A superior photocatalytic performance of a novel Bi$_2$SiO$_5$ flower-like microsphere via a phase junction†

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A phase junction over a Bi$_2$SiO$_5$ photocatalyst with the orthorhombic Bi$_2$SiO$_5$ and the tetragonal Bi$_2$SiO$_5$ structure was successfully synthesized via an ion exchange method using BiOBr solid microspheres as the sacrificial template. In the meantime, the as-prepared Bi$_2$SiO$_5$ phase junction possesses a novel morphology of a flower-like microsphere with nanoparticles evenly embedded in its nano-petals. It was found that the Bi$_2$SiO$_5$ phase junction not only showed a highly enhanced photocatalytic activity and excellent durability under UV or simulated solar irradiation, but also showed a remarkable visible-light activity for photo-degradation of phenol. Experimental results reveal that the tetragonal Bi$_2$SiO$_5$ phase in this phase junction possesses a narrower band gap, thus leading to its extended light absorption. The efficient charge separation via a phase junction would make a great contribution to its highly enhanced photocatalytic activity under UV or simulated solar irradiation. The high efficiency in the degradation of organic pollutants makes the as-prepared photocatalyst a promising candidate for photocatalytic environmental purification.

Introduction

Bi$_2$SiO$_5$ is one of the newly found compounds within the Aurivillius family. It has been reported as a promising material with relatively good dielectric properties and piezoelectric and nonlinear optical effects. Furthermore, Bi$_2$SiO$_5$ has also been reported as a good photocatalyst for the degradation of pollutants in water. To date, solid-state-reaction methods are the most common synthesis route for Bi$_2$SiO$_5$. However, this route typically results in high energy consumption, large agglomerated particles with irregular morphologies and low specific surface areas. Besides, some impurities were obtained spontaneously because of the metastable properties of Bi$_2$SiO$_5$. Although Bi$_2$SiO$_5$ with different morphologies such as nanoparticles, nanosheets, mesoporous microspheres and nanoflowers have been synthesized under hydrothermal conditions, these synthetic strategies suffered from the drawbacks of containing a capping agent which requires additional removal, tedious synthetic procedures and a low photocatalytic performance. Therefore, it is of significance to develop a facile route to fabricate Bi$_2$SiO$_5$ nanostructures with novel structures and fascinating properties.

Two Aurivillius-type oxides, BiOBr and Bi$_2$SiO$_5$ are crystallized in layered structures composed of [Bi$_2$O$_2$]$^{2+}$ slabs interlaced with anion layers. As a result, it is possible for these two semiconductors to come in contact or transformation through sharing the [Bi$_2$O$_2$]$^{2+}$ unit and then experiencing an ion exchange. Recently, an ion exchange, which permits the exchange of the component ions with the incoming species, has paved a new way to engender various inorganic nanostructures from the existing materials. In this work, a transformation process was realized through introducing the as-prepared BiOBr solid microspheres as the sacrificial templates followed by ion exchange treatments. A novel Bi$_2$SiO$_5$ flower-like microsphere with nanoparticles evenly embedded in its nano-petals was obtained successfully. Furthermore, the as-prepared Bi$_2$SiO$_5$ microsphere was found to contain two Bi$_2$SiO$_5$ phases and exhibited an extended range of spectral response, excellent photocatalytic activity and good stability for photo-degradation of phenol. The formation mechanism of this special morphology is proposed, while a systematic research on the enhanced photocatalytic activity of the Bi$_2$SiO$_5$ microsphere is revealed in detail.

Experimental

Materials preparation

All chemicals of analytical-grade reagents were used without further purification. Deionized water (85 mL), glacial acetic
acid (45 mL), and bismuth nitrate (14.55 g, 30 mmol) were placed into a 250 mL beaker and stirred at room temperature for 15 min until a clear, transparent solution was formed. Then cetyltrimethylammonium bromide (CTAB) (10.93 g dissolved in 40 mL of water, 30 mmol) was added to the above solution in one batch, and the mixture was stirred for an additional 30 min at room temperature. The precipitate thus formed was filtered and washed several times with ethanol and water to remove the nonreactive species. The white solid was then dried (in air) and ready for use. In a typical reaction, 0 mmol, 1.5 mmol, and 2 mmol Na2SiO3 was dissolved separately in 80 mL distilled water and stirred at room temperature for 10 min to obtain clear solutions. Then, BiOBr (1.22 g) was dispersed respectively in each of the above solutions with stirring. Each mixture was kept at room temperature for 30 min with stirring and then transferred into a Teflon-lined autoclave with a capacity of 100 mL, and heated at 160 °C for 24 h. After reaction, the autoclave was cooled to room temperature naturally. The precipitates were collected by centrifugation, washed with deionized water and ethanol several times, and finally dried in air at 80 °C for 10 h. Products with different amounts of Na2SiO3 ranging from 0 to 2 mmol were prepared according to this method and were marked as BiOBr, S-1.5, and S-2, respectively.

For the synthesis of pure Bi2SiO5, 4 mmol Bi(NO3)3·5H2O and 2 mmol Na2SiO3 were added to 75 mL deionized water with stirring. The pH was adjusted to ca. 9 by 10% ammonia solution. The mixture was then transferred into a Teflon-lined autoclave with a capacity of 100 mL, and heated at 160 °C for 24 h. After reaction, the autoclave was cooled to room temperature naturally. The precipitates were collected by centrifugation, washed with deionized water and ethanol several times, and finally dried in air at 80 °C for 10 h. The pure Bi2SiO5 synthesized above was labeled as Bi2SiO5.

Characterizations

X-ray diffraction (XRD) patterns of the powders were recorded at room temperature on a Bruker D8 Advance X-ray diffractometer. The sizes and morphologies of the samples were characterized with the aid of a LEO-1530 field Scanning Electron Microscope (SEM) and a HITACHI HT7700 Transmission Electron Microscope (TEM). High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL JEM-2010F field emission transmission electron microscope with an accelerating voltage of 200 kV. Fourier Transform Infrared Spectra (FT-IR) were recorded on a Bruker VERTEX 700 spectrometer in the frequency range of 4000–600 cm−1 with a resolution of 4 cm−1. The Brunauer–Emmett–Teller (BET) surface area measurements were performed using a Micromeritics (ASAP 2010V5.02H) surface area analyzer. The nitrogen adsorption and desorption isotherms were measured at 77 K after degassing the samples on a Sorptomatic 1900 Carlo Erba Instrument. The Diffuse Reflectance Spectroscopy (DRS) of the samples were recorded in the range from 200 to 800 nm using a Hitachi U-3010 spectroscope equipped with an integrated sphere attachment and BaSO4 was used as a reference. X-ray Photoelectron Spectroscopy (XPS) was performed using a PHI 5300 ESCA system. The beam voltage was 3.0 kV, and the energy of the Ar ion beam was 1.0 keV. The binding energies were normalized to the signal for adventitious carbon at 284.8 eV.

Photocatalytic experiments

The photocatalytic activities were evaluated by the decomposition of phenol under UV light irradiation (λ≈ 365 nm), simulated sunlight irradiation and visible light irradiation (λ≥ 420 nm). UV irradiation was produced by a 100 W high pressure Hg lamp with the main wave crest at 365 nm. The simulated sunlight irradiation and visible irradiation were both obtained from a 500 W Xe lamp (Institute for Electric Light Sources, Beijing), whereas the latter was obtained through the addition of a 420 nm cutoff filter. For the photocatalytic experiments, the samples (30 mg) were dispersed in the 50 mL aqueous phenol solution (5 ppm). Before the light irradiation, the suspensions were first ultrasonically dispersed in the dark for 15 min and then magnetically stirred for 1 h to reach the absorption–desorption equilibrium. At certain time intervals, 2 mL of the mixed suspension were extracted and centrifuged to remove the photocatalyst. The degradation process was monitored by HPLC analysis with a UV detector at 270 nm. The mobile phase used methanol and water (60% : 40%), and the flow rate was 1 mL min⁻¹.

Results and discussion

Formation of the Bi2SiO5 microsphere

XRD patterns of the as-prepared samples are shown in Fig. 1. The pure BiOBr and Bi2SiO5 are listed for comparison. For S-2, all of the observed peaks of the pattern can be indexed to the
pure orthorhombic Bi$_2$SiO$_5$ phase (JCPDS no. 36-0287). However, the XRD peaks of S-1.5 can be indexed to two mixed phases of Bi$_2$SiO$_5$ (orthorhombic, JCPDS no. 36-0288 & tetragonal, JCPDS no. 36-0287), indicating the existence of a phase junction. Further confirmation on the phase composition of S-1.5 is provided in the ESI.† The XRD results of S-1.5 and S-2 demonstrate the successful transformation into Bi$_2$SiO$_5$ from the sacrificial template (BiOBr) via ion exchange.

Fig. 2a–c show the TEM images of BiOBr, S-1.5 and S-2, respectively. It is found that they all possess sphere-like structures assembled by nanosheets. However, small particles with uniform distribution in the sheets were only found in S-1.5. SEM images for S-1.5 and the sacrificial template of BiOBr are shown in Fig. 2d and 2e, respectively. Sample BiOBr and S-1.5 both exhibit uniform sphere-like structures, indicating the successful transformation from the sacrificial template of BiOBr into Bi$_2$SiO$_5$ without the collapse of the shape. It is known that Bi$_2$SiO$_5$ which is composed of (SiO$_3$)$_2^{-}$ pyroxene file layers inserted between (Bi$_2$O$_2$)$_2^{+}$ layers$^{7a}$ has a similar structure and lower solubility to BiOBr. Therefore, BiOBr could adopt a thermo-dynamically favored direction to transform into Bi$_2$SiO$_5$ by reacting with SiO$_3$$^{2-}$ ions. The schematic diagram of the anion exchange is shown in Scheme 1. As discussed above, S-1.5 is composed of two Bi$_2$SiO$_5$ phases, and small particles embedded in the sheets are absent in the sample S-2 which contains one single phase of Bi$_2$SiO$_5$ (JCPDS no. 36-0287). At the same time, as shown in Fig. 2f, elemental analysis of S-1.5 revealing its components has been done through EDS. No residual of Br in S-1.5 can be found through the experimental result, suggesting that the sacrificial template of BiOBr has been completely transformed into Bi$_2$SiO$_5$. Hence, this unique and special morphology of S-1.5 suggests that the nanoparticles should belong to an intermediate and metastable phase. As shown in Fig. 3d, through the lattice identification for S-1.5, the sphere-like particles embedded in the sheets can be attributed to the tetragonal Bi$_2$SiO$_5$ phase (JCPDS no. 36-0288) and the sheets can be identified as the orthorhombic Bi$_2$SiO$_5$ phase (JCPDS no. 36-0287). It is also worth noting that the sacrificial template of BiOBr belongs to

**Fig. 2** TEM images of BiOBr (a), S-1.5 (b) and S-2 (c); SEM images of S-1.5 (d) and BiOBr (e); EDS analysis of S-1.5 (f).
the tetragonal phase, thus it is reasonable and easy for the sacrificial template of BiOBr firstly transforming into the tetragonal Bi$_2$SiO$_5$ phase (JCPDS no. 36-0288) through ion exchange. Furthermore, the tetragonal Bi$_2$SiO$_5$ phase which has been reported to be a metastable phase is easy to transform into a more stable phase. At the same time, less clear lattice fringes of the nanoparticles embedded in the surrounding sheets can be seen in Fig. 3d, indicating a low crystallization quality of these nanoparticles. This just suggests that the nanoparticles which are attributed to a metastable phase of Bi$_2$SiO$_5$ (JCPDS no. 36-0288) would experience a process of transforming into a more stable phase of the orthorhombic Bi$_2$SiO$_5$ (JCPDS no. 36-0287). As a result, the phase junction (S-1.5) should be a product originating from the phase evolution process. Further confirmation is conducted in the following part.

In order to further investigate the morphology of S-1.5, additional electron microscope analyses have been done and the results are shown in Fig. 3. Flower-like microspheres composed of crossed nanosheets are observed and a significant uniformity in the morphology can be confirmed by the SEM image shown in Fig. 3c. Fig. 3b and d depict the sheet-like structures comprising Bi$_2$SiO$_5$ microspheres, small particles with uniform distribution embedded in the sheets can be obviously found. Lattice match is known to play a significant role in the growth of hetero-structures. A high degree of lattice mismatch will prevent the nucleation and growth of an overlayer due to the high structural strain. As shown in Fig. 3d, the atomic spacing of (110) planes of Bi$_2$SiO$_5$ (JCPDS no. 36-0288) is 0.265 nm, which is quite close to the atomic spacing (0.262 nm) at the Bi$_2$SiO$_5$ (JCPDS no. 36-0287) (020) facet.

Therefore, the two Bi$_2$SiO$_5$ phases not only have closely contacted interfaces, but also have excellent compatibility in lattices. The structural topotactic relationship, originating from the close matching of lattice constants of these two Bi$_2$SiO$_5$ phases, could favor the formation of a phase junction and facilitate the interfacial charge transfer. Furthermore, obviously distinct characteristics in the morphology of the two Bi$_2$SiO$_5$ phases were achieved for the first time in this work.

FT-IR results are shown in Fig. 3a.† The peak located around 1029 cm$^{-1}$ is related to the stretching vibration mode of the Si-O bond while the band located around 945 cm$^{-1}$ is assigned to the stretching vibration mode of isolated (SiO$_3$)$_{6-}$ groups forming a distorted tetrahedron. The absorption band located around 856 cm$^{-1}$ is due to absorption by the stretching vibration mode of Bi–O–Si bonds.† This result confirmed the formation of Bi–O–Si and Si–O bonds with increasing amount of SiO$_3^{2-}$. BET surface area results shown in Fig. S3b† show that with increasing amount of SiO$_3^{2-}$, the BET specific surface area of the as-prepared products first increases and then decreases. S-1.5 got the most of the BET specific surface area which is almost twice that of BiOBr. As discussed above, S-1.5 has a hierarchical structure in which nanoparticles were found embedded in the self-assembled nano-sheets, thus leading to an obvious surface roughness. It can be concluded that the surface roughness of S-1.5 together with its hierarchical frameworks would help to harvest more photons to participate in photocatalytic reactions.

**Electronic structure of the Bi$_2$SiO$_5$ microsphere**

The optical properties of the as-prepared products were measured by UV–vis DRS. As shown in Fig. 4a, the absorption edges of the samples are blue shifted with increasing amount of SiO$_3^{2-}$. The band gaps ($E_g$) of the samples were estimated from the onsets of the absorption edges using the formula $\lambda_g = 1239/E_g$, where $\lambda_g$ is the band-gap wavelength. On the basis of DRS results, the estimated band gaps are 2.93, 3.01, 3.73 and 3.49 eV for BiOBr, S-1.5, S-2 and Bi$_2$SiO$_5$, respectively. It is worth noting that S-1.5 which is composed of two mixed Bi$_2$SiO$_5$ phases has a much narrower band gap in comparison with the sample Bi$_2$SiO$_5$ or S-2 (Fig. 4a). The VB top of the semiconductor could be investigated directly by valence band X-ray photoelectron spectroscopy (VB-XPS), which can directly probe the total density of the state (DOS) distribution in the

**Fig. 4** DRS spectra (a) and valence band spectra of X-ray photoelectron spectroscopy (b) for the as-prepared products.
valence band. In our investigation, VB-XPS spectra were used for the observation of extra electronic states above the valence band of BiOBr, S-1.5 and S-2. A comparison in the range of binding energies $= -1$–$4$ eV (Fig. 4b) showed the difference between the valence band of these three samples. The VB top of BiOBr, S-1.5 and S-2 was found to be $1.53$ eV, $1.64$ eV and $1.64$ eV vs. the vacuum level, respectively. $E_{g}$ is the band gap energy of the semiconductor; and $E_{CBM}$ can be determined by $E_{CBM} = E_{VBM} - E_{g}$. The values used for calculating the CBM and VBM potentials of the samples are listed in Table S1.† The band positions of the orthorhombic Bi$_2$SiO$_5$ phase (JCPDS no. 36-0287) can be achieved by the result of S-2. Then, based on the calculation results, it can be obviously seen that the conduction band (CB) potential of S-1.5 is more positive relative to that of the orthorhombic Bi$_2$SiO$_5$ phase (JCPDS no. 36-0287), indicating that the other Bi$_2$SiO$_5$ phase (JCPDS no. 36-0288) in S-1.5 should have a much shallower CB band potential than the orthorhombic Bi$_2$SiO$_5$ phase. It was reasonable to conclude that the Bi$_2$SiO$_5$ phase (JCPDS no. 36-0288) would have the same VB potential as the S-1.5 and the Bi$_2$SiO$_5$ phase (JCPDS no. 36-0287), and have the most positive CB potential, thus leading to its narrowest band gap which can respond to the visible light ($\lambda \geq 420$ nm) in the following photocatalytic experiments. As a result, the CB edge potentials of the two Bi$_2$SiO$_5$ phases enable electrons from Bi$_2$SiO$_5$ (JCPDS no. 36-0287) to easily transfer to Bi$_2$SiO$_5$ (JCPDS no. 36-0288). In such a way, long-lived reactive photo-charges can be yielded and thus the enhanced charge separation efficiency at the interface of the phase junction can be achieved. This result agrees well with other reports insisting that the formation of a phase junction would efficiently accelerate the separation efficiency of the photo-generated charges and improve the photocatalytic performance. In addition, it is reasonable to conclude that the inner electric field across the phase junction region would exist, which can improve the separation efficiency of photo-induced carriers. Scheme 2 shows the schematic diagram of the separation and transfer of photo-generated charges in the phase junction.

**Photocatalytic performance**

The photocatalytic properties of the as-prepared samples were studied under irradiation of UV light ($\lambda \approx 365$ nm), simulated solar light and visible light ($\lambda \geq 420$ nm). It can be seen that S-1.5 exhibits the best photocatalytic activity under irradiation of UV light ($\lambda \approx 365$ nm) and simulated solar light. Furthermore, as shown in Fig. 5, S-1.5 has a noticeable photocatalytic activity under visible light irradiation, whereas no activity can be detected in Bi$_2$SiO$_5$ S-2 and Bi$_2$SiO$_5$ products reported in other literature. Thus, it can be speculated that the new Bi$_2$SiO$_5$ phase (JCPDS no. 36-0288) in S-1.5 would have a much narrower band gap, thus leading to its visible light activity. It is well known that the photocatalytic activity of a catalyst is related to its microstructure, such as crystal plane, crystallinity, surface properties, BET specific surface area and so on. The highly enhanced photocatalytic activity of S-1.5 under UV and simulated solar light and irradiation can be attributed to (1) the existence of a new Bi$_2$SiO$_5$ phase (JCPDS no. 36-0288), which may act as a photosensitizer in this phase junction and consequently widen the range of spectral response, (2) the hierarchical structure with a rough surface which can benefit for light harvesting, (3) a large BET specific surface area which increases the abundant sites for the photocatalytic reactions, (4) the highly enhanced charge separation efficiency at the interface of the phase junction which helps to yield long-lived reactive charges, and ultimately improve the phenol degradation rate.

In view of practical applications, besides efficiency, the stability and durability are also indispensable to photocatalysts. The catalyst recovered from the 1st cycle is reused in the second cycle and the same is continued up to 4 cycles. In the case of sample S-1.5, the photodegradation rate of 4 rounds of the continuous recycle photodegradation test is 86.85%, 85.72%, 83.19%, and 79.78%, respectively (Fig. S4a†), indicating a good stability of the photocatalytic performance. In addition, XRD patterns of S-1.5 before and after 4 cycles of the photocatalytic reactions were also investigated, as shown in Fig. S4b.† A decreased intensity of XRD peaks suggests that the crystal structure of the sample has been affected in some way.
Conclusions

In summary, a novel Bi$_2$SiO$_5$ phase junction with an interesting microsphere structure has been successfully prepared through the ion exchange method using BiOBr microspheres as the sacrificial template. Moreover, it exhibits a narrowed band gap, noticeable visible light activity and highly enhanced UV or simulated solar light activity compared with pure Bi$_2$SiO$_5$ and other reported Bi$_2$SiO$_5$ products. The exceptional photocatalytic activity of phenol degradation under visible light irradiation of the Bi$_2$SiO$_5$ phase junction was ascribed to the existence of the tetragonal Bi$_2$SiO$_5$ phase (JCPDS no. 36-0288) with a narrower band gap. The efficient separation of photo-generated carriers via a phase junction, highlight harvesting efficiency due to its hierarchical structure with a rough surface together with a large BET specific surface area are supposed to be responsible for its highly enhanced photocatalytic activity under UV and simulated solar light irradiation.

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Notes and references

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