University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

1-1-2016

A ferroelectric photocatalyst Ag₁₀Si₄O₁₃ with visible-light photooxidation properties

Amar Al-Keisy

University of Wollongong, ahjak378@uowmail.edu.au

Long Ren

University of Wollongong, lr289@uowmail.edu.au

Dandan Cui

Beihang University

Zhongfei Xu

Beihang University

Xun Xu

University of Wollongong, xun@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>

Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

A ferroelectric photocatalyst Ag₁₀Si₄O₁₃ with visible-light photooxidation properties

Abstract

Ferroelectric p-block semiconductors are regarded as a new family of visible-light photocatalysts because of their dispersive and anisotropic band structures, as well as their intrinsic internal electric field. Silver silicates belong to this family and have band structures and an internal electric field that can be engineered by modulating the stoichiometry of Ag and SiO₄. Here, we have developed a new ferroelectric p-block photocatalyst, Ag₁₀Si₄O₁₃, by materials design and band engineering, which exhibits excellent photocatalytic activity towards the degradation of organic compounds, which is driven by visible light. Owing to the unique d¹⁰ and sp³/p configurations in its electronic structure, Ag₁₀Si₄O₁₃ possesses an indirect band gap of 1.72 eV with a highly dispersive conductive band and a flat valence band. This electronic structure promotes the generation, separation, and mobility of photo-induced charge carriers under visible-light illumination, which has been verified experimentally and theoretically. The compatible energy level of the conduction band determines its strong photo-oxidative capability. Moreover, the charge transfer process takes advantage of the existence of an internal electric field in Ag₁₀Si₄O₁₃, which is attributed to the distorted SiO₄ chain structure.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Al-Keisy, A., Ren, L., Cui, D., Xu, Z., Xu, X., Su, X., Hao, W., Dou, S. X. & Du, Y. (2016). A ferroelectric photocatalyst Ag₁₀Si₄O₁₃ with visible-light photooxidation properties. *Journal of Materials Chemistry A*, 4 (28), 10992-10999.

Authors

Amar Al-Keisy, Long Ren, Dandan Cui, Zhongfei Xu, Xun Xu, Xiangdong Su, Weichang Hao, S X. Dou, and Yi Du

A Ferroelectric Photocatalyst Ag₁₀Si₄O₁₃ with Visible-light Photooxidation Properties†

Amar Al-keisy,^{⊥ a} Long Ren,^{⊥ a} Dandan Cui,^b Zhongfei Xu,^b Xun Xu,^{a d} Xiangdong Su,^c Weichang Hao,^{b d *} Shi Xue Dou,^a Yi Du^{a d *}

The ferroelectric *p*-block semiconductors are regarded as a new family of visible-light photocatalysts because of their dispersive and anisotropic band structures, as well as their intrinsic internal electric field. Silver silicates belong to this family and have band structures and internal electric field that can be engineered by modulating the stoichiometry of Ag and SiO₄. Here, we have developed a new ferroelectric *p*-block photocatalyst, Ag₁₀Si₄O₁₃, by material design and band engineering, which exhibits excellent photocatalytic activity towards the degradation of organic compounds, which is driven by visible light. Owing to the unique *d*¹⁰ and *sp/p* configurations in its electronic structure, Ag₁₀Si₄O₁₃ possesses an indirect band gap of 1.72 eV with a highly dispersive conductive band and a flat valence band. This electronic structure promotes the generation, separation, and mobility of photo-induced charge carriers under visible-light illumination, which has been verified experimentally and theoretically. The compatible energy level of the conduction band determines its strong photo-oxidative capability. Moreover, the charge transfer process takes advantage of the existence of an internal electric field in Ag₁₀Si₄O₁₃, which is attributed to the distorted SiO₄ chain structure.

INTRODUCTION

Photocatalysis is one of the most promising ways to solve the energy crisis and environmental pollution issues by using solar energy.¹⁻¹¹ A number of photocatalysts have been proposed and prepared using materials design and band engineering techniques. Some have achieved excellent photocatalytic performance in either water splitting or the elimination of organic pollution. Nevertheless, most of the high-performance photocatalysts proposed so far are transition metal oxide (TMO) based materials. Generally, TMOs have wide band gaps (> 3.0 eV) due to partially filled d-orbitals,¹²⁻¹⁵ which limits the absorption of visible light. In addition, their valence bands (VBs) and conduction bands (CBs) are less dispersive due to the isotropic d orbitals of transition metals (TM). The photo-induced charge carriers are hence given a large effective mass, which hinders charge separation and mobility, and results in low quantum conversion efficiency in photocatalysis, especially in the visible light spectrum. Consequently, their visible-light photocatalytic performances are not as high as desired. Therefore, the exploration and

development of new visible-light responsive photocatalysts with high quantum conversion efficiency through materials design and band engineering have emerged as an urgent and challenging task in the field of photocatalysis.

Recently, AgO-based compounds have been reported with excellent visible-light-driven photocatalytic activities,¹⁶⁻²⁴ because of their unique electronic configurations. Since the *d* orbitals of Ag are fully filled, the *p* orbitals in these compounds play an important role in the energy levels and dispersion of the VB and CB. Generally, *p* orbitals lift the top of the VB and/or lower the bottom of the CB in AgO-based photocatalysts, and promote generation of photo-induced electrons and holes under visible light. Moreover, highly dispersive VBs or CBs can be formed due to anisotropic *p* or hybridized *sp* states. As a result, the effective mass of photo-induced charge carriers is much smaller in AgO-based compounds, which facilitates charge transfer in the photocatalytic process under visible-light irradiation.^{25,26} Nevertheless, the narrow band gap and dispersive electronic structure also facilitate the recombination of electrons and holes in the photocatalytic process and, in turn, would limit the photocatalytic activities of these compounds. Therefore, AgO-based compounds with efficient charge separation in photocatalysis are still desired, although their visible-light photocatalytic performance is much higher than those of the TMOs. Among these AgO-based compounds, an Ag-incorporated *p*-block family, silver silicate (Ag_xSi_yO_z),^{19,20,24} has captured our attention recently. Besides the unique *d*¹⁰ state of Ag, both Si and O in Ag_xSi_yO_z have typical *sp/p* electronic configurations, which make the band gap, and the VB and CB in Ag_xSi_yO_z very likely to conform to the optimum electronic structure for visible-light-driven photocatalysts. In particular,

^a Institute for Superconducting and Electronic Materials (ISEM), Australian Institute for Innovative Materials (AIIM), University of Wollongong, Wollongong, NSW 2525, Australia * E-mail for Y. D. : yi_du@uow.edu.au

^b Department of Physics and Key Laboratory of Micro-nano Measurement, Manipulation and Physics, Ministry of Education (MOE), Beihang University, Beijing 100191, China * E-mail for W. H. : whao@buaa.edu.cn

^c School of Materials and Metallurgy, Guizhou Institute of Technology, Guizhou 550007, China

^d UOW-BUAA Joint Research Centre, University of Wollongong, Wollongong, NSW 2525, Australia

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

[⊥] Authors contributed equally.

an internal electric field is expected in $\text{Ag}_x\text{Si}_y\text{O}_z$ compounds, owing to the spontaneous electronic polarization induced by the distorted tetrahedral unit (SiO_4) arrangement.²⁷⁻²⁹ This internal electric field can effectively promote spatial charge separation, which addresses the electron-hole recombination issues that are found in the other AgO-based compounds. Moreover, the strength of the internal electric field can be feasibly modulated by the number of distorted arrangements of SiO_4 tetrahedral, and enhances the photocatalytic activity of silver silicate. As a consequence, $\text{Ag}_x\text{Si}_y\text{O}_z$ is regarded as a promising compound family for exploring new visible-light-driven photocatalysts because of these unique crystal and electronic structures. Nevertheless, there have been very few investigations aimed at the design and development of $\text{Ag}_x\text{Si}_y\text{O}_z$ photocatalysts so far.

In this work, we report a new visible-light-driven silver silicate photocatalyst, $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, which demonstrates high photocatalytic activity towards the elimination of organics. It was found that the excellent photocatalytic performance of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ originates from its anisotropic and highly dispersive band structure due to its *p*-block electronic configuration. Moreover, $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ is expected to have a large ferroelectric polarization due to long distorted SiO_4 chains in comparison to the other $\text{Ag}_x\text{Si}_y\text{O}_z$ ferroelectric materials. It induces an intrinsic internal electric field in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, which further enhances the photocatalytic activity by effective separation of photo-induced charges. Our experimental and theoretical results suggest that silver silicates are promising candidate materials to explore visible-light-active photocatalysts through structural and electronic engineering.

EXPERIMENTAL SECTION

Sample preparation. In a typical experimental process, AgNO_3 and Na_2SiO_3 (99.9%, Sigma-Aldrich Company) were mixed in a mortar in a molar ratio of 2:1 and then pressed into a disk 1 cm in diameter and 3 mm in thickness. The disk was heated in air at 400 °C for 2 h. After that, the product was washed three times with distilled water and ethanol to remove residual NaNO_3 and AgNO_3 . The sample was dried at 60 °C for 12 h. For comparison, the photocatalytic activity of N doped TiO_2 was synthesized according to the original report.²

Sample characterizations.

The purity and crystallinity of the sample were investigated by X-ray diffraction (XRD, GBC, MMA) using $\text{Cu K}\alpha$ radiation with $\lambda = 1.5418 \text{ \AA}$. The sample morphology and elemental analysis were investigated by field emission scanning electron microscopy (FESEM, JEOL-7500). The composition of the samples was examined by energy dispersive spectroscopy (EDS) attached to the FESEM. Transmission electron microscope (TEM) images and SAED patterns were obtained using a JEOL ARM-200F. X-ray photoelectron spectroscopy (XPS, PHI660) was performed using a monochromatic $\text{Mg K}\alpha$ X-ray source. An ultraviolet-visible spectrophotometer (UV-Vis, Shimadzu-3600) was used to measure diffuse reflectance spectra (DRS) by adding an integrating sphere attachment to

the instrument, with BaSO_4 providing a background between 200 nm and 800 nm. The polarization as a function of electric field was obtained using an Easy Check 300 (aixACCT Systems GmbH) equipped with a Trek 610E high voltage source. In the photocurrent-time response system, a 300 W Xe lamp with a monochromator and a cut-off filter ($\lambda > 400 \text{ nm}$) was used as the light source. The photocurrent as a function of irradiation time under visible light was collected by a KEITHLEY 2400 source meter. The surface photovoltage (SPV) spectroscopy apparatus is composed of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), and a photovoltaic cell. A 500 W Xe lamp (CHFXQ500W, Global Xenon Lamp Power) and a grating monochromator (Omni-5007, no. 09010, Zolix) provide monochromatic light. The construction of the photocurrent-time-response cell and the photovoltaic cell was in the form of a sandwich-like structure of indium tin oxide (ITO)-sample-ITO. The Mott-Schottky curves were collected with a PARSTAT-2273 Advanced Electrochemical System (Princeton Applied Research). The $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ film, Pt foil, SCE, and saturated KCl solution were used as working, counter, and reference electrodes, and as the electrolyte, respectively. The working electrode was prepared via the dip-coating method. The Mott-Schottky measurements were monitored at a fixed frequency of 100 Hz with 10 mV amplitude at various potentials.

Photocatalytic activity measurements. Rhodamine B (RhB), methyl orange (MO), methylene blue (MB), and phenol were used as target organics in photocatalytic degradation tests. All the dyes and the phenol were purchased from Sigma-Aldrich. The photocatalytic activity was carried out at room temperature using $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ as photocatalyst. The light source used in the photocatalytic measurements was a 300 W W-Xe lamp with a UV cut-off filter ($\lambda > 420 \text{ nm}$). In a typical process, 100 ml of RhB, MO, or MB solution (10 mg/L for all dyes) and 0.1 g $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ were added together in a 250 ml beaker. The suspensions were magnetically stirred in the dark for 30 min to reach adsorption-desorption equilibrium, and then the mixture was exposed to the light source. The photodegradation of the dye solutions was analysed by UV-Vis spectrophotometer. To stand in for real organic pollutants, phenol was used under the same conditions, but the concentration and volume were 20 mg/L and 50ml respectively, a sample taken every 20 min. For comparison, the photocatalytic activity of N doped TiO_2 was measured under the same conditions.

Theoretical calculations. The calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) based on density functional theory with the projector augmented wave (PAW) pseudopotential method. We applied hybrid functional calculations to simulate ferroelectricity in this work. The short-range exchange potential was calculated by mixing a fraction of nonlocal Hartree-Fock exchange with the generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE). A conjugate-gradient algorithm was used to relax the ions into their ground states, and the energies and

the forces on each ion were converged within 1×10^{-5} eV/atom and 0.01 eV/Å, respectively. The Koln-Sham orbitals were expanded by a plane wave basis set, and an energy cut-off of 550 eV was used throughout. The Brillouin-zone integration was performed by using the Gamma-centered Monkhorst-Pack scheme with $6 \times 4 \times 3$ k-points.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern of the as-prepared sample is shown in Fig. 1a. All the diffraction peaks can be indexed to $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ with a triclinic structure (space group $P-1$), according to the Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 01-071-1365. The sample consists of phase-pure reddish powders without any observable impurities. In the triclinic structure of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, as illustrated in the inset of Fig. 1a, four tetrahedral SiO_4 units are connected through a corner-shared oxygen atom, forming a distorted Si_4O_{13} chain which is coordinated with the Ag ions. The field emission scanning electron microscope (FESEM) images reveal that the as-prepared $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ sample consists of micron-sized irregular particles (Fig. 1b). As shown in Fig. S1†, the selected area electron diffraction (SAED) pattern verifies excellent crystallinity of the $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ sample. HRTEM results clearly show the lattice fringes of as-prepared $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ particles with d-spacing of 0.197 and 0.279 nm, which can be assigned to (-104) and (-411) directions of triclinic structure, respectively. The elemental composition and chemical states of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ were further analysed by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 1c. The survey spectrum demonstrates that the main peaks correspond to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, O 1s, and Si 2p orbitals for the $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ sample. Detailed spectra providing the fine information for Ag, Si, and O are presented in (Fig. S1c, S1d and S1e†) in which the peaks of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ are located at 367 eV and 373 eV, whereas the peaks of Si 2p and O 1s are located at 100.8 eV and 530.6 eV, respectively. The valences of Ag and Si are thus identified as +1 and +4, respectively. The energy dispersive spectroscopy (EDS) spectrum shows (Fig. S1f†) that the atomic percentages of Ag, Si, and O in the sample are 26%, 12%, and 42%, respectively, which further confirms the composition of phase-pure $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. Fig. 1d shows the diffuse reflectance spectrum of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ collected by ultraviolet-visible (UV-Vis) spectroscopy. The absorption edge is located at about 700 nm. The band gap (E_g) of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ was then estimated to be 1.72 eV according to the Tauc formula,³⁰ as is shown in the upper right inset of Fig. 1d. It indicates that $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ can absorb almost all the visible-light spectrum.

The narrow band gap of the as-prepared $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ sample is believed to have arisen from the hybridization of different orbitals in this Ag-incorporated p -block compound. Thus, density functional theory (DFT) calculations were carried out in order to reveal the electronic structure of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. The calculated band structure is shown in Fig. 2a. The band gap is calculated as 1.71 eV, which agrees well with our experimental results based on the photo-absorption edge. The high symmetry points of the CB and VB are located at the Γ and Z

points, respectively, giving $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ the features of a typical indirect band-gap semiconductor. It is well known that the excited electrons in an indirect-band-gap semiconductor have a longer lifetime. The separation and migration of photo-induced charge carriers are thus expected to be more efficient. Moreover, a typical signature band structure of the p -block configuration is revealed by our DFT results, in which the CB is highly dispersive whereas the VB shows much less dispersion in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. As shown in Fig. 2b, the CB of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ mainly consists of Ag 5s and 5p orbitals. The large amount of hybridization between Ag s and Ag p occurs due to short Ag-Ag bonds. This indicates that the CB is constructed without the “contamination” of less dispersive d states. As a result, the photo-excited electrons have a small effective mass, which enables photo-excited electrons to easily move to surface active sites due to their high mobility. In contrast, the VB of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ is mainly contributed by Ag 4d orbitals. This leads to a flatter band (as compared to the CB) and thus generates “heavy” holes in the photo-excitation process. This electronic configuration suggests high quantum conversion efficiency for $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ under visible light. It is well known that the energy positions of the CB and VB are the primary factors that determine whether the semiconductor can be used in photocatalytic reduction or oxidation. We therefore carried out Mott-Schottky measurements of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, as shown in Fig. 2c. The relative position of the CB edge can be calculated from the empirical equation³¹: $E_c = \chi - 0.5 E_g + E_0$, where E_0 is a scale factor relating the reference electrode redox level to the absolute vacuum scale ($E_0 = -4.5$ eV for normal hydrogen electrode (NHE)), E_g is the band gap, and χ is the absolute electronegativity of the semiconductor. The calculated E_c from this equation is empirical and theoretical. Therefore, electrochemical flat-band potential measurements were adopted. The flat-band potential values are obtained by the Mott-Schottky equation^{32,33}:

$$\frac{1}{C^2} = \frac{2}{\epsilon \epsilon_0 N_D} \left(E - E_{fb} - \frac{k_B T}{q} \right)$$

where C is the space charge capacitance, N_D is the donor density, ϵ and ϵ_0 are the dielectric constants of free space and the film electrode, respectively, E is the applied potential, E_{fb} is the flat-band potential, k_B is Boltzmann’s constant, T is the temperature, and q is the electronic charge. The E_{fb} value can be determined from the extrapolation to $1/C^2 = 0$, as shown in Fig. 2c. The flat potential is calculated to be 0.523 V versus saturated calomel electrode (SCE), which is equivalent to 0.729 V (NHE vs. Ag/AgCl = 0.206 V). It is well accepted that the CB of n -type semiconductors is about -0.1 V higher than the flat potentials, depending on the electron effective mass and carrier concentration. With an applied voltage difference of 0.05 eV between the conduction band and the flat potential, the bottom of the CB is derived as 0.679 eV. The inset in Fig. 2c shows a schematic diagram of the redox potential of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, corresponding to the Mott-Schottky fitting result. The CB and VB edges (inset Fig. 2c) of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ are +0.679 eV and +2.4 eV vs. NHE, respectively. The lower potential of the VB with respect to the $\text{O}_2/\text{H}_2\text{O}$ redox potential indicates that

Ag₁₀Si₄O₁₃ possesses strong photo-oxidative capabilities and can be used as an oxidative photocatalyst.

In view of the possible strong photo-oxidative capability, the photocatalytic activity of Ag₁₀Si₄O₁₃ was evaluated by the photodegradation of organic compounds, including Rhodamine B (RhB), Methyl orange (MO), methylene blue (MB), and phenol, under visible light irradiation. The results are shown in Fig. 3 and in (Fig. S2a and S2b†). All the photocatalytic degradation measurements were carried out after the dark reaction, in which the equilibrium adsorption states were reached.

The Ag₁₀Si₄O₁₃ sample exhibits excellent visible-light photocatalytic degradation activity, which is better than that of N doped TiO₂ and the other AgO-based reference samples. For example, under visible-light irradiation, the absorption peak of MB at 664 nm decreased rapidly with increasing irradiation time and eventually disappeared after 40 min, suggesting excellent photocatalytic performance of the Ag₁₀Si₄O₁₃ (Fig. 3a). This demonstrates that the MB can be completely degraded by Ag₁₀Si₄O₁₃ under visible light. The inset in Fig. 3a shows the visible changes in the color concentration of the MB solution during the photo-oxidation process. The excellent photocatalytic degradation activities of Ag₁₀Si₄O₁₃ were also demonstrated with the other dyes, which are shown in (Fig. S2a, S2b†). By monitoring the signature absorption peaks of RhB, MB, and MO at 556 nm, 664 nm, and 470 nm, respectively, plots of the visible-light degradation ratio versus reaction time were obtained and are shown in Fig. 3b. We note that the complete degradation of MB and RhB, and the 80% degradation of MO can be achieved after 30 min, 40 min, and 40 min, respectively. The photocatalytic degradation reaction of the samples followed the pseudo-first-order linear relationship with reaction rate constants (*k*) as shown in the inset of Fig. 3b. The photocatalytic stability of Ag₁₀Si₄O₁₃ in photodegradation was also studied by a photocatalytic cycling test, as shown in (Fig. S3†). Ag₁₀Si₄O₁₃ shows stable photocatalytic performance for eight photocatalytic degradation cycles. The decreased photocatalytic activity in the first several rounds is due to initial instability of Ag₁₀Si₄O₁₃, which is general for the other Ag-based photocatalysts.^{34,35} It is believed that a small amount of Ag nanoparticles form on the surface of Ag₁₀Si₄O₁₃ at the very beginning photocatalytic cycles. These Ag nanoparticles then function as electron trapping centres to suppress further photocorrosion of the samples, which is evident by stable photocatalytic performance after third run. It should be noted that our Ag₁₀Si₄O₁₃ sample shows much higher photo-oxidation activity than the N doped TiO₂ reference sample under visible-light, as shown in Fig. 3c, which verifies its excellent visible-light photocatalytic activity towards degradation of organics. We also carried out photocatalytic degradation of colorless phenol over our Ag₁₀Si₄O₁₃ sample under visible light irradiation. As shown in Fig. 3d and Fig. S4a†, it is found that the phenol can be completely degraded in 80 min. The inset in Fig. 3d shows the plots of the rate constants (*k*) versus reaction time. The above results confirm that the photocatalytic dye degradation activity of Ag₁₀Si₄O₁₃ cannot be attributed to the

dye-sensitization effect because the colorless phenol only absorbs light with wavelengths of 260-280 nm. The *k* of MB, MO, RhB and phenol were 6, 2.68, 5.7, 2.7 s⁻¹ respectively as shown in (Table S1†). and the apparent quantum efficiency were 0.78, 0.83, 1.23, 5.9 respectively.³⁶

The mechanism behind the excellent visible-light photocatalytic activity of our Ag₁₀Si₄O₁₃ sample was investigated. It is well known that the photocatalytic activity is dominated by several chemical dynamic processes in photocatalysis, including charge excitation, charge separation, and charge transfer. In our photocatalytic degradation measurements, Ag₁₀Si₄O₁₃ shows superior photocatalytic activity relative to N doped TiO₂ and the other Ag-based *p*-block photocatalysts (see Fig. S4b†). This indicates that one or several key steps involved in the photocatalytic dynamics under visible light would be promoted by the electronic structure of Ag₁₀Si₄O₁₃. We carried out photocurrent response measurements of Ag₁₀Si₄O₁₃ under visible light irradiation, as shown in (Fig. S5a†). It can be seen that the photocurrent generated in Ag₁₀Si₄O₁₃ under visible light is 1.4×10^{-1} mA/cm², which is higher than that (1×10^{-1} mA/cm²) of a typical visible-light-driven AgO-based photocatalyst Ag₃PO₄.³⁷ The ON-OFF cycles measurement of photocurrent demonstrates that Ag₁₀Si₄O₁₃ possesses high quantum conversion efficiency, and there is a low recombination rate of photo-induced charge carriers under visible-light illumination. It should note that gradually decrease of photocurrent at first three cycles is due to photocorrosion of sample as a result of formation of Ag nanoparticles. We went on to collect surface photovoltage spectra (Fig. S5b†), which confirms the high separation rate of photo-induced charge carriers in Ag₁₀Si₄O₁₃, especially in the spectral range from 300 to 600 nm. The efficient separation of photo-induced charges is most likely the key factor contributing to the excellent photocatalytic activity of Ag₁₀Si₄O₁₃, as compared to the other *p*-block photocatalysts.

In fact, the separation of electron-hole pairs in Ag₁₀Si₄O₁₃ would not be expected to be so effective if one only considered its electronic structure. The reasons for the greater efficiency are as follows: Firstly, the charge recombination process also takes advantage of the dispersive band structure in Ag₁₀Si₄O₁₃. The chances for separation and recombination would be traded off in the photocatalytic process. Secondly, our DFT results reveal that photo-induced holes in Ag₁₀Si₄O₁₃ possess a large effective mass due to the relatively flat VB. This would be expected to limit the movement of photo-induced holes to surface active sites of Ag₁₀Si₄O₁₃, and thereby, limit the photo-oxidative activity of Ag₁₀Si₄O₁₃. Nevertheless, this is obviously contradictory to our results on the photocatalytic degradation of dyes and phenol in Fig. 3. Therefore, it is suspected that the effective separation of photo-induced charge carriers in Ag₁₀Si₄O₁₃ is caused by another mechanism in addition to the *p*-block electronic configuration.

In Ag₃Si₂O₇ compounds, an internal electric field may exist due to the distorted SiO₄ tetrahedral chains that are formed in the crystal structure. This internal electric field can overcome charge recombination and promote spatial separation of electrons and holes. Interestingly, Ag₁₀Si₄O₁₃ has the longest

distorted SiO_4 chains in the $\text{Ag}_x\text{Si}_y\text{O}_z$ family. They most likely induce an internal field due to spontaneous polarization. In order to verify this, a ferroelectric polarization measurement was conducted. As shown in Fig. 4a, we observed the ferroelectric polarization-electric field (P - E) hysteresis loops of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, which were obtained through a pulsed positive-up-negative-down (PUND) polarization measurement. A typical unsaturated ferroelectric hysteresis loop with a remanent polarization (P_r) of $0.05 \mu\text{C}/\text{cm}^2$ was obtained in electric field of $100 \text{ V}/\text{cm}$, as shown in Fig. 4a. This result verifies the existence of an internal electric field in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ due to an intrinsic electric polarization. Corresponding to the DFT-simulated three-dimensional (3D) charge density distribution (Fig. 4b), the spontaneous electric polarization in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ is attributed to misaligned positive and negative charge centers in the $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ unit cells, in which O is the charge acceptor and Si is the main charge donor, with little charge decrease for Ag in the crystal. This result suggests that the spontaneous electric polarization in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ is attributable to misaligned positive and negative charge centers, which are mainly induced by the asymmetrical Si-O tetrahedral chains in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ unit cells. Given this structure, the calculated spontaneous polarization is about $64.78 \mu\text{C}/\text{cm}^2$, and the polarization direction is indicated in Fig. 4(c). We also find that the O1-O1 bonds in the chains are twisted with angles of 143° and 166.4° (Fig. S6[†]), accompanied by a coherent displacement of the Ag ions, as well as a distortion of the O3. The SiO_4 tetrahedra show a spiral distortion with respect to each other on the SiO_4 chains. The spontaneous polarization along the c direction is induced by the relative displacement of these anionic SiO_4 tetrahedral units and cationic Ag-O layers. Concurrently, the Ag ions are slightly shifted to a direction normal to the O3, thereby also creating electronic polarization along the a direction. The internal electric field is believed to be the main driving force for charge separation in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. Our investigation has demonstrated that the excellent visible-light photocatalytic activity of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ is attributable to its p -block electronic structure as well as structural distortion, which provides a new strategy to design and develop visible-light-driven photocatalysts to eliminate pollution.

Conclusions

The visible-light-driven photocatalyst $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ was synthesized by the ion-exchange method. It was found that $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ possesses excellent photocatalytic performance towards degradation of dyes and phenol over the entire visible light spectrum. The photocatalytic activity of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ is attributed to high quantum conversion efficiency because of its narrow band gap, dispersive band structure, and internal electric field. This unique electronic structure and internal electric field originate from the p -block electronic configuration and distorted SiO_4 chains in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$.

Acknowledgements

This work is supported by the Australian Research Council (ARC) through a Discovery Project (DP 140102581), the National Natural Science Foundation of China (Grant No. 51072012, No. 51272015), the Fundamental Research Funds for the Central Universities (Grand No.: YWF-16-JCTD-B-03), and the Beijing Key Discipline Foundation of Condensed Matter Physics). The authors acknowledge the service supported by Electronic Microscopy Centre at the University of Wollongong. The authors thank Dr. T. Silver for her valuable comments on this work.

References

- 1 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37-38.
- 2 V. Vaiano, O. Sacco, D. Sannino and P. Ciambelli, *Chem. Eng. J.*, 2015, **261**, 3-8.
- 3 O. Sacco, V. Vaiano, C. Han, D. Sannino and D. D. Dionysiou, *Appl. Catal. B*, 2015, **164**, 462-472.
- 4 M. Takeuchi, H. Yamashita, M. Matsuoka, M. Anpo, T. Hirao, N. Itoh and N. Iwamoto, *Catal. Lett.*, 2000, **66**, 185-187.
- 5 S. Klosek and D. Raftery, *J. Phys. Chem. B*, 2001, **105**, 2815-2819.
- 6 M. Khan, S. R. Gul, J. Li, W. Cao and A. G. Mamalis, *Mater. Res. Express*, 2015, **2**, 066201.
- 7 Q. Wang, M. Chen, N. Zhu, X. Shi, H. Jin, Y. Zhang and Y. Cong, *J. Colloid Interface Sci.*, 2015, **448**, 407-416.
- 8 K. M. Cho, K. H. Kim, H. O. Choi and H.-T. Jung, *Green Chem.*, 2015, **17**, 3972-3978.
- 9 M. Aslam, I. M. I. Ismail, S. Chandrasekaran and A. Hameed, *J. Hazard. Mater.*, 2014, **276**, 120-128.
- 10 D. Lang, Q. Xiang, G. Qiu, X. Feng and F. Liu, *Dalton Trans.*, 2014, **43**, 7245-7253.
- 11 J. Shang, W. Hao, X. Lv, T. Wang, X. Wang, Y. Du, S. Dou, T. Xie, D. Wang and J. Wang, *ACS Catal.*, 2014, **4**, 954-961.
- 12 C. Janáky, K. Rajeshwar, N. R. de Tacconi, W. Chanmanee and M. N. Huda, *Catal. Today*, 2013, **199**, 53-64.
- 13 F. Meng, J. Li, Z. Hong, M. Zhi, A. Sakla, C. Xiang and N. Wu, *Catal. Today*, 2013, **199**, 48-52.
- 14 Z. Shu, X. Jiao and D. Chen, *CrystEngComm*, 2013, **15**, 4288-4294.
- 15 H. Yan, X. Wang, M. Yao and X. Yao, *Prog. Nat. Sci.*, 2013, **23**, 402-407.
- 16 C. Xu, Y. Liu, B. Huang, H. Li, X. Qin, X. Zhang and Y. Dai, *Appl. Surf. Sci.*, 2011, **257**, 8732-8736.
- 17 S. Ouyang, N. Kikugawa, Z. Zou and J. Ye, *Appl. Catal. A*, 2009, **366**, 309-314.
- 18 Y. Maruyama, H. Irie and K. Hashimoto, *J. Phys. Chem. B*, 2006, **110**, 23274-23278.
- 19 T.-G. Kim, D.-H. Yeon, T. Kim, J. Lee and S.-J. Im, *Appl. Phys. Lett.*, 2013, **103**, 043904.
- 20 X. Zhu, Z. Wang, B. Huang, W. Wei, Y. Dai, X. Zhang and X. Qin, *APL Mater.*, 2015, **3**, 104413.
- 21 J. Zhao, Z. Ji, C. Xu, X. Shen, L. Ma and X. Liu, *Cryst. Res. Technol.*, 2014, **49**, 975-981.
- 22 J. Tang, D. Li, Z. Feng, Z. Tan and B. Ou, *RSC Adv.*, 2014, **4**, 2151-2154.
- 23 K. Yu, S. Yang, C. Liu, H. Chen, H. Li, C. Sun and S. A. Boyd, *Environ. Sci. Technol.*, 2012, **46**, 7318-7326.
- 24 Z. Lou, B. Huang, Z. Wang, X. Ma, R. Zhang, X. Zhang, X. Qin, Y. Dai and M.-H. Whangbo, *Chem. Mater.*, 2014, **26**, 3873-3875.
- 25 H. Feng, Z. Xu, L. Wang, Y. Yu, D. Mitchell, D. Cui, X. Xu, J. Shi, T. Sannomiya, Y. Du, W. Hao and S. X. Dou, *ACS Appl. Mater. Interfaces*, 2015, **7**, 27592-27596.

- 26 L. Wang, J. Shang, W. Hao, S. Jiang, S. Huang, T. Wang, Z. Sun, Y. Du, S. Dou, T. Xie, D. Wang and J. Wang, *Sci. Rep.*, 2014, **4**, 7384.
- 27 H. Taniguchi, A. Kuwabara, J. Kim, Y. Kim, H. Moriwake, S. Kim, T. Hoshiyama, T. Koyama, S. Mori, M. Takata, H. Hosono, Y. Inaguma and M. Itoh, *Angew. Chem. Int. Ed.*, 2013, **52**, 8088-8092.
- 28 D. Seol, H. Taniguchi, J.-Y. Hwang, M. Itoh, H. Shin, S. W. Kim and Y. Kim, *Nanoscale*, 2015, **7**, 11561-11565.
- 29 T. H. Akira SAHASHI, Hiroaki TAKEDA and Takaaki TSURUMI, *J. Ceram. Soc. Jpn.*, 2014, **122**, 389-392.
- 30 J. Tauc, R. Grigorovici and A. Vancu, *Phys. Status Solidi B*, 1966, **15**, 627-637.
- 31 M. A. Butler and D. S. Ginley, *J. Electrochem. Soc.*, 1978, **125**, 228-232.
- 32 K. Gelderman, L. Lee and S. W. Donne, *J. Chem. Educ.*, 2007, **84**, 685.
- 33 F. Cardon and W. P. Gomes, *J. Phys. D: Appl. Phys.*, 1978, **11**, L63.
- 34 D. Xu, B. Cheng, J. Zhang, W. Wang, J. Yu, W. Ho, *J. Mater. Chem A*, 2015, **3**, 20153-20166.
- 35 Z. Yi, J. H. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuart-Williams, H. Yang, J. Cao, W. Luo, Z. Li, Y. Liu and R. L. Withers. *Nat. Mater.*, 2010, **9**, 559-564.
- 36 J. M. Buriak, P. V. Kamat and K. S. Schanze, *ACS Appl. Mater. Interfaces*, 2014, **6**, 11815-11816.
- 37 C. Cui, Y. Wang, D. Liang, W. Cui, H. Hu, B. Lu, S. Xu, X. Li, C. Wang and Y. Yang, *Applied Catalysis B: Environmental*, 2014, **158-159**, 150-160.

Figures, Scheme, Charts

Figure 1 (a) XRD pattern of as-prepared $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. The inset is the crystal structure of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. (b) SEM image of as-prepared $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ sample. (c) XPS result of as-prepared $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. (d) UV-vis diffuse reflectance spectra of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. Inset at right top of (d) is the derivation of the band gap value of as-prepared $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ which is derived from diffuse reflectance spectrum. Inset at left bottom of (d) is photograph of the as-prepared photocatalyst.

Figure 2 (a) DFT calculated electronic structure of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, in which a dispersive CB and flat VB can be observed. (b) Partial density of states calculated by DFT. (c) Mott-Schottky plot of pure $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. The flat band potential is determined to be about 0.523 V. The inset is a schematic diagram of the redox potential of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$, corresponding to the Mott-Schottky fitting results schematic of band-edge potentials of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$.

Figure 3 (a) UV-Visible absorbance spectra for photodegradation of MB dye over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ under visible light, recorded after different degradation times. The inset shows the color changes of the MB solutions corresponding to the five degradation times from 0 min to 40 min. (b) Photodegradation rate of organic dyes over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ under visible light. The inset show kinetic study of photocatalytic degradation process of organic dyes under visible light over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. (c) Comparison of photodegradation percentages of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ and N doped TiO_2 (N-TiO₂) under visible light for different organic dyes. (d) Photodegradation rate of phenol under visible light over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. The inset show kinetic study of photocatalytic degradation process of phenol under visible light over $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$.

Figure 4 (a) P–E hysteresis loop of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ at different applied voltage and frequency 1 kHz. (b) Charge density maps, the isosurfaces are $0.01e / \text{\AA}^3$ of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$. (c) Crystal structure of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ to show polarization direction.