In-situ synthesis of amorphous silver silicate/carbonate composites for selective visible-light photocatalytic decomposition

Ruya Cao, Hongcen Yang, Xiaolong Deng, Shouwei Zhang & Xijin Xu

Coupling two different semiconductors to form composite photocatalysts is an extremely significant technique for environmental remediation. Here, a one-step in-situ precipitation method has been developed to prepare amorphous silver silicate/carbonate (AgSiO/Ag$_2$CO$_3$) nanoparticles (NPs) composites, which are well dispersed sphere-like particles with the sizes of around ~50–100 nm. The high-efficiency photocatalytic activities under visible light (VL) have been carefully evaluated, and the AgSiO/Ag$_2$CO$_3$ NPs composites exhibit selective photocatalytic degradations on Methylene Blue (MB) and Rhodamine B (RhB). The maximum degradation rate for MB can reach ~99.1% within ~40 min under VL irradiation, much higher than that of RhB (~12%) in the same condition, which can be ascribed to (I) the smaller molecule size of MB than that of RhB, (II) the fast charge separation between AgSiO NPs and Ag$_2$CO$_3$ NPs, abundant heterojunction interfaces as well as fully exposed reactive sites. These composites are proposed to be an example for the preparation of other silicate composite photocatalysts for practical applications in environmental remediation.

Photocatalytic technology has become one of the most promising green technology as it can degrade organic pollutants in water to produce non-toxic substances such as CO$_2$, H$_2$O and so on with no secondary pollution, mild reaction conditions, and low energy consumption. Especially, semiconductor photocatalysts have attracted wide attention in the field of environmental purification and a lot of achievements have been achieved. Among them, silver carbonate (Ag$_2$CO$_3$) has received great research interests, but is restricted by its photocorrosion and lower photocatalytic degradation efficiency. Therefore, it is significantly worthy to make great efforts to solve the problem for the real industrial application. Recently, it has been reported that introducing an electron acceptor in the photocatalytic reaction system can efficiently restrain the photocorrosion. The silicates have been found to be the effective one, which can not only enhance the photogenerated charge transfer but also broaden the spectral response range. Furthermore, the excited electron–hole pairs can readily transfer between the particles due to the internal polar electric field in the silicate NPs. Among them, silver silicate (AgSiO) has been one of the most famous silicates due to its good stability, high efficiency, nontoxicity, low cost, and it has row band gap which can extend the large of light absorption. Therefore, visible-light-driven photocatalysts can be exploited by coupling AgSiO with Ag$_2$CO$_3$ NPs. Furthermore, the heterojunctions by coupling them favor the separation of photogenerated electron-hole pairs resulting in the improvement of the photocatalytic activity.

In this paper, AgSiO/Ag$_2$CO$_3$ composites with different ratios have been successfully synthesized by an in-situ method. The final samples with different molar ratios of SiO$_2$ and CO$_3$$_2$$_2$ exhibit the optimal photocatalytic activities. Besides, the selective photodegradation of two cationic dyes Methylene Blue (MB), Rhodamine B (RhB), and two another anionic dyes Methyl Orange (MO) and Congo Red (CZ) have been carefully investigated. Finally, the photocatalytic mechanisms of these AgSiO/Ag$_2$CO$_3$ composites are carefully discussed.

Experimental Sections

Preparation of the amorphous silver silicates (AgSiO). The AgSiO was synthesized via an in-situ method. For a typical synthesis, 0.2 M AgNO$_3$ (40 mL) was added into 0.1 M Na$_2$SiO$_3$·9H$_2$O (40 mL) under
continuously stirring for 1.0 h. The precipitates were collected and washed with distilled water and ethanol, and finally dried at room temperature.

**Preparation of the silver carbonate (Ag$_2$CO$_3$).** 0.2 M AgNO$_3$ (40 mL) was slowly drop by drop added into 0.1 M NaHCO$_3$ (20 mL) under continuously stirring for 1.0 h. The precipitates were collected and washed with distilled water and ethanol, and finally dried at room temperature.

**Preparation of the amorphous silver silicate/carbonate heterostructure (AgSiO/Ag$_2$CO$_3$).** The AgSiO/Ag$_2$CO$_3$ composites were synthesized via an *in-situ* precipitation method. In a typical synthetic procedure, 0.1 M Na$_2$SiO$_3$·9H$_2$O (40 mL) were added to 0.1 M NaHCO$_3$ (20 mL) under stirring for 5 min. Then, 0.2 M AgNO$_3$ (40 mL) was slowly added to the mixture under stirring for 1.0 h. The precipitates were collected and washed with distilled water and ethanol, and dried at room temperature. The AgSiO/Ag$_2$CO$_3$ composites prepared with different molar ratios of Na$_2$SiO$_3$·9H$_2$O and NaHCO$_3$ in 40, 60, 80, 100 and 120 ml are denominated as AgSiO/Ag$_2$CO$_3$-2:1, AgSiO/Ag$_2$CO$_3$-3:1, AgSiO/Ag$_2$CO$_3$-4:1, AgSiO/Ag$_2$CO$_3$-5:1, and AgSiO/Ag$_2$CO$_3$-6:1, respectively.

**Characterization.** Powder X-ray diffraction (XRD) patterns were collected using a D/MAX2500 V diffractometer equipped with Cu K$_\alpha$ radiation (\(\lambda = 1.5418 \text{ Å}\)). The morphologies of the materials were observed using a FEI QUANTA FEG 250 field emission scanning electron microscope (SEM). The structural information of the samples was measured with the standard KBr disk method by a Fourier transform spectrophotometer (FT-IR, Avatar 370, Thermo Nicolet). X-ray photoelectron spectroscopy (XPS) was carried out on ESCALAB250 with Mg K$_\alpha$ as the source and the C$_1$s peak at 284.6 eV as an internal standard. UV-vis diffuse reflection spectroscopy (DRS) was recorded with a Shimadzu UV-2500 spectrophotometer using BaSO$_4$ as the reference. The Brunauer–Emmett–Teller (BET) specific surface areas were explored by nitrogen adsorption in a Micromeritics Tristar II 3020 nitrogen adsorption–desorption apparatus in accordance with the Barret–Joyner–Halenda (BJH) technique from the N$_2$ adsorption isotherms.

**Photocatalytic tests.** Photocatalytic degradation experiments were conducted in a photocatalytic reactor equipped with a 420 nm cut-off filter and a 500 W Xe lamp as the light source. For the photocatalytic reaction, the photocatalysts (20 mg) were mixed into a MB and RhB solution (50 mL, 10 mg/L). To guarantee the adsorption-desorption counterpoise, the mixed solution was stirred for 60 min in the darkness. Then, the solution was illuminated by VL and a small portion of the suspension (~3.0 mL) was sampled at 10 min illumination spacing. The catalytic efficiency was tested by using a UV-vis spectrophotometer (UV-2500, Shimadzu) for the degradation of RhB and MB.

**Results and Discussion**

A facile *in-situ* precipitation method was designed to synthesize AgSiO/Ag$_2$CO$_3$ nanoparticles as illustrated in Fig. 1. The chemical reaction process can be described as follows:

$$\text{Ag}^+ + \text{SiO}_3^{2-} + \text{CO}_3^{2-} + \text{OH}^- \rightarrow \text{AgSiO/Ag}_2\text{CO}_3 + \text{H}_2\text{O}$$

(1)

By adding AgNO$_3$ to the NaHCO$_3$ solution, the CO$_3^{2-}$ present in the solution will react with the added Ag$^+$ by electrostatic interaction to produce Ag$_2$CO$_3$. Then, the fixed Ag$^+$ cations will further react with SiO$_3^{2-}$ to generate AgSiO with the addition of Na$_2$SiO$_3$ solution, resulting in the formation of AgSiO/Ag$_2$CO$_3$.$^5$-$^7$

The XRD patterns of pure AgSiO, Ag$_2$CO$_3$, and AgSiO/Ag$_2$CO$_3$ composites are shown in Fig. 2. The broad peak at about 34° could be indexed to the (−124) and (−115) planes for pure AgSiO in Fig. 2A, suggesting its amorphous structure.$^6$ For the pure Ag$_2$CO$_3$ NPs (Fig. 2B), the positions and intensities of the diffraction peaks are well matched with the standard JCPDS card.$^2$-$^3$,$^11$ The XRD pattern of AgSiO/Ag$_2$CO$_3$ composites is shown in Fig. 2A. Obviously, the diffraction peaks of AgSiO and Ag$_2$CO$_3$ NPs can be clearly found in curve and without any other
peaks. The peaks of Ag₂CO₃ decreased with increasing AgSiO contents, and the characteristic peak intensity of AgSiO increases with the increase of the AgSiO contents, indicating that AgSiO/Ag₂CO₃ composites with high purity have been successfully synthesized by an in-situ precipitation.

FTIR spectra of AgSiO, Ag₂CO₃ and AgSiO/Ag₂CO₃ composites were recorded as shown in Fig. 3. In comparison to pure AgSiO, the absorption bands of AgSiO/Ag₂CO₃ composites obtained at around ~705 cm⁻¹, ~893 cm⁻¹, ~1382 cm⁻¹, and ~1451 cm⁻¹ are attributed to CO₃²⁻ in Ag₂CO₃. Compared with pure Ag₂CO₃, strong absorption band at around ~1382 cm⁻¹ is found for AgSiO/Ag₂CO₃ composites, which belongs to the Si-O-Si stretching vibrations. Moreover, there is also another shoulder peak indexed to the Si-O-Si bonds at ~1630 cm⁻¹, which confirms the successful introduction of AgSiO in the composites. Nevertheless, the characteristic peak located at ~1382 cm⁻¹ shifts to higher wavenumbers (Fig. 3). The observed blue shift in the composites after introducing AgSiO (Fig. 3) indicates the weakened bond strengths of Si-O-Si owing to the conjugation between Ag₂CO₃ and AgSiO. This result demonstrates the strong interfacial coupling effect in the AgSiO/Ag₂CO₃ composites. Compared with the aggregated or large-size nanoparticles, the nature of AgSiO nanoparticles on Ag₂CO₃ acted as nano-islands can facilitate the formation of the heterojunction interfaces and guarantee the higher contact areas. Both characters are essentials to promote photocatalytic activity and to enhance the separation efficiency of photogenerated charges.

The UV-vis diffuse reflectance spectra of AgSiO/Ag₂CO₃ composites together with pure AgSiO and Ag₂CO₃ are shown in Fig. 3. The light absorption edge of Ag₂CO₃ is measured to be ~480 nm, and mainly absorptions are ultraviolet light. In addition, the peak at 520 nm can be indexed to the Ag nanocrystals. Therefore, we can see that a broad absorption ranging from ~480 to ~750 nm is detected, which is due to the generation of Ag nanocrystals. The AgSiO/Ag₂CO₃ composites exhibit the stronger absorption than that of the Ag₂CO₃ NPs in both the visible and ultraviolet light region. Obviously, the introduction of AgSiO can significantly enhance the absorption in the visible-light region and can even extend to near-infrared region, which is attributed to the SPR of Ag nanoparticles. It is inferred that the heterojunction of AgSiO/Ag₂CO₃ composites results in significantly
decreased interfacial contact barrier and strengthened electronic coupling of the semiconductors to generate more photogenerated electrons/holes with improved photocatalytic performance.

The surface chemical compositions of AgSiO, Ag2CO3, and AgSiO/Ag2CO3-5:1 composite were investigated by XPS (Fig. 4). The full-scan XPS spectra of pure AgSiO, Ag2CO3, and AgSiO/Ag2CO3-5:1 composite (Figure S1) indicate the presence of Ag, Si, O in AgSiO, Ag, C, O in Ag2CO3, and Ag, Si, O, C in AgSiO/Ag2CO3-5:1 composite, respectively. Figure 4A depicts the Si 2p peak of AgSiO/Ag2CO3-5:1 composite. The divided peaks located at ~96.9, ~102.8 and ~101 eV can be indexed into Ag 4s, Si 2p1/2 and Si 2p3/2, respectively. Figure 4B shows two XPS peaks located at ~368.1 eV and ~374.1 eV, which can be indexed to Ag 3d5/2 and Ag 3d3/2 of pure AgSiO, Ag2CO3, and the AgSiO/Ag2CO3-5:1 composite. These two peaks can be further divided into four peaks, ~368.1 and ~374.1 eV for Ag+ 3d5/2 and 3d3/2, and ~368.8 and ~374.7 eV for Ag0 3d5/2 and 3d3/2, respectively. The peaks at ~368.8 and ~374.7 eV confirm the existence of metallic Ag0 in our AgSiO/Ag2CO3-5:1 composite. The carbon element in AgSiO is mostly ascribed to the adventitious hydrocarbon from XPS itself. Therefore the strength of C 1s obeys the decreasing order of Ag2CO3 > AgSiO/Ag2CO3 > AgSiO20. Figure 4D demonstrates that O 1s peak in AgSiO/Ag2CO3 contains two distinguishable shoulders in the spectrum, demonstrating that two chemical states of oxygen are present on the surface.

The morphologies of Ag2CO3, AgSiO, and AgSiO/Ag2CO3 with different ratios are shown in Fig. 5. It can be observed that Ag2CO3 are composed of microcubes with the length of ~1.0–5.0 μm. The lattices of AgSiO are clearly visible in the HRTEM images. The close interface between AgSiO and Ag2CO3 nanoparticles reveals the formation of nano-heterojunction26. From the figure, we can see that Ag2CO3 is uniformly packaged by an amorphous AgSiO, limiting the growth of Ag2CO3. The intimate contact between AgSiO and Ag2CO3 will strengthen the photogenerated charge separation and transfer. Compared with traditional aggregated or large contact structures, this AgSiO/Ag2CO3 composites can not only provide more surface active sites for sequential photocatalytic reactions, but also shorten the migration distance of photogenerated charges.

The HRTEM images in Figure S2(A, B) show that the size of AgSiO/Ag2CO3 NPs is of 10 to 20 nm. The lattices of AgSiO/Ag2CO3 NPs are clearly visible in the HRTEM images. The close interface between the AgSiO and Ag2CO3 nanoparticles reveals the formation of nano-heterojunction. From the figure, we can see that Ag2CO3 is uniformly packaged by an amorphous AgSiO, limiting the growth of Ag2CO3. Figure S2(B) shows the lattice spacing of uniformly dispersed Ag2CO3 nanoparticles. The lattice fringes of 0.275 nm is in agreement with the...
spacings of the (−101) plane of Ag₃CO₃ and consistent with JCPDS Card No. 26–0339. No lattice fringes of AgSiO can be observed. This kind of heterojunction, which is favorable for the transport of photoexcited carriers, is formed between AgSiO and Ag₃CO₃. Meanwhile, the composites can be further characterized by element mapping and EDS images (Fig. 6), where the Ag, Si, O and C elements are homogeneously distributed over the

Figure 5. SEM images of (A) pure Ag₃CO₃, (B) pure AgSiO, (C) AgSiO/Ag₃CO₃-3:1 composite, (D) AgSiO/Ag₃CO₃-4:1 composite, (E) AgSiO/Ag₃CO₃-5:1 composite and (F) AgSiO/Ag₃CO₃-6:1 composite.

Figure 6. Elemental mapping images and EDS spectrum of the AgSiO/Ag₃CO₃-5:1 composite.
can be attributed to its heterogeneous structure.

Figure 7 for a better understanding of the composite nanostructure. It can be seen that the surface area of Ag$_2$CO$_3$-5:1 composite; Figure 7B respectively, the characteristic peaks of cationic dyes MB disappeared quickly, while the characteristic peaks of all the photocatalytic performance of AgSiO/Ag$_2$CO$_3$ composites. With further increase of the AgSiO content, the adsorbed volume drops obviously indicating that the enhancement in adsorption volume is not driven solely by the small particles. The surface areas of the different AgSiO/Ag$_2$CO$_3$ composites and pure AgSiO and Ag$_2$CO$_3$ are also calculated as shown in Figure 7B for a better understanding of the composite nanostructure. It can be seen that the surface area of Ag$_2$CO$_3$ is ~11.4 m$^2$·g$^{-1}$. With further increasing of the amount of the AgSiO, the surface area values of the AgSiO/Ag$_2$CO$_3$ composites increase obviously. The surface area of AgSiO/Ag$_2$CO$_3$-6:1 composite can be achieved ~107.9 m$^2$·g$^{-1}$. Although the AgSiO/Ag$_2$CO$_3$-5:1 composite specific surface area isn’t the largest, the degradation is best, which can be attributed to its heterogeneous structure.

Photocatalytic tests. The photocatalytic activities of pure AgSiO, Ag$_2$CO$_3$, and AgSiO/Ag$_2$CO$_3$ composites with different ratios under VL irradiation are shown in Figure 8. The degradation reaches as ~99.1% under VL irradiation within ~40 min (Fig. 8A,B). The degradation of RhB is only ~12% in the same condition (Fig. 8C,D). All AgSiO/Ag$_2$CO$_3$ composites exhibit higher photocatalytic activities than either AgSiO or Ag$_2$CO$_3$ with the order of AgSiO/Ag$_2$CO$_3$-5:1 > AgSiO/Ag$_2$CO$_3$-6:1 > AgSiO/Ag$_2$CO$_3$-4:1 > AgSiO/Ag$_2$CO$_3$-3:1 > AgSiO/Ag$_2$CO$_3$-2:1 > AgSiO > Ag$_2$CO$_3$, indicating the positive effect of AgSiO contents on enhancing the photocatalytic activities of the composites. Full degradation of MB can be observed within ~40 min by VL irradiation in the presence of AgSiO/Ag$_2$CO$_3$-5:1 composite (Fig. 8A), illustrating the significantly improved photocatalytic activity of the AgSiO/Ag$_2$CO$_3$ composites. However, further increment of proportion (AgSiO/Ag$_2$CO$_3$-6:1) results in decreased photocatalytic activity, which may be attributed to the recombination of photogenerated electrons and holes, and then the photocatalytic efficiency is restrained.

Figure 9 shows the variation of the absorption spectra of MB under VL irradiation by AgSiO/Ag$_2$CO$_3$-5:1 composite. The characteristic peak intensities of MB gradually decrease by prolonging the irradiation time, and the adsorption peaks disappear within ~40 min irradiation. The corresponding optical photographs of MB degradation using different photocatalysts under different irradiation times are collected and displayed in Fig. 9B. The color of MB gradually becomes lighter by prolonging the irradiation time, it can be seen that the color of AgSiO/Ag$_2$CO$_3$-5:1 composite becomes transparent while pure color for AgSiO and Ag$_2$CO$_3$ turns into azury. The variation of the absorption spectra of RhB under VL irradiation by AgSiO/Ag$_2$CO$_3$-5:1 composite is shown in Figure 9C. The characteristic peak intensities of RhB gradually decreased by prolonging the irradiation time, and the adsorption peaks became constant within ~40 min irradiation indicating the very slow degradation of RhB. These corresponding optical photographs of RhB degradation using different photocatalysts under different irradiation times are in Fig. 9D, showing that the color of RhB almost keeps unchanged.

The selective photocatalytic phenomenon of the AgSiO/Ag$_2$CO$_3$-5:1 composite was examined by photodegradation of MB and RhB. The absorption peaks of MB located at ~664 nm almost disappear after irradiation within ~40 min. However, the absorption peaks of RhB located at ~554 nm doesn't change too much (Fig. 9). As for two cationic dyes MB and RhB, we speculate that the discrepancy in adsorption capacities among them can be ascribed to the molecule size. That is, because the size of MB molecules is smaller than those of RhB, MB can be intercalated into the space, while RhB are too large to intercalate into the NPs.

Similarly, we used MB&MO, MO&RhB and MO&CR mixture dyes to further research the selectivity of the material. As shown from the figure S4, When AgSiO/Ag$_2$CO$_3$ composites were added into the binary mixtures, respectively, the characteristic peaks of cationic dyes MB disappeared quickly, while the characteristic peaks of all other cationic dyes remained.
anionic dyes remained unchanged. These results demonstrated excellent selective removal of cationic dyes over anionic dyes due to the electrostatic effect.

Photocatalytic mechanism. The electrons and holes produced by photocatalysis have strong reduction and oxidation capacities. The main active species of different photocatalysts may vary due to their different band structure and phase compositions. Thus, to explore the mechanism of the high photocatalytic activities and to assess the contribution of the reactive species, trapping experiments of reactive species were conducted using ethylenediaminetetraacetate (EDTA-2Na), iso-propyle alcohol (IPA) and N\(_2\) as h\(^+\) and OH\(^-\) and e\(^-\) scavengers, respectively. By adding scavengers into the degradation solutions, the reactive species in the degradation process can be revealed. As shown in Fig. 10, the degradation rate decreases clearly to ~8.8% in the presence of EDTA-2Na (h\(^+\) scavenger) and the degradation rate is ~98% in the absence of scavengers, which indicates that h\(^+\) is the major reactive specie for MB degradation (Fig. 10A,B). Introducing IPA displays a significant effect on the k\(_{app}\). It decrease from ~0.102 min\(^{-1}\) to ~0.055 min\(^{-1}\) (Fig. 10C), suggesting that the radical is also a dominant reactive species. And the degradation rate decreases obviously to ~53% and ~66% in the presence of N\(_2\) (O\(_2\) scavenger) and AgNO\(_3\) (e\(^-\) scavenger), which suggests that O\(_2\)\(^-\) and e\(^-\) is the partly reactive species for MB degradation (Fig. 10D,E). Through Fig. 10F, we can visually see that the O\(_2\)\(^-\), e\(^-\) and h\(^+\) are reactive species.

The recyclability of the photocatalysts is significant factors in their practical applications. Figure 11A indicates that the recyclability for AgSiO/Ag\(_2\)CO\(_3\)-5:1 composite. After six successive cycles, AgSiO/Ag\(_2\)CO\(_3\)-5:1 composite still possesses ~89% degradation rate of MB after ~40 min VL irradiation, indicating its high recyclability. The results indicate that the incorporation of AgSiO with Ag\(_2\)CO\(_3\) photocatalyst successfully improves the VL photocatalytic performance and restrains the photocorrosion in a large level. To further confirm the separation and recombination of electron-hole pairs in pure AgSiO, Ag\(_2\)CO\(_3\) and AgSiO/Ag\(_2\)CO\(_3\) composites, the photocurrent test is carried out under visible light. In this study, electrochemical and photoelectrochemical measurements were performed in 1 M Na\(_2\)SO\(_4\) electrolyte solution in a three-electrode quartz cell. Pt sheet was used as a counter electrode and Hg/Hg\(_2\)Cl\(_2\)/sat. KCl was used as a reference electrode. The pure AgSiO, Ag\(_2\)CO\(_3\) and AgSiO/Ag\(_2\)CO\(_3\) composites on ITO was used as the working electrode for investigation. The photoelectrochemical response was recorded with a CHI 660E electrochemical system. The photocurrent-potential plots of these samples are shown in Fig. 11B. The figure shows the obvious photocurrent intensity of different samples under illumination by 250 lumens LED for 30 second intervals. The best photocurrent intensity (0.7 \(\mu A\cdot g^{-1}\)) of AgSiO was obtained when the applied potential is 1.3 V. And the best photocurrent intensity of Ag\(_2\)CO\(_3\) was 1.2 \(\mu A\cdot g^{-1}\). However, the photocurrent intensity was improved to 1.8 \(\mu A\cdot cm^{-1}\) with the same applied potential after
a heterojunction formed from AgSiO and Ag₂CO₃, which was three times greater than pure Ag₂CO₃. This phenomenon reveals that the AgSiO/Ag₂CO₃ heterostructures possess a larger carrier concentration than the pure AgSiO and Ag₂CO₃ NPs, and more electron-hole pairs are generated for the charge separation process. These results of the photocurrent tests are in agreement with the results of the photodegradation of MB. The obvious photocurrent demonstrates that the interfacial charge separation between AgSiO and Ag₂CO₃ NPs exists in this composite.

Based on experimental results, Fig. 12 depicts a diagrammatic sketch for photocatalytic mechanism. Under VL irradiation, AgSiO can absorb VL, leading to the excitation of e⁻ to the conduction band (CB) and whilst keeping h⁺ in the valence bands (VB). For AgSiO/Ag₂CO₃ heterojunctions, the photogenerated e⁻ on the CB of AgSiO can easily migrate to the CB of Ag₂CO₃, while the photogenerated h⁺ in the VB of Ag₂CO₃ migrates to AgSiO. That is to say, the appropriately aligned band edges of AgSiO and Ag₂CO₃ indicates that the migration of effective photogenerated charges can occur via the heterojunctions with strong interfacial coupling effect in
Figure 10. The typical visible absorption spectra (A–E) and concentration changes (F) of MB over AgSiO/Ag$_2$CO$_3$-5:1 composite in the presence of EDTA-2Na, IPA, N$_2$ and in the absence scavengers.

Figure 11. (A) The photocatalytic stability of AgSiO/Ag$_2$CO$_3$-5:1 composite in recycling reactions; Photocurrent response curves of pure Ag$_2$CO$_3$, AgSiO and AgSiO/Ag$_2$CO$_3$ composites under visible light irradiation (B).
the composite. The migration of photogenerated charges limits the transmission of photogenerated electron-hole pairs and improves the abundance and stability of photogenerated charge in the composite. At the same time, the isolated photogenerated charges promote the production of reactive oxidative species, i.e. $\cdot$O$_2^-$ and $\cdot$OH, which are responsible for degrading MB confirmed by Fig. 12.

Conclusions
In summary, a facile in-situ precipitation method has been designed and developed to synthesize a series of AgSiO/Ag$_2$CO$_3$ composites with the sizes in the range of 100 nm. The as-synthesized AgSiO/Ag$_2$CO$_3$-5:1 composite shows superior VL photocatalytic activities, and the degradation of MB reach as ~99.1% under VL irradiation within ~40 min, which can be ascribed to the synergetic effect between AgSiO and Ag$_2$CO$_3$, including the maximum heterojunction interface with intimate contact, enhanced photogenerated charge separation efficiency, fully exposed reactive sites as well as excellent VL response in the composite. For the selectivity for degradation, we speculate that the discrepancy in degradation capacities among the two anionic dyes can be ascribed to the molecule size. This work will give insights into the importance of rational design of heterojunction systems, and provide a potential method for the construction of efficient heterojunction photocatalysts with controllable sizes and space distributions.

References
1. Shi, L., Liang, L., Wang, F., Liu, M. & Sun, J. Enhanced visible-light photocatalytic activity and stability over g-C$_3$N$_4$/Ag$_2$CO$_3$ composites. J. Mater. Sci. 50, 1718–1727 (2015).
2. Li, Y. et al. Preparation and enhanced visible light photocatalytic activity of novel g-C$_3$N$_4$ nanosheets loaded with Ag$_2$CO$_3$ nanoparticles. Nanoscale 7, 758–764 (2015).
3. Panthi, G. et al. Electrospun composite nanofibers of polyacrylonitrile and Ag$_2$CO$_3$ nanoparticles for visible light photocatalysis and antibacterial applications. J. Mater. Sci. 50, 4477–4485 (2015).
4. Xu, X., Zhai, T., Shao, M. & Huang, J. Anodic formation of anatase TiO$_2$ nanotubes with rod-formed walls for photocatalysis and field emitters. Phys. Chem. Chem. Phys. 14, 16371–16376 (2012).
5. Dai, G., Yu, J. & Liu, G. A new approach for photocorrosion inhibition of Ag$_2$CO$_3$ photocatalyst with highly visible-light-responsive reactivity. J. Phys. Chem. C 116, 15519–15524 (2012).
6. Liu, J. et al. Anchoring of Ag$_x$Si$_2$O$_7$ nanoparticles on α-Fe$_2$O$_3$ short nanotubes as a Z-scheme photocatalyst for improving their photocatalytic performances. Dalton T. 45, 12745–12755 (2016).
7. Lou, Z. et al. Ag$_2$SiO$_3$: a silicate photocatalyst for the visible region. Chem. Mater. 26, 3873–3875 (2014).
8. Zhang, S. et al. Hybrid 0D–2D nanoheterostructures: in-situ growth of amorphous silver silicates dots on g-C$_3$N$_4$ nanosheets for full spectrum photocatalysis. ACS Appl. Mater. Inter. 8, 35138–35149 (2016).
9. Zheng, Y., Lin, L., Ye, X., Guo, F. & Wang, X. Helical graphitic carbon nitrides with photocatalytic and optical activities. Angew. Chem. Int. Edit. 53, 11926–11930 (2014).
10. Mehrjui, O., Mir, N. A., Pirzada, B. M., Sabir, S. & Muneeb, M. In-situ anion exchange synthesis of AgBr/Ag$_2$CO$_3$ hybrids with enhanced visible light photocatalytic activity and improved stability. J. Mol. Catal. A: Chem. 395, 16–24 (2014).
11. Yang, H. et al. Constructing the novel ultrafine amorphous iron oxyhydroxide/g-C$_3$N$_4$ nanosheets heterojunctions for highly improved photocatalytic performance. Sci. Rep. 7, 8686 (2017).
12. Shu, D., Feng, F., Han, H. & Ma, Z. Prominent adsorption performance of amino-functionalized ultra-light graphene aerogel for methyl orange and amaranth. Chem. Eng. J. 324, 1–9 (2017).
13. Chen, F. et al. Novel ternary heterojunction photocatalyst of Ag nanoparticles and g-C$_3$N$_4$ nanosheets co-modified BiVO$_4$ for wider spectrum visible-light photocatalytic degradation of refractory pollutant. Appl. Catal. B: Environ. 205, 133–147 (2017).
14. Zhao, Q. et al. One-pot synthesis of Zn-doped SnO$_2$ nanosheet-based hierarchical architectures as a glycol gas sensor and photocatalyst. CrystEngComm 17, 4394–4401 (2015).
15. Yu, C. et al. Enhancing the photocatalytic performance of commercial TiO2 crystals by coupling with trace narrow-band-gap Ag2CO3. Ind. Eng. Chem. Res. 53, 5759–5766 (2014).
16. Liu, L. et al. A stable Ag2PO4@g-C3N4 hybrid core@shell composite with enhanced visible light photocatalytic degradation. Appl. Catal. B: Environ. 183, 133–141 (2016).
17. Han, S. W., Kim, Y. & Kim, K. Dodecanethiol-derivatized Au/Ag bimetallic nanoparticles: TEM, UV/VIS, XPS, and FTIR analysis. J. Colloid Interf. Sci. 208, 272–278 (1998).
18. Kaushik, V. K. XPS core level spectra and Auger parameters for some silver compounds. J. Electron Spectrosc. 56, 273–277 (1991).
19. Yu, C., Li, G., Kumar, S., Yang, K. & Jin, R. Phase transformation synthesis of novel Ag2O/Ag2CO3 heterostructures with high visible light efficiency in photocatalytic degradation of pollutants. Adv. Mater. 26, 892–898 (2014).
20. Epling, W. S., Hollund, G. B. & Salata, G. N. Surface characterization study of the thermal decomposition of Ag2CO3. J. Phys. Chem. B 102, 2263–2268 (1998).
21. Dong, S. et al. Self-assembled hollow sphere shaped Bi2WO6/RGO composites for efficient sunlight-driven photocatalytic degradation of organic pollutants. Chem. Eng. J. 316, 778–789 (2017).
22. Jin, X., Mok, E. K., Baek, J.-W., Park, S.-H. & Hwang, S.-J. Importance of the tuning of band position in optimizing the electronic coupling and photocatalytic activity of nanocomposite. J. Solid State Chem. 230, 175–181 (2015).
23. Frey, G. et al. A chromium terephthalate-based solid with unusually large pore volumes and surface area. Science 309, 2040–2042 (2005).
24. Sun, J. et al. Bioinspired hollow semiconductor nanospheres as photosynthetic nanoparticles. Nat. Commun. 3, 1139 (2012).
25. Gaumet, M., Vargas, A., Gurny, R. & Delie, F. Nanoparticles for drug delivery: the need for precision in reporting particle size parameters. Eur. J. Pharm. Biophar. 69, 1–9 (2008).
26. Fang, S. et al. Fabrication of BiOCl@CdS/Ag2CO3 heterojunctions with enhanced photocatalytic activity under visible-light irradiation. J. Mater. Sci.-Mater. El. 1–9 (2017).
27. Al-Keisy, A. et al. A ferroelectric photocatalyst Ag8Si5O13 with visible-light photooxidation properties. J. Mater. Chem. A 4, 10992–10999 (2016).
28. Yang, M.-Q. et al. Self-surface charge exfoliation and electrostatically coordinated 2D hetero-layered hybrids. Nat. Commun. 8, 14224 (2017).
29. Yu, C.-L. et al. Novel AgCl/Ag2CO3 heterostructured photocatalysts with enhanced photocatalytic performance. Rare Metals 35, 475–480 (2016).
30. Yu, B. et al. Preparation of electrosyn Ag/g-C3N4 loaded composite carbon nanofibers for catalytic applications. Mater. Res. Express 4, 1 (2017).
31. Zhu, X. et al. Synthesis of novel visible light response Ag2SiO3 photocatalyst. Appl. Catal. B: Environ. 199, 315–322 (2016).
32. Chem, Q., Wu, S. & Xin, Y. Synthesis of Au@Cu2TiO4 nanobelts photocatalyst for efficient photocatalytic degradation of antibiotic oxetacycline. Chem. Eng. J. 302, 377–387 (2016).
33. Yang, M.-Q. et al. Ultrathin nickel boron oxide nanosheets assembled vertically on graphene: a new hybrid 2D material for enhanced photo/electro-catalysis. Mater. Horiz. 4, 885–894 (2017).
34. Liu, J. et al. 2D ZnO mesoporous single-crystal nanosheets with exposed [0001] polar facets for the depollution of cationic dye molecules by highly selective adsorption and photocatalytic decomposition. Appl. Catal. B: Environ. 181, 138–145 (2016).
35. Yao, Z. et al. Preparation, characterization, and antibacterial activity of shell waste loaded with silver. J. Mater. Sci. 48, 8580–8587 (2013).
36. Cui, W. et al. Microwave-assisted synthesis of Ag@AgBr-intercalated K2Nb2O7 composite and enhanced photocatalytic degradation of Rhodamine B under visible light. Chem. Eng. J. 230, 10–18 (2013).
37. Hou, R. et al. Coupling system of Ag/BiOBr photocatalysis and direct contact membrane distillation for complete purification of N-containing dye wastewater. Chem. Eng. J. 317, 386–393 (2017).
38. Shu, J. et al. One-pot synthesis of AgCl@Ag hybrid photocatalyst with high photocatalytic activity and photostability under visible light and sunlight irradiation. Chem. Eng. J. 252, 374–381 (2014).
39. Ma, X. et al. Comparison of photocatalytic reaction-induced selective corrosion with photocorrosion: Impact on morphology and stability of Ag-ZnO. Appl. Catal. B: Environ. 201, 348–358 (2017).
40. Orge, C., Pereira, M. & Faria, J. Photocatalytic-assisted ozone degradation of metolachlor aqueous solution. Chem. Eng. J. 318, 247–253 (2017).
41. Liang, H., Jia, Z., Zhang, H., Wang, X. & Wang, J. Photocatalysis oxidation activity regulation of Ag/TiO2 composites by evaluated the selective oxidation of Rhodamine B. Appl. Surf. Sci. 422, 1–10 (2017).
42. Suyama, P. et al. Co3O4-C3N4-p-n nano-heterojunctions for the simultaneous degradation of a mixture of pollutants under solar irradiation. Environ. Sci. Nano. 4, 212–221 (2017).
43. Zhang, D., Li, J., Wang, Q. & Wu, Q. High [001] facets dominated BiOBr lamellas: facile hydrolysis preparation and selective visible-light photocatalytic activity. J. Mol. Catal. A 41, 8622–8629 (2013).
44. Gou, W., Wu, P., Jiang, D. & Ma, X. Synthesis of AgBr@Bi2O3 composite with enhanced photocatalytic performance under visible light. J. Alloy. Compd. 646, 437–445 (2015).
45. Han, C., Quan, Q., Chen, H. M., Sun, Y. & Xu, Y. J. Progressive Design of Plasmonic Metal–Semiconductor Ensemble toward Regulated Charge Flow and Improved Vis-NIR-Driven Solar-to-Chemical Conversion. Small 13, 14 (2017).
46. Xu, K. et al. Ag-CuO-ZnO metal-semiconductor multiconcentric nanotubes for achieving superior and perdurable photodegradation. Nanoscale 9, 11574–11583 (2017).
47. Chen, F. et al. Facile preparation of ternary Ag2CO3/Ag/PANI composite nanorods with enhanced photocatalytic performance and stability. J. Mater. Sci. 52, 4521–4531 (2017).
48. Zhang, P. et al. Synthesis of sandwich-structured AgBr@Ag2TiO3 composite photocatalyst and study of its photocatalytic performance for the oxidation of benzyl alcohols to benzaldehydes. Chem. Eng. J. 306, 1151–1161 (2016).
49. Yang, M.-Q., Zhang, N., Wang, Y. & Xu, Y.-J. Metal-free, robust, and regenerable 3D graphene–organics aerogel with high and stable photosensitization efficiency. J. Catal. 346, 21–29 (2017).

Acknowledgements

Financial supports from NSFC (Grant Nos 51672109, 21505050) and the Natural Science Foundation of Shandong Province (Grant No. ZR2016JL015, ZR2016FM30).

Author Contributions

C.R.Y. performed the experiments. D.X.L. and Y.H.C. performed the SEM observations and TEM observations. Z.S.W. and X.X.J. discussed and commented on the experiments and results, and wrote the paper.

Additional Information

Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-017-15405-6.

Competing Interests: The authors declare that they have no competing interests.
