peak at 284.60 eV as a reference. A diffusive reflectance UV-vis spectrophotometer (UVIKON XL/XS) was used to measure the diffuse reflectance spectra of the samples. BaSO₄ was taken as a reference, and the spectra were recorded in the range of 190–800 nm. The band gap of the samples was estimated from the onset of the absorption using the formula E_g (eV) = 1240/ λ_g (nm). Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode cell with a working electrode, platinum wire as a counter electrode, and Ag/AgCl in saturated KCl as a reference electrode. Electrochemical impedance spectroscopy (EIS) was carried out at the open circuit potential. The



amplitude of the sinusoidal wave was 5 mV, and frequency range was from 100 kHz to 0.1 Hz. During all measurements, the electrolyte was 0.2 M Na₂SO₄. The charge transfer resistance of the materials was calculated by fitting the impedance data from the equivalent circuit using EIS.

Photocatalytic activity evaluation

The photocatalytic activities of the as-prepared samples were evaluated by tetracycline oxidation and Cr(VI) ion reduction. Tetracycline (TC) degradation was tested in a XPA-7 photochemical reactor containing 30 mg of catalyst sample and 100 mL of 20 mg L⁻¹ tetracycline aqueous solution, which was adjusted to pH = 1. A 300 W Hg lamp with a UV-cutoff filter ($\lambda > 400$ nm) was placed inside the reactor. Water was circulated through the annulus to avoid heating during the reaction. The suspension was stirred continuously for 120 min in the dark to establish an equilibrium of tetracycline hydrochloride absorption/desorption on the samples before light irradiation. At certain time intervals, 4 mL of solution was centrifuged to investigate the changes in the absorption peak using a UVIKON XL/XS spectrometer and this was used to determine the concentration of TC. The photocatalytic degradation rate (D_r) was calculated using the following equation:

$$D_r = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of tetracycline solution and C_t is the concentration at irradiation time t .

Cr(VI) ion reduction was evaluated by analyzing the decreased concentration of Cr(VI) ions in the solution. 30 mg of catalyst sample was added into a K₂Cr₂O₇ aqueous solution (5 mg L⁻¹) together with the color-developing agent diphenylcarbazide (DPCI). The mixture solution was kept for 60 min in the dark, with constant stirring, to reach adsorption equilibrium. The reduction rate can be calculated according to the above eqn (1).

The synergic effect of removing both tetracycline and Cr(VI) ions was measured with similar photocatalytic activity experiments, by simultaneous degradation of a mixed solution containing tetracycline (20 mg L⁻¹) and Cr(VI) ions (5 mg L⁻¹) over 0.3 mg L⁻¹ catalyst samples. The reactive active species were detected using trapping experiments. The process was similar to the above photodegradation experiments.

Results and discussion

Fig. 1 shows the XRD patterns of Bi₂WO₆/NSTO10 together with Bi₂WO₆ and N-SrTiO₃. The diffraction peaks of the Bi₂WO₆/NSTO10 composite were well matched to the standard values of the cubic phase of SrTiO₃ (ICOD no. 01-089-4934) and the tetragonal phase of Bi₂WO₆ (ICOD no. 01-079-2381). In addition, the characteristic peaks of Bi₂WO₆ were all weak in intensity in the as-prepared composites with different weight ratios of W : Ti = 5%, 8%, 10%, 15%, and 20%, respectively (Fig. S1†). This indicated the smaller amount of Bi₂WO₆ in the composites.³³ No other characteristic peaks were detected,

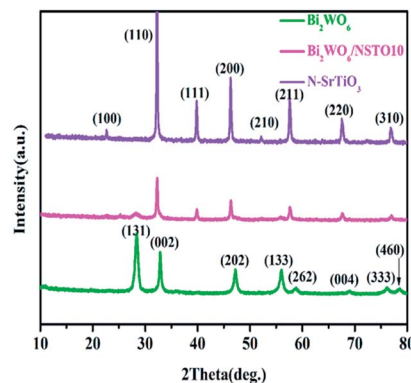


Fig. 1 XRD patterns of Bi₂WO₆/NSTO10, Bi₂WO₆, and N-SrTiO₃.

which demonstrated that Bi₂WO₆/N-SrTiO₃ composites were successfully fabricated without other impurities.

The morphologies of pure Bi₂WO₆, N-SrTiO₃ and Bi₂WO₆/NSTO10 were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A good layer structure was observed visually for the prepared Bi₂WO₆, which was constructed from many 2D interlaced nanosheets (Fig. 2a). The N-SrTiO₃ particles exhibited a sphere-like shape with an average size of 30–50 nm, as shown in Fig. 2b. Fig. 2c intuitively indicated that nanosheets of Bi₂WO₆ were evenly inserted into the massive N-SrTiO₃ nanoballs. The HRTEM image of Bi₂WO₆/NSTO10 (Fig. 2d) clearly shows crystal lattice stripes with a spacing of 0.28 nm, corresponding to the (0 1 1) crystal plane of SrTiO₃ particles, while the lattice spacing of 0.31 nm was ascribed to the (1 3 1) crystal plane of Bi₂WO₆, in accordance with the XRD results. To further confirm the composition, the

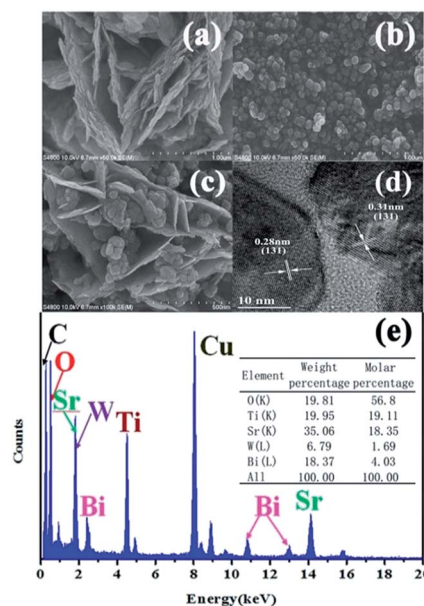


Fig. 2 SEM images of (a) Bi₂WO₆, (b) N-SrTiO₃, and (c) Bi₂WO₆/NSTO10, (d) HRTEM image of Bi₂WO₆/NSTO10, and (e) EDX spectrum of Bi₂WO₆/NSTO10, and EDS element content analysis of Bi₂WO₆/NSTO10 (inset).



element distribution of the as-prepared composite was analyzed by energy dispersive X-ray spectroscopy (EDS) (Fig. 2e). The existence of C, Cu, O, Sr, Ti, Bi, and W elements was observed in the EDS data, in which the C element was from the carbon film and Cu came from the copper wire mesh.³⁴ N was not detected, which was explained by the lower doping amount. From the inset of Fig. 2e, the atomic ratio of Sr/Ti is calculated to be approximately 1 : 1, very close to the theoretical value of SrTiO₃, while the atomic ratio of Bi/W is calculated to be approximately 2 : 1, corresponding to the theoretical value of Bi₂WO₆. Furthermore, the atomic ratio of W/Ti is close to 1 : 13, which is in agreement with the initial molar ratio of the composite. The growth process of Bi₂WO₆/N-SrTiO₃ could be approximately deduced and is schematically represented in Fig. S2.† The Bi₂WO₆ nanosheets were generated immediately when Bi³⁺ and WO₆⁶⁻ collided under hydrothermal reaction conditions. Then they were inserted into the massive as-prepared N-SrTiO₃ nanospheres to construct Bi₂WO₆/N-SrTiO₃, forming accumulated nano-balls segmented by nanosheets. This construction provided more active points for the adsorption of organic pollutants and separated redox active sites to completely remove the mixed pollutants through both oxidative degradation and reductive reaction.³⁵

To investigate the light adsorption, UV-vis diffuse reflectance spectra of Bi₂WO₆, N-SrTiO₃, and Bi₂WO₆/N-SrTiO₃ composites with different W : Ti ratios were measured (Fig. 3a). Bi₂WO₆ exhibited light absorption from the UV to the visible light region, with an absorption edge at about 430 nm, which was assigned to the intrinsic band gap transition. N-SrTiO₃ showed

a strong absorption in the range of 200–400 nm, as well as a stronger peak at around 420 nm. The optical absorption near the band edge follows the formula $(\alpha h\nu)^2 = A(h\nu - E_g)$, where α , h , ν , E_g , and A are the absorption coefficient, Planck's constant, the light frequency, the band gap, and a constant, respectively.³⁶ The band gap energy (E_g) is 2.83 eV for pure Bi₂WO₆ and 3.08 eV for N-SrTiO₃ as estimated by extrapolating the line (Fig. 3b), consistent with a previous study.^{37,38} Apparently, compared with both pure Bi₂WO₆ and N-SrTiO₃, Bi₂WO₆/N-SrTiO₃ showed enhanced light absorption in the UV-vis region.

The XPS results (Fig. 4) and FT-IR spectra (Fig. S3†) provided further insight into the chemical composition and groups of the as-prepared Bi₂WO₆ and Bi₂WO₆/NSTO10. The XPS survey spectra indicated the existence of Bi, O, W, Sr, Ti, and C elements in the surface of Bi₂WO₆/NSTO10 (Fig. 4a). The C 1s peak at a binding energy of about 284.9–285.9 eV is derived from the carbon tape used for fixing the sample and from atmospheric CO₂ adsorbed on the sample surface.³⁹ The high-resolution Bi 4f spectra of the Bi₂WO₆/NSTO10 and pure Bi₂WO₆ samples are shown in Fig. 4b. Two strong peaks located at 159.2 and 164.6 eV for both samples are attributed to Bi 4f_{7/2} and Bi 4f_{5/2} of Bi³⁺, respectively. The peaks at binding energies of 35.4 and 37.5 eV are the signals of W 4f_{7/2} and 4f_{5/2} of W⁶⁺ in Bi₂WO₆ (Fig. 4c). In the same way, the binding energies of 132.6 and 134.4 eV with a doublet separation of 1.8 eV were assigned to 3d_{5/2} and 3d_{3/2} of Sr³⁺, respectively (Fig. 4d).⁴⁰ The results indicate the consistent surface component of Bi³⁺ in the pure Bi₂WO₆ and Bi₂WO₆/NSTO10. The peaks in the FT-IR spectrum of Bi₂WO₆/NSTO10 were mainly matched with N-SrTiO₃ due to the enormous N-SrTiO₃ content in the composite (Fig. S4†). However, the peak at 1633 cm⁻¹ was stronger in the composite than in the individual component, suggesting that the hydrophilic ability of the composite was enhanced.

TC was used as a model reagent to evaluate the oxidation ability of the as-prepared samples. Fig. 5a displays the UV

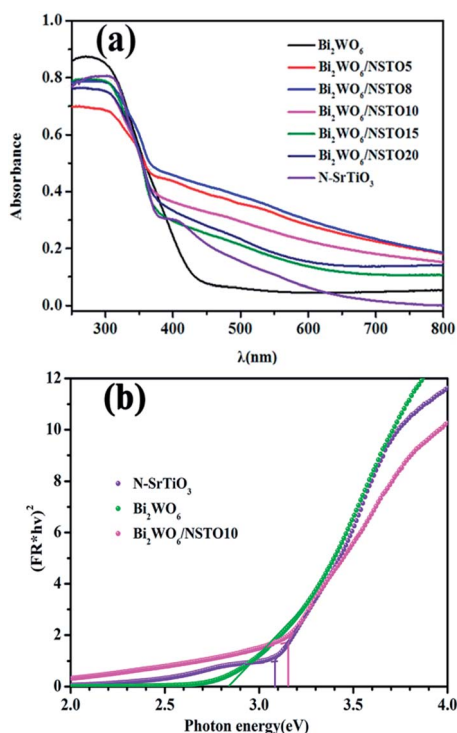


Fig. 3 (a) UV-visible diffuse reflectance spectra of the as-prepared samples, and (b) the optical bandgap of pristine Bi₂WO₆ and N-SrTiO₃.

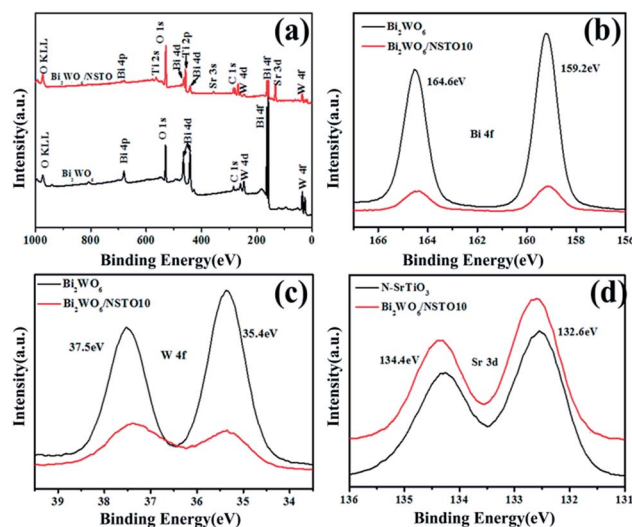


Fig. 4 The XPS spectra of Bi₂WO₆ and Bi₂WO₆/NSTO10: (a) survey, (b) Bi 4f orbitals, (c) W 4f orbitals, and (d) Sr 3d orbitals of N-SrTiO₃ and Bi₂WO₆/NSTO10.



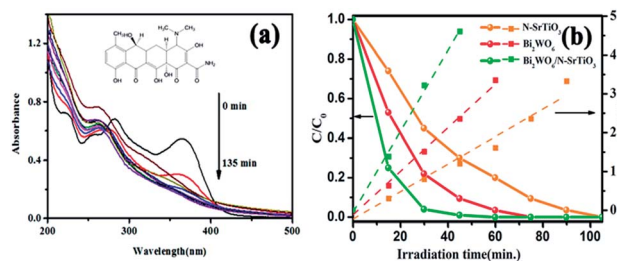


Fig. 5 (a) UV-vis absorption spectrum recorded during TC degradation over $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ under visible light irradiation and structural formula of TC (inset). (b) Concentration of TC versus visible light irradiation time and the apparent reaction kinetic curve linear transformation.

spectra taken in the course of the photodegradation experiments of TC over $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ under visible light illumination ($\lambda > 420$ nm). There is enough time in the dark for 2 h to ensure the establishment of an adsorption/desorption equilibrium of TC on the catalyst surface. A rapid decrease of TC at the wavelength of 360 nm was observed, accompanied by an absorption band shift to a shorter wavelength of 270 nm. The peaks at 270 nm and 360 nm corresponded to the E_2 and B bands of the benzene ring, respectively, indicating that the sample could degrade TC into small molecules.⁴¹ In comparison with Bi_2WO_6 and N-SrTiO_3 in Fig. 5b, the conversion of TC was approximately 98% after 30 min of irradiation under visible light for $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$, higher than that of pure Bi_2WO_6 (79%) and N-SrTiO_3 (55%). According to the formula $\ln(C_0/C_t) = kt$, the lines were clearly well fitted with the pseudo-first-order kinetics model. The observed rate constant (k) for the degradation of TC is 5.76 h^{-1} for $\text{Bi}_2\text{WO}_6/\text{NSTO10}$, while that for N-SrTiO_3 is 2.91 h^{-1} and that for Bi_2WO_6 is 3.68 h^{-1} . It was proved that the oxidation of TC over Bi_2WO_6 surpassed that of N-SrTiO_3 . More importantly, $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ could gain an advantage over any sole component for the photocatalytic degradation of TC.

$\text{Cr}(\text{vi})$ ions were used as a model reagent to evaluate the reduction ability of the as-prepared samples. Fig. 6 shows the photo-reductive activities of $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ composites together with pure Bi_2WO_6 and N-SrTiO_3 . Opposite to TC oxidation, weak reduction (only 15%) was observed for Bi_2WO_6 , whereas N-SrTiO_3 showed a higher photo-reductive efficiency (about 58% in 40 min) under visible light irradiation. Importantly, on assembling Bi_2WO_6 and N-SrTiO_3 (mass ratio from 5 to 10%), $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ showed an obviously increased photo-reductive activity; 5 mg L^{-1} $\text{Cr}(\text{vi})$ ions were completely reduced in 90 min under visible light irradiation. However, it should be noted that when the mass ratio continues to increase (that is, the amount of Bi_2WO_6 becomes higher), there is a decrease in the photo-reductive activity. The kinetic rate constants under visible light were calculated (Fig. S4†). The photo-reduction of $\text{Cr}(\text{vi})$ ions can be fitted to a pseudo-first-order reaction and the rate constant (k_{ap}) is 2.33 h^{-1} for $\text{Bi}_2\text{WO}_6/\text{NSTO10}$, obviously higher than that of N-SrTiO_3 (0.908 h^{-1}) and Bi_2WO_6 (0.155 h^{-1}). As a result, the constructed heterojunction of $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ presented the highest photo-reductive activity compared with either component.

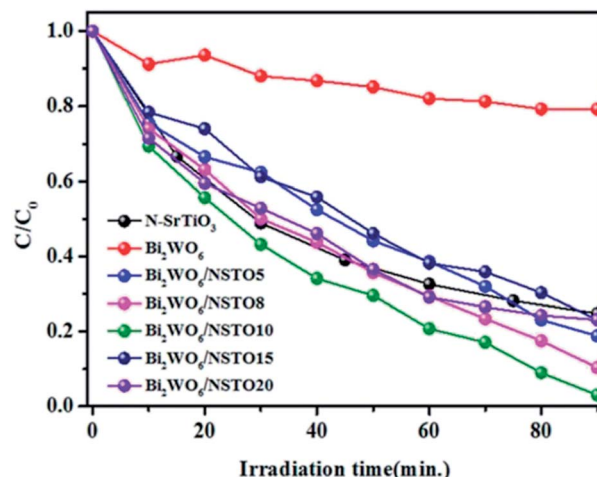


Fig. 6 Concentration of $\text{Cr}(\text{vi})$ versus visible light irradiation time in the presence of Bi_2WO_6 , N-SrTiO_3 and $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ with various ratios of W : Ti = 5%, 8%, 10%, 15%, and 20%, respectively.

Finally, the feasibility of simultaneous tetracycline oxidation and $\text{Cr}(\text{vi})$ ion reduction over $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ was tested in a simulated complicated solution that contained tetracycline and $\text{Cr}(\text{vi})$ ions. Firstly, the reduction rate of $\text{Cr}(\text{vi})$ ions in the mixed solution is shown in Fig. 7a. The $\text{Cr}(\text{vi})$ ions (5 mg L^{-1}) were completely reduced in 20 min under visible light for the $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ composite, which is about 2 and 10 times faster than the reaction with pure N-SrTiO_3 and Bi_2WO_6 , respectively. Secondly, the oxidation of TC in the mixed solution is shown in Fig. 7b. For $\text{Bi}_2\text{WO}_6/\text{NSTO10}$, the oxidation of TC was accelerated in the mixture of $\text{Cr}(\text{vi})$ and TC under visible light, and up to 100% of the TC was oxidized within 20 min, indicating about 1.45 and 2.5 times better activity than the sole

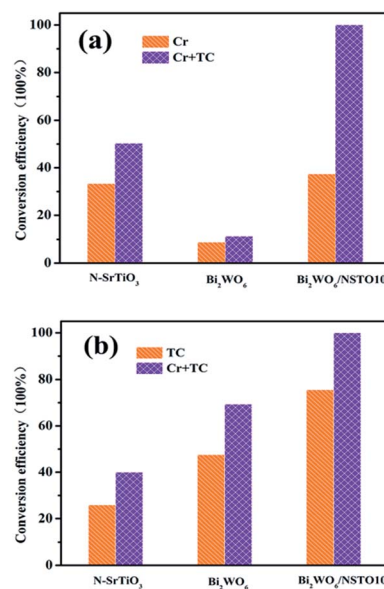


Fig. 7 (a) $\text{Cr}(\text{vi})$ and (b) TC conversion efficiencies in the first 20 minutes over the as-prepared photocatalysts in a single solution (TC or $\text{Cr}(\text{vi})$) and mixed solution (TC and $\text{Cr}(\text{vi})$).



components Bi_2WO_6 (69%) and N-SrTiO_3 (40%). Thirdly, all samples, $\text{Bi}_2\text{WO}_6/\text{NSTO10}$, Bi_2WO_6 , and N-SrTiO_3 , showed better activity for TC oxidation (or Cr^{6+} ion reduction) in the mixed pollutant environment than in the single pollutant solution. Thus, two conclusions were derived from the above results. (1) The integrated $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ composite was obviously more efficient for both TC oxidation and $\text{Cr}(\text{vi})$ ion reduction than any sole component, indicating that both the oxidative and reductive performance were substantially improved through coupling design. (2) The coexistence of tetracycline and $\text{Cr}(\text{vi})$ ions was conducive to the removal of either constituent contaminant, confirming that the designed $\text{Bi}_2\text{WO}_6/\text{N-SrTiO}_3$ was absolutely superior for the removal of mixed contaminants. Besides, compared with other references regarding the photocatalytic reduction of $\text{Cr}(\text{vi})$ ions^{42–45} and the degradation of TC,^{46–48} the removal efficiency of the present work showed outstanding advantages (Tables S1 and S2†).

To assess the stability of the as-prepared composite, the photocurrent under 300 W xenon lamp irradiation was recorded and shown in Fig. 8a. Among all the samples, N-SrTiO_3 presented the highest photocurrent density, implying higher light harvesting. However, the photocurrent response was continuously decreased during several on-off cycles. Combining Bi_2WO_6 and N-SrTiO_3 into a composite, the photo-responsive phenomenon of $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ was entirely reversible upon each light irradiation, exhibiting more excellent stability. We also conducted recycling experiments for the mixed contaminants over $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ under visible light irradiation and

the results are illustrated in Fig. 8b. No noticeable activity change is observed during four successive cycles, suggesting that the $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ composite is recyclable with good stability during the photocatalytic remediation of complicated toxic residuals.

As is well known, the specific surface area and porosity are important factors to enhance catalytic performance. The isotherm curves of Bi_2WO_6 , N-SrTiO_3 , and $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ were characterized as type III with an H_3 hysteresis loop according to Brunauer–Deming–Deming–Teller (BDDT) classification,⁴⁹ as shown in Fig. 9. The BET surface area of the $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ nanocrystals is about $31.0 \text{ cm}^2 \text{ g}^{-1}$, slightly larger than the value of $27.7 \text{ cm}^2 \text{ g}^{-1}$ for N-SrTiO_3 , whereas it is obviously smaller than that of Bi_2WO_6 (inset of Fig. 9). Combined with the photocatalytic results (Fig. 8), it was deduced that the change in electron structure played a significant role in enhancing the photocatalytic performance, instead of the high BET surface area in the as-prepared composite.

Radical-trapping experiments were performed to determine the active species in TC degradation by using different scavengers, including benzoquinone (BQ, superoxide anion $\text{O}_2^{\cdot-}$ radical scavenger), *tert*-butanol (TBA, $\cdot\text{OH}$ radical scavenger), silver nitrate (AgNO_3 , electron scavenger) and ammonium oxalate (AO, hole scavenger).⁵⁰ As shown in Fig. 10, TC photodegradation was greatly restrained in the presence of AO, compared with the reaction without radical scavengers. Furthermore, the degradation of TC was slightly decreased when TBA was added into the reaction system. These results revealed that h^+ plays a more significant role, while $\cdot\text{OH}$ gives a secondary contribution in TC degradation under visible light irradiation, confirming that an oxidative reaction of TC occurred for $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ in aqueous solution.

EIS is an efficient electrochemical method to explain the electron-transfer efficiency at electrodes.⁵¹ N-SrTiO_3 showed the biggest diameter, implying that it has poor electrical conductivity (Fig. 11a). In comparison, $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ exhibited the smallest diameter, indicating a faster charge transfer shift through the composite electrode interface. This suggested a significant promotion of the photo-response ability due to the effective restraint of photo-generated charge recombination. The charge transfer resistance of the materials was obtained

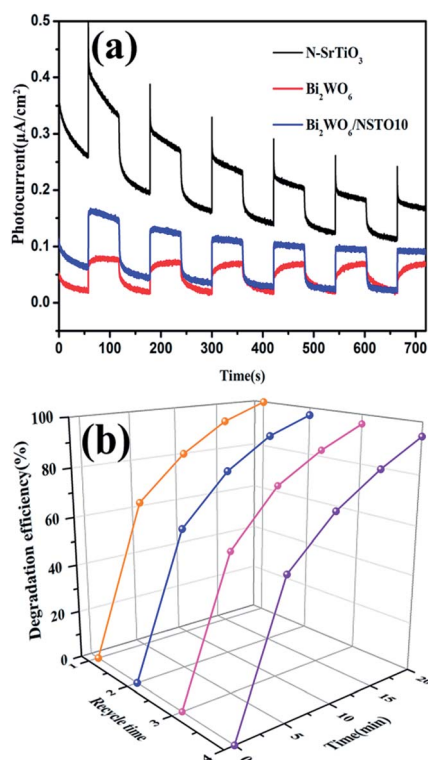


Fig. 8 (a) Photocurrent responses of N-SrTiO_3 , Bi_2WO_6 and $\text{Bi}_2\text{WO}_6/\text{NSTO10}$ electrodes. (b) Cycling degradation of TC in a mixed solution (TC and $\text{Cr}(\text{vi})$) using $\text{Bi}_2\text{WO}_6/\text{NSTO10}$.

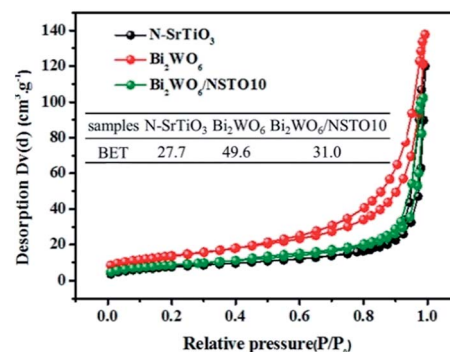


Fig. 9 Nitrogen adsorption/desorption isotherms and BET of the as-prepared samples (inset).

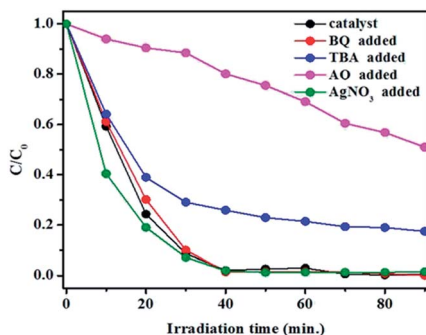


Fig. 10 Effects of different scavengers on TC degradation in the presence of Bi₂WO₆/NSTO10 under visible light irradiation.

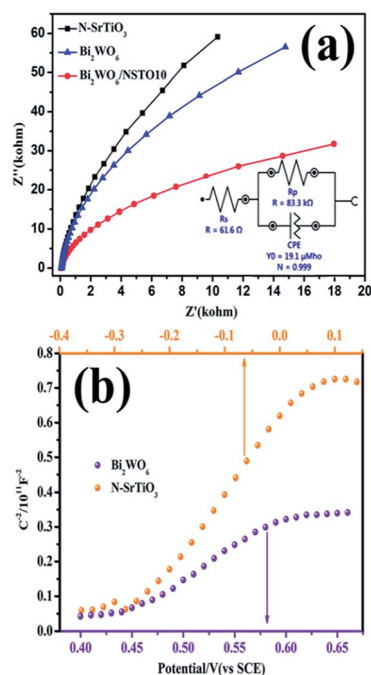


Fig. 11 (a) Electrochemical impedance spectroscopy (EIS) plots, and (b) Mott-Schottky (MS) plots of the Bi₂WO₆ and N-SrTiO₃ film electrodes.

from the equivalent circuit by fitting the impedance data using EIS. The fitted impedance value of Bi₂WO₆/NSTO10 (83.3 kΩ) is smaller than that of Bi₂WO₆ (136 kΩ) or N-SrTiO₃ (184 kΩ) alone, attributed to the accelerated formation of charge-transfer states and depletion layers within the nanocomposites through the internal electrostatic field in the heterojunction. The reduced resistance of Bi₂WO₆/N-SrTiO₃ suggested an increased transmission rate of photogenerated charge carriers. Fig. 11b shows the electrochemical Mott-Schottky plot of Bi₂WO₆ and N-SrTiO₃ films on a platinum electrode substrate. The positive slopes revealed a typical n-type characteristic for both Bi₂WO₆ and N-SrTiO₃. Thus, a Z-type n-n heterojunction is constructed by assembling N-SrTiO₃ and Bi₂WO₆, in which the conduction band potential is -0.28 eV for N-SrTiO₃ and 0.43 eV of Bi₂WO₆, respectively, in terms of the equivalence of the Fermi level and

conduction band potential in an n-type semiconductor. According to the band gaps of N-SrTiO₃ (3.08 eV) and Bi₂WO₆ (2.83 eV), their valence band (E_{VB}) positions are estimated to be 2.80 and 3.26 eV, respectively. Based on the above experiment, the probable mechanism for the photocatalytic removal of the mixed tetracycline and Cr(vi) ions over Bi₂WO₆/N-SrTiO₃ under visible light irradiation is described in Fig. 12. (1) Under visible light illumination, electrons (e^-) are excited into the CB and holes located at the valence band of N-SrTiO₃. The same occurs for Bi₂WO₆. (2) The conduction band potentials of Bi₂WO₆ and N-SrTiO₃ are higher compared with the reductive potential of Cr₂O₇²⁻/Cr³⁺ (1.27 eV *versus* NHE), and thus they both exhibit reducing capacity for Cr(vi) to Cr(III) ions, which was demonstrated in the Cr(vi) reduction experiment. However, N-SrTiO₃ exhibited excellent reducing ability due to its high conduction band level, whereas the reducing activity of Bi₂WO₆ was poor due to its slightly lower conduction band compared to N-SrTiO₃ (Fig. 7). (3) On the other hand, the valence band potentials of N-SrTiO₃ and Bi₂WO₆ are all lower than the oxidation potential of TC (-3.28 eV), as shown in Fig. S5.† As a result, the holes in the valence band of N-SrTiO₃ and Bi₂WO₆ could degrade TC directly. However, the valence band potential of Bi₂WO₆ is much lower than the redox potential of \cdot OH/H₂O (2.73 eV *versus* NHE), indicating that its holes could transform H₂O into \cdot OH and then oxidize TC. This was confirmed by the radical-trapping experimental results. At the same time, N-SrTiO₃ exhibits poor performance for the oxidation of TC due to its not very low valence band energy. (4) If we combine the two separate components, band bending was not obvious, due to the close Fermi energy level in the present n-n junction. The conduction band (CB) of Bi₂WO₆ was slightly shifted upwards. In this case, the redox abilities of each component were not changed very much, unlike in p-n type junctions.^{20,21} As a result, while maintaining the greater transition tendency of the charges between Bi₂WO₆ and N-SrTiO₃, the reductive ability of N-SrTiO₃ did not obviously decrease. The same case is observed for the oxidative performance of Bi₂WO₆.⁵² Therefore, the photo-generated charge carriers are effectively separated by the heterojunction between Bi₂WO₆ and N-SrTiO₃, and the photocatalytic activity is also significantly improved.

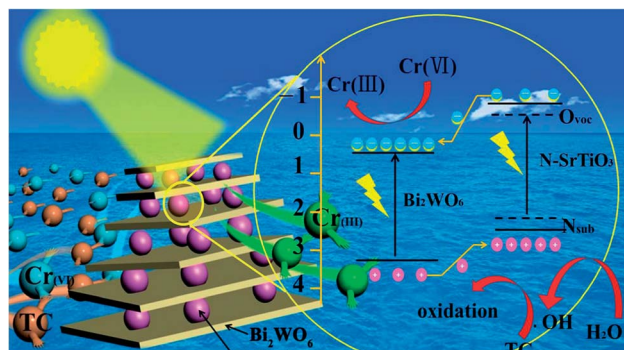


Fig. 12 Possible mechanism for Cr(vi) photoreduction and tetracycline oxidation over the Bi₂WO₆/NSTO10 photocatalytic system under visible light irradiation.



Conclusions

In summary, we have successfully fabricated a series of n-n Bi₂WO₆/N-SrTiO₃ heterojunctions with different mass ratios of W to Ti using a hydrothermal method. The as-prepared samples were composed of massive N-SrTiO₃ nanoballs with a diameter of about 10–20 nm, segmented by a small amount of 2D interlaced Bi₂WO₆ nanosheets. As established in the UV-vis experiment, the capacity to absorb visible light was significantly improved in the composite. Moreover, this Bi₂WO₆/N-SrTiO₃ composite showed obviously superior visible light photocatalytic efficiency and stability for the simultaneous removal of tetracycline and Cr(VI) compared with the individual Bi₂WO₆ or N-SrTiO₃, confirming that the high reductive and oxidative ability could be holistically improved through coupling design. This is particularly useful for the remediation of mixed contaminants in complicated aquatic environments. The results of free radical trapping experiments revealed that photo-excited h⁺ and e[−] were responsible for the oxidation of TC and reduction of Cr(VI) ions, respectively. The Z type n-n heterojunction of Bi₂WO₆/N-SrTiO₃ exhibited an excellent bipolar photo-oxidative and photo-reductive ability, while retaining a good visible light response, and simultaneously promoted the separation of the photogenerated electron-hole pairs. The present work could offer a new strategy to develop more efficient binary catalysts for practical application in the elimination of pharmaceutical and heavy metal pollutants in aquatic environments.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grants 21567017 and 21777078), the open project of the state key laboratory of inorganic synthesis and preparative chemistry of Jilin University (2016-10), and the Project of Research and Development of the Applied Technology for Inner Mongolia 2017.

References

- 1 R. Hirsch, T. Ternes, K. Haberer and K. Kratz, *Sci. Total Environ.*, 1999, **225**(1–2), 109–118.
- 2 B. Li and T. Zhang, *Water Res.*, 2013, **47**, 2970–2982.
- 3 A. Sarmah, M. Meyer and A. Boxall, *Chemosphere*, 2006, **65**(5), 725–759.
- 4 J. Bound and N. Voulvoulis, *Chemosphere*, 2004, **56**(11), 1143–1155.
- 5 T. Wang, W. Liu, L. Xiong, N. Xu and J. Ni, *Chem. Eng. J.*, 2013, **215–216**, 366–374.
- 6 X. Yu, Z. Lu, D. Wu, P. Yu, M. He, T. Chen, W. Shi, P. Huo, Y. Yan and Y. Feng, *React. Kinet., Mech. Catal.*, 2014, **111**, 347–360.
- 7 L. Minh, N. Khan, J. Drewes and R. Stuetz, *Water Res.*, 2010, **44**, 4295–4323.
- 8 T. Aarthi and G. Madras, *Catal. Commun.*, 2008, **9**(5), 630–634.
- 9 D. Kolpin, E. Furlong, M. Meyer, E. Thurman, S. Zaugg, L. Barber and H. Buxton, *Environ. Sci. Technol.*, 2002, **36**, 1202–1211.
- 10 Q. Yuan, L. Chen, M. Xiong, J. He, S. Luo, C. Au and S. Yin, *Chem. Eng. J.*, 2014, **255**, 394–402.
- 11 F. Lian, Z. Song, Z. Liu, L. Zhu and B. Xing, *Environ. Sci. Pollut. Res.*, 2013, **178**, 264–270.
- 12 Z. Zhang, H. Liu, L. Wu, H. Lan and J. Qu, *Chemosphere*, 2015, **138**, 625–632.
- 13 T. Yan, J. Tian, W. Guan, Z. Qiao, W. Li, J. You and B. Huang, *Appl. Catal., B*, 2017, **202**, 84–94.
- 14 P. Huo, M. Zhou, Y. Tang, X. Liu, C. Ma, L. Yu and Y. Yan, *J. Alloys Compd.*, 2016, **670**, 198–209.
- 15 D. Ma, J. Wu, M. Gao, Y. Xin, T. Ma and Y. Sun, *Chem. Eng. J.*, 2016, **290**, 136–146.
- 16 X. Liu, Q. Lu and J. Liu, *J. Alloys Compd.*, 2016, **662**, 598–606.
- 17 P. Ju, Y. Wang, Y. Sun and D. Zhang, *Dalton Trans.*, 2016, **45**, 4588–4602.
- 18 Y. Xiang, P. Ju, Y. Wang, Y. Sun, D. Zhang and J. Yu, *Chem. Eng. J.*, 2016, **288**, 264–275.
- 19 X. Wang, S. Li, Y. Ma, H. Yu and J. Yu, *J. Phys. Chem. C*, 2011, **115**(30), 14648–14655.
- 20 Y. Zhang, Y. Yu, X. Wang, G. Tong, L. Mi, Z. Zhu, X. Geng and Y. Jiang, *J. Mater. Chem. C*, 2017, **5**, 140–148.
- 21 N. Zhang, Y. Zhang, X. Pan, M. Yang and Y. Xu, *J. Phys. Chem. C*, 2012, **116**, 18023–18031.
- 22 K. Yu, C. Zhang, Y. Chang, Y. Feng, Z. Yang, T. Yang, L. Lou and S. Liu, *Appl. Catal., B*, 2017, **200**, 514–520.
- 23 C. Zhang, K. Yu, Y. Feng, Y. Chang, T. Yang, Y. Xuan, D. Lei, L. Lou and S. Liu, *Appl. Catal., B*, 2017, **210**, 77–87.
- 24 W. Dong, X. Li, J. Yu, W. Guo, B. Li, L. Tan, C. Li, J. Shi and G. Wang, *Mater. Lett.*, 2012, **67**, 131–134.
- 25 G. Xing, L. Zhao, T. Sun, Y. Su and X. Wang, *SpringerPlus*, 2016, **5**, 1132.
- 26 W. Chen, T. Liu, T. Huang, X. Liu, J. Zhu, G. Duan and X. Yang, *Appl. Surf. Sci.*, 2015, **355**, 379–387.
- 27 J. Zhu, S. Liu, Q. Yang, P. Xu, J. Ge and X. Guo, *Colloids Surf., A*, 2016, **489**, 275–281.
- 28 M. Li, L. Zhang, X. Fan, Y. Zhou, M. Wu and J. Shi, *J. Mater. Chem. A*, 2015, **3**(9), 5189–5196.
- 29 D. Yue, D. Chen, Z. Wang, H. Ding, R. Zong and Y. Zhu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 26314.
- 30 Y. Zhou, Y. Zhang, M. Lin, J. Long, Z. Zhang, H. Lin, J. Wu and X. Wang, *Nat. Commun.*, 2015, **6**, 8340.
- 31 Y. Huang, S. Kang, Y. Yang, H. Qin, Z. Ni, S. Yang and X. Li, *Appl. Catal., B*, 2016, **196**, 89–99.
- 32 J. Xu, Y. Wei, Y. Huang, J. Wang, X. Zheng, Z. Sun, L. Fan and J. Wu, *Ceram. Int.*, 2014, **40**, 10583–10591.
- 33 L. Chen, D. Jiang, T. He, Z. Wu and M. Chen, *CrystEngComm*, 2013, **15**(37), 7556–7563.
- 34 M. Sun, D. Li, W. Zhang, Z. Chen, H. Huang, W. Li, Y. He and X. Fu, *J. Phys. Chem. C*, 2009, **113**, 14916–14921.



- 35 L. Qu, J. Lang, S. Wang, Z. Chai, Y. Su and X. Wang, *Appl. Surf. Sci.*, 2016, **388**, 412–419.
- 36 L. Ye, X. Jin, C. Liu, C. Ding, H. Xie, K. Chu and P. Wong, *Appl. Catal., B*, 2016, **187**, 281–290.
- 37 S. Kumar, S. Tonda, A. Baruah, B. Kumar and V. Shanker, *Dalton Trans.*, 2014, **43**, 16105–16114.
- 38 J. Li, H. Hao and Z. Zhu, *Mater. Lett.*, 2016, **168**, 180–183.
- 39 H. Li, Q. Deng, J. Liu, W. Hou, N. Du, R. Zhang and X. Tao, *Catal. Sci. Technol.*, 2014, **4**, 1028–1037.
- 40 L. Zhang, W. Tian, Y. Chen, J. Chen, H. Teng, J. Zhou, J. Shi and Y. Sun, *RSC Adv.*, 2016, **6**, 83471.
- 41 M. Liu, G. Lv, L. Mei, X. Wang, X. Xing and L. Liao, *Adv. Mater. Sci. Eng.*, 2014, **2014**, 409086.
- 42 H. Xu, W. Zhang, M. Ding and X. Gao, *Mater. Des.*, 2017, **114**, 129–138.
- 43 L. Liu, C. Luo, J. Xiong, Z. Yang, Y. Zhang, Y. Cai and H. Gu, *J. Alloys Compd.*, 2017, **690**, 771–776.
- 44 J. Qu, D. Chen, N. Li, Q. Xu, H. Li, J. He and J. Lu, *Appl. Catal., B*, 2017, **207**, 404–411.
- 45 M. Naimi-Joubani, M. Shirzad-Siboni, J. K. Yang, M. Gholami and M. Farzadkia, *J. Chem. Eng.*, 2015, **22**, 317–323.
- 46 M. Cao, P. Wang, Y. Ao, W. Chao, J. Hou and Q. Jin, *J. Colloid Interface Sci.*, 2016, **467**, 129–139.
- 47 P. Huo, Z. Ye, H. Wang, Q. Guan and Y. Yan, *J. Alloys Compd.*, 2017, **696**, 701–710.
- 48 Z. Ye, J. Li, M. Zhou, H. Wang, Y. Ma, P. Huo, L. Yu and Y. Yan, *Chem. Eng. J.*, 2016, **304**, 917–933.
- 49 Y. Su, L. Hou, C. Du, L. Peng, K. Guan and X. Wang, *RSC Adv.*, 2012, **2**, 6266.
- 50 B. Luo, D. Xu, D. Li, G. Wu, M. Wu, W. Shi and M. Chen, *ACS Appl. Mater. Interfaces*, 2015, **7**, 17061–17069.
- 51 S. Zhang, J. Li, M. Zeng, G. Zhao, J. Xu, W. Hu and X. Wang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 12735–12743.
- 52 J. Lee, Y. Kim, J. Kim, S. Kim, D. Min and D. Jang, *Appl. Catal., B*, 2017, **205**, 433–442.

