# Amorphous Materials

# One-Step Synthesis of Amorphous Silver Silicates with Tunable Light Absorption Spectra and Photocatalytic Activities in the Visible Region

Zaizhu Lou,<sup>[a]</sup> Zeyan Wang,<sup>\*[a]</sup> Baibiao Huang,<sup>\*[a]</sup> Ying Dai,<sup>[b]</sup> Gang Wang,<sup>[a]</sup> Zaiyong Jiang,<sup>[a]</sup> Xiaoyang Zhang,<sup>[a]</sup> Xiaoyan Qin,<sup>[a]</sup> and Yanqing Li<sup>[a]</sup>

**Abstract:** A series of amorphous silver silicates with different compositions were synthesized for the first time by one-step co-precipitation. Silicate ions were found to have important role on determining visible light absorption and photocatalytic activities of amorphous silver silicates, and the sample with Ag/Si ratio of 3.20 exhibits optimal photocatalytic activity.

As a promising approach to utilizing solar energy, photocatalysis has attracted increasing interest owing to its potential applications in water splitting for hydrogen evolution,<sup>[1]</sup> decomposition of organic contaminants,<sup>[2]</sup> and carbon dioxide reduction.<sup>[3]</sup> In the past forty years, various photocatalysts have been developed, among which  ${\rm TiO}_{\rm 2}$  is still the most investigated, owing to its high reactivity and stability. However, limited by its wide band gap, TiO<sub>2</sub> can only absorb and utilize UV light, which only account for a small portion of the entire solar spectrum.<sup>[4]</sup> Although various strategies have been developed to expand the light-absorption range of wide band-gap photocatalysts,<sup>[4,5]</sup> such as ion doping, solid solutions, sensitization by organic dyes, or narrow band-gap semiconductors, and various visible-light-responsive photocatalysts have also been developed, including those based on bismuth<sup>[6]</sup> and silver.<sup>[7]</sup> The efficiencies of current photocatalysts still fail to satisfy the criteria for commercial application on a large scale. Therefore, it is still a great challenge to develop new photocatalysts with wide light-absorption spectra and high reactivities.

Present investigations into photocatalysts are mainly focused on crystalline materials and it is commonly accepted that highly crystalline materials are required for high photocatalytic activities. However, recent investigations have given rise

[a]	Dr. Z. Lou, Prof. Z. Wang, Prof. B. Huang, G. Wang, Z. Jiang, X. Zhang,
	X. Qin, Y. Li
	State Key Laboratory of Crystal Materials, Shandong University
	Jinan, 250100 (P. R. China)
	E-mail: bbhuang@sdu.edu.cn
	wangzeyang@sdu.edu.cn
[b]	Prof. Y. Dai
	School of Physics, Shandong University
	Jinan, 250100 (P. R. China)
	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201406673.

to some unexpected results, demonstrating that amorphous materials could also be photocatalytically active. Guo et al. reported that amorphous/crystallite ZnO/TiO<sub>2</sub> nanocomposites were highly photocatalytically active for H<sub>2</sub> generation without noble metal cocatalyst.<sup>[8]</sup> The presence of amorphous ZnO not only promoted charge separation but also facilitated the adsorption and surface reactions, thus improving the photocatalytic performance. Furthermore, the disordered atomic arrangements of amorphous materials also provided more compatibility to tailor the electronic structures and band gaps of the materials, thus, greatly expanding the light absorption spectra. By introducing a thin layer of disordered structure onto the surface of the TiO<sub>2</sub> nanocrystallite, the absorption spectra of TiO<sub>2</sub> can be extended from UV to the whole visible and near-IR region.<sup>[9]</sup> Moreover, amorphous materials can be easily synthesized and scaled up at low cost, which is favorable for practical applications. Therefore, the exploration of highly active amorphous photocatalysts would be of great importance for the future development of photocatalysis and stimulate its practical applications.

As the most abundant class of minerals on earth, silicates are one of the most important amorphous materials and have been widely used in a variety of fields.<sup>[10]</sup> However, silicate photocatalysts have not to date been extensively studied. We previously reported that Ag<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> is highly reactive in nearly the whole visible-light region owing to its special electronic structure.<sup>[11]</sup> Herein we report, for the first time, the synthesis of amorphous silver silicate photocatalysts with tunable light-absorption spectra by using a simple one-step co-precipitation method. With wide visible-light absorption and appropriate band structure, the amorphous silver silicate with Ag/Si ratio of 3.20 exhibited optimal photocatalytic activity that is also higher than those of bulk Ag<sub>2</sub>O and N-doped TiO<sub>2</sub> under visible light irradiation. The effect of silicate ions on the Aq-O bond was investigated and proposed to give rise to the tunable visible absorption and photocatalytic activities of amorphous silver silicates.

To synthesize the amorphous silver silicates, silicate ions were introduced into  $Ag_2O$  gradually by tuning the pH values of the reaction solution. The reaction process can be described by the Equation (1) as follows:

$$xAg^{+} + H_2SiO_3 + xOH^{-} = Ag_xSiO_{(2+\frac{x}{2})} + (\frac{x}{2} + 1)H_2O$$
 (1)

Chem. Eur. J. 2015, 21, 8706-8710

Wiley Online Library



With reduction of pH values, the content of silicate ions in the obtained samples is increased gradually and sample colors change from black to greenish yellow (see the Supporting Information, S1). As shown by SEM images (see the Supporting Information, S2), the obtained samples were irregular particles with sizes becoming smaller as the pH values decreased. XRD patterns of samples prepared with different pH values were also investigated (Figure 1 A). When silver nitrate was mixed



**Figure 1.** XRD patterns (A), Ag 3d XPS spectra (B), and UV/Vis diffuse reflectance spectra (C) of as-prepared Ag<sub>2</sub>O and silver silicates prepared with different pH values: 12.94 (**a**), 12.50 (**b**), 12.18 (**c**), 11.94 (**d**), 11.45 (**e**), 10.98 (**f**), 10.27 (**g**), 9.96 (**h**). Estimated band gap ( $E_g$ ) of amorphous silver silicates with different Ag/Si atomic ratios x (D).

with NaOH solution directly in the absence of silicate ions, the obtained samples were pure Ag<sub>2</sub>O. In the presence of silicate ions, and with a pH value of 12.94, the XRD pattern of sample a have four peaks that match those of as-prepared Ag<sub>2</sub>O with a little migration along high-angle direction. When the pH value has been reduced to 12.5, the XRD pattern of obtained sample **b** has a wide peak, implying an amorphous structural character. On continued decrease of the pH value, wide peaks can be observed in all XRD patterns of obtained samples c-h, in a similar manner to the wide peak of amorphous silicate oxides,<sup>[12]</sup> indicating the amorphous character of those samples. For better understanding of the crystal structures of the samples, Ag 3d XPS spectroscopy was carried out (Figure 1 B). The Ag 3d peaks of sample a matched with those of Aq<sub>2</sub>O. On decreasing the pH value, the Aq 3d peaks of asprepared samples **b**-**h** gradually shifted along the high-energy direction, suggesting that the Ag-O bond in the samples was becoming stronger. Peaks in the O 2p and Si 2p XPS spectra of as-prepared samples **a**-**h** also shifted gradually along the highenergy direction (see the Supporting Information, S3 and S4). A weak peak observed in Si 2p XPS spectrum of sample a indicates the presence of silicate ions, resulting in lattice changes of Aq<sub>2</sub>O, which can explain the shift of peaks in its XRD pattern. From sample **b** to **h**, the peaks of Si 2p gradually become stronger, implying that more silicate ions are introduced resulting in their amorphous characters. The XPS results indicate that introduction of silicate ion can influence the Ag–O bond. Compositions of as-prepared samples can be measured by the EDS, and the results are listed in Table 1. With the decrease in

Table 1. Element composition of as-prepared amorphous silver silicates.							
Samples	рН	E	x (Ag/Si)				
		Ag	Si	0			
a	12.94	49.71	1.25	49.03	39.77		
b	12.50	65.56	5.59	28.85	11.73		
c	12.18	32.66	9.82	57.52	3.33		
d	11.94	30.01	9.39	60.59	3.20		
e	11.45	29.48	10.08	60.44	2.92		
f	10.98	30.32	11.89	57.79	2.55		
g	10.27	24.91	12.34	62.75	2.02		
h	9.96	29.49	16.52	53.99	1.79		

pH value, the content of silicate ions in as-prepared samples gradually increases. At pH 12.94, sample **a** contains only 1.6 at.% silicate. At pH values below 12.5, the content of silicate increases from 5.70 at.% to 37.24 at.%.

The light absorption of prepared samples was investigated by the UV/Vis diffuse reflectance spectroscopy (Figure 1C). At pH 12.94, the absorption edge of sample a has a blue shift compared to that of as-prepared Ag<sub>2</sub>O. On continual decrease of the pH value, the absorption edge of obtained samples undergoes a further blueshift, which can be observed clearly in Figure 1C. At pH 9.97, the obtained silver silicates (sample h) exhibit a visible light response with an edge at  $\lambda\!\approx\!557\,\text{nm}$  $(\lambda = wavelength of absorption edge)$ . Based on the light absorption, the energy band gap  $E_{\alpha}$  of the obtained samples can be estimated simply by using the expression  $E_q = h\nu = 1240/$  $\lambda$ .<sup>[13]</sup> Band gap energies  $E_{g}$  of amorphous silver silicates with different Ag/Si ratios (x) are shown in Figure 1 D. The band gap of sample a is 1.26 eV, which is little larger than that of Ag<sub>2</sub>O (1.2 eV). On decreasing the pH value from 12.94 to 9.97, x decreased from 39.77 to 1.79. Furthermore, the band gap of silver silicates (samples **b**-**h**) is widened from 1.37 to 2.25 eV.  $E_{a}$ underwent a great change when x was decreased from 3.33 to 1.79 (Figure 1 D, inset). The main cause for this change in band gap can be attributed to increase in silicate ions in the samples. Therefore, silicate ions play a critical role in determining the light absorption and band structures of silver silicates, which will be discussed in detail below.

The photocatalytic activities of as-prepared silver silicates were tested by the photodegradation of organic contaminant methylene blue (MB) under visible light irradiation ( $\lambda$  > 420 nm). More than 45% of MB decomposed within 40 min over sample **a** as photocatalyst (Figure 2 A). From sample **b** to **d**, the photocatalytic degradation of MB increases gradually in rent and sample **d** exhibited the optimal photocatalytic activity and more than 95% MB decomposed within 8 min under the irradiation of visible light. UV/Vis spectroscopic changes of MB solution over time in the presence of sample **d** are shown in

~					
Chem.	Eur. J.	2015,	21,	8706 - 8710	

www.chemeurj.org





Figure 2. A) Photocatalytic degradation of MB over silver silicates (a-h; Table 1); B) kinetic plots for silver silicates; C) overall MB degradation rate constant k over silver silicates with different Ag/Si atomic ratios x: D) photocatalytic MB degradation rate over silver silicate (sample d), as-prepared Ag\_2O, and N-doped P25 under visible light irradiation ( $\lambda\!>\!420$  nm).

S5 (see the Supporting Information). However, from sample d to **h**, the MB photodegradation rate decreases(Figure 2A). To exclude the influence of adsorption on the MB degradation rate, kinetic plots over different silver silicates were investigated (Figure 2B). The photocatalytic reaction can be simply described by dC/dt = kC, where C is the concentration of MB and k denotes the overall degradation rate constant.<sup>[14]</sup> The k values for samples a to h are 0.0222, 0.0508, 0.2504, 0.2758, 0.1642, 0.1373, 0.0920, and 0.0661 min<sup>-1</sup>, respectively. It can be observed clearly that sample **d** has the highest k value of 0.2758 min<sup>-1</sup>, which is 13 times higher than that of sample  $\mathbf{a}$ (0.0222 min<sup>-1</sup>). To investigate the relationship between content of silicate ions and photocatalytic activities of silver silicates, k values for degradation of MB vs. Ag/Si atomic ratio (x) plots were assembled (Figure 2 C). When x is decreased 39.77 to 3.2, the content of silicate ions increases and photocatalytic activity is gradually enhanced. When x=3.2, the silver silicates have the highest activity in degradation of MB. On continued decrease of x from 3.2 to 1.79, the MB degradation becomes gradually slower. Therefore, silicate ions also play a critical role in determining the photocatalytic activities of silver silicates. The BET surface areas of samples **a-h** (see the Supporting Information, Table S1) show that surface area is not the main cause for enhancement of the samples' photocatalytic activity. To understand in depth the photocatalytic activity of the asprepared silver silicates, as-prepared Ag<sub>2</sub>O and N-doped P25 were used as references. Sample d (Ag/Si ratio of 3.2) showed higher photocatalytic activity than either Ag<sub>2</sub>O aor N-doped P25 (Figure 2D). The MB degradation rate over sample d was 142.14 mg  $g^{-1}h^{-1}$ , which is 6 and 16 times faster than those of Ag<sub>2</sub>O (22.94 mg  $g^{-1}h^{-1}$ ) and N-doped TiO<sub>2</sub> (8.4 mg  $g^{-1}h^{-1}$ ), respectively.







Figure 3. A) Changes in silver silicate structure with increasing silicate ion content; B) effect of silicate ions on tunable light absorption and photocatalytic activity of silver silicates; C) band structures of silver silicates with different compositions (a-h; Table 1).

To better understand the effect of silicate ions on visible light absorption and photocatalytic properties of silver silicates, a possible mechanism is proposed (Figure 3). In the crystal structure of Ag<sub>2</sub>O, one O atom is coordinated to four Ag atoms (Figure 3 A). When the silicate ion is introduced into Ag<sub>2</sub>O, the silica tetrahedron is connected with Ag atoms by O bridges. Further introduction of tetrahedral silica can break the unique atomic arrangement in the crystal structure of Aq<sub>2</sub>O, resulting in amorphous structures of silver silicates. The bonding energy is enhanced with the increase in silicate ions, which is confirmed by the Ag 3d, O 2p and Si 2p XPS spectra of the silver silicates. Compared with the Ag-O bond, the Si-O bond has a higher bonding energy, which can influence the Ag-O bonding via the O bridge.<sup>[15]</sup> For the band structures of silver oxides and silver silicates, Ag atoms provide the main contributions to the conduction band (CB) and O atoms provide the main contributions to the valence band (VB).<sup>[11, 16]</sup> The light absorption of semiconductor materials can be described as the absorption of photons by electrons on the VB causing their



transfer to the CB, and this process can also be described as electron transfer from O atoms to coordinated Ag atoms in the view of the molecular structure.(Figure 3B) Therefore, the transfer of electrons on O atoms plays a critical role in light absorption by silver silicates. The presence of silicate ions can restrict the electron transition of O atoms, resulting in wide band gaps and blueshift of the absorption edge. More silicate ions would induce a widening of the band gap and further blueshift in light absorption of silver silicates, as is consistent with experimental results (Figure 1C and D). The CB and VB of silver silicates were estimated by calculation (Figure 3C and Table S2 in the Supporting Information). Positions of the CB and VB, which determine the redox ability of photogenerated carriers, are dependent on the composition of silver silicates. On increasing the silicate ion content, the band gap of silver silicates becomes wider, with opposing movements of the CB and VB positions (Figure 3C). This means that photogenerated carriers have higher redox ability and the visible absorption region is reduced. Furthermore, the presence of silicate ions can facilitate the transfer of photogenerated electrons, as reported previously.<sup>[11]</sup> Therefore, when x = 3.2, the silver silicates have wide visible light absorption and high redox ability of carriers, leading to its optimal photocatalytic activity. However, with continuous increase in silicate ion content, the further blueshift of the visible absorption edge reduces the utilization of visible light, resulting in weakening in the photocatalytic activity of silver silicates.

In summary, a series of amorphous silver silicates were obtained by a one-step co-precipitation method. Light absorption spectra and band structures of amorphous silver silicates could be tuned over a wide range by changing the content of silicate ions. With wide visible light absorption and appropriate band structures, amorphous silver silicates with a Ag/Si ratio of 3.20 exhibited the optimal photocatalytic activity compared to other samples, as-prepared Ag<sub>2</sub>O, and N-doped TiO<sub>2</sub>. A plausible mechanism was proposed to explain the tunable visible light absorption and photocatalytic activities of the amorphous silver silicates, based on the effect of silicate ions on the Ag–O bond.

## **Experimental Section**

All reagents were analytical grade. AgNO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O, methylene blue, and NaOH were purchased and used without further purification.

#### Synthesis of amorphous silver silicates

General procedure:  $Na_2SiO_3 \cdot 9H_2O$  (0.284 g) was mixed with deionized water (70 mL) under constant stirring. The pH of the solution was adjusted to a given value by addition of NaOH solid. 0.1 m AgNO<sub>3</sub> (30 mL) was added to the solution quickly and precipitates were formed in the solution. After 30 min stirring, the samples were separated from solution by filtering. The obtained sample powders were washed with deionized water (3×10 mL) and ethanol (3×10 mL) and dried at room temperature for 6 h. For comparison, Ag<sub>2</sub>O was prepared by direct precipitation method. 0.1 m AgNO<sub>3</sub> (20 mL) solution was mixed with a 2 mmol aqueous NaOH solution (70 mL) and stirred for 30 min. The precipitates were separated from the solution by the filtering and the Ag<sub>2</sub>O was collected, washed with the deionized water (3×10 mL) and ethanol (3×10 mL), and dried at room temperature for 6 h.

#### Photocatalytic reactions

Samples (0.1 g) were mixed with MB solution ( $20 \text{ mg L}^{-1}$ , 100 mL) in a 200 mL beaker. The resultant solution was stirred for 20 min in the dark to achieve a dye absorption equilibrium on the surface of the catalysts. Photocatalytic reactions were then carried out with stirring under visible light provided by a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd.) equipped with cut-off filter to cut off wavelengths of < 420 nm. A 5 mL aliquot of solution was removed for a given time, until the solution was blanched, and the concentration of MB was tested by measuring the absorption of aqueous MB solution with a Shimadzu UV2550 recording spectro-photometer.

#### Characterization

The X-ray diffraction patterns (XRD) of samples were obtained on Bruker D8 advanced X-ray powder diffractometer with Cu<sub>Ka</sub> radiation  $\lambda = 1.5418$  Å. Scanning electron microscopy (SEM) measurements were carried out by Hitachi S-4800 microscope. UV/Vis diffusion reflectance spectra light absorbance curves were recorded for the dry-pressed disk samples by a Shimadzu UV2550 recording spectrophotometer in the wavelength range 200–800 nm.

## Acknowledgements

This work was financially supported by research grants from the National Basic Research Program of China (the 973 Program; No. 2013CB632401),the National Natural Science Foundation of China (No. 21333006, 11374190 and 51321091) and Shandong Provincial Natural Science Foundation (No. ZR2014BM024).

**Keywords:** absorption spectroscopy · amorphous materials · photocatalysis · silicates · silver

- [1] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38.
- [2] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, Chem. Rev. 1995, 95, 69–96.
- [3] T. Inoue, A. Fujishima, S. Konishi, K. Honda, Nature 1979, 277, 637-638.
- [4] X. B. Chen, S. S. Mao, Chem. Rev. 2007, 107, 2891-2959.
- [5] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 2001, 293, 269–271.
- [6] H. F. Cheng, B. B. Huang, P. Wang, Z. Y. Wang, Z. Z. Lou, J. P. Wang, X. Y. Qin, X. Y. Zhang, Y. Dai, *Chem. Commun.* **2011**, *47*, 7054–7056; H. F. Cheng, B. B. Huang, Y. Dai, *Nanoscale* **2014**, *6*, 2009–2026.
- [7] P. Wang, B. B. Huang, X. Y. Qin, X. Y. Zhang, Y. Dai, J. Y. Wei, M. H. Whangbo, Angew. Chem. Int. Ed. 2008, 47, 7931–7933; Angew. Chem. 2008, 120, 8049–8051; Z. Z. Lou, Z. Y. Wang, B. B. Huang, Y. Dai, ChemCatChem 2014, 6, 2456–2476.
- [8] S. Y. Guo, S. Han, B. Chi, J. Pu, J. Li, ACS Appl. Mater. Interfaces 2014, 6, 4743–4751; S. Y. Guo, S. Han, H. F. Mao, S. M. Dong, C. C. Wu, L. C. Jia, B. Chi, J. Pu, J. Li, J. Power Sources 2014, 245, 979–985.
- [9] X. B. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science* **2011**, *331*, 746–750.
- [10] M. Bejblová, D. Prochazkova, J. Cejka, ChemSusChem 2009, 2, 486-499.
- [11] Z. Z. Lou, B. B. Huang, Z. Y. Wang, X. C. Ma, R. Zhang, X. Y. Zhang, X. Y. Qin, Y. Dai, M. H. Whangbo, *Chem. Mater.* **2014**, *26*, 3873–3875.
- [12] S. Musić, N. Filipović-Vinceković, L. Sekovanić, Braz. J. Chem. Eng. 2011, 28, 89–94.

Cham	Eur	-	0015	21	0706	0710
Chem.	EUI. J	. 4	2013,	21,	0/00-	0/10

www.chemeurj.org



- [13] Z. Y. Wang, Y. Y. Liu, B. B. Huang, Y. Dai, Z. Z. Lou, G. Wang, X. Y. Zhang, X. Y. Qin, Phys. Chem. Chem. Phys. 2014, 16, 2758–2774.
- [14] J. C. Liu, O. Margeat, W. Dachraoui, X. J. Liu, M. Fahlman, and J. Ackermann, Adv. Funct. Mater. 2014, 24, 6029-6037.
- [15] Y. R. Luo, Comprehensive Handbook of Chemical Bond Energies, 2007, CRC Press, Boca Raton, FL, p. 462–993.
- [16] G. Wang, X. C. Ma, B. B. Huang, H. F. Cheng, Z. Y. Wang, J. Zhan, X. Y. Qin, X. Y. Zhang, Y. Dai, J. Mater. Chem. 2012, 22, 21189–21194.

Received: December 30, 2014 Published online on April 23, 2015