Engineering the metathesis and oxidation-reduction reaction in solid state at room temperature for nanosynthesis

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It is a long-standing goal to explore convenient synthesis methodology for functional materials. Recently, several multiple-step approaches have been designed for photocatalysts AgnX@Ag (X = Cl−, PO43−, etc.), mainly containing the ion-exchange (metathesis) reaction followed by photoreduction in solution. But they were obsessed by complicated process, the uncontrollability of composition and larger sizes of Ag particles. Here we show a general solid-state route for the synthesis of AgnX@Ag catalysts with hierarchical structures. Due to strong surface plasmon resonance of silver nanoparticles with broad shape and size, the AgnX@Ag showed high photocatalytic activity in visible region. Especially, the composition of AgnX@Ag composites could be accurately controlled by regulating the feed ratio of (NH2OH)2·H2SO4 to anions, by which the performance were easily optimized. Results demonstrate that the metathesis and oxidation-reduction reactions can be performed in solid state at room temperature for nanosynthesis, greatly reducing the time/energy consumption and pollution.

Photocatalytic technology has become an important method to degrade organic pollutants. Recently, Ag-based photocatalyst AgnX@Ag-NPs has been attracted much attention due to their photocatalytic activity under visible-light irradiation1–15. Firstly, silver nanoparticles (Ag-NPs) demonstrate strong visible absorbance in virtue of the strong localized surface plasmon resonance (LSPR) effect16–20. Moreover, due to the low Fermi level (EF) of Ag-NPs7,10,11,21, the photo-excited electrons tend to move to the surface of Ag-NPs, resulting in effective segregation of photo-generated electrons and holes. The recombination of photo-generated electron-hole pairs and photo-reduction of AgnX is suppressed. Therefore, Ag-based composite catalysts exhibit higher visible absorbance and stability. Several multiple-steps strategies have been designed to synthesize these hybrid photocatalysts. Among these, ion-exchange1,3,5,6,10,11,24,27, liquids-assisted hydrothermal7, and solvothermal reaction8 were adopted firstly to prepare AgnX, and then some Ag+ ions of as-prepared AgnX were converted to Ag via UV irradiation. Furthermore, these multiple-steps methods increased the complexity of the procedures, and the sizes of resultant Ag particles were usually in micron scale, reducing the photocatalytic effectiveness of the materials. Especially the composition of prepared AgnX@Ag composites could not be controlled accurately, making it difficult to optimize the performance of the materials.

In the nanosynthesis of functional materials, the exchange (metathesis) reaction and redox reaction are usually adopted. The former is a traditional solution-processed synthesis, while the latter is a process happening in solution, or in solid phase at high temperature. If the synthesis can be achieved in solid state at room temperature (mechanochemistry synthesis), the time/energy consumption and pollution in the synthesis process will be markedly reduced. Featured with convenient and eco-friendly, the room-temperature solid-state chemical synthesis technique has sparked intense research interest of scientists22–27. In our previous research26, AgCl@Ag composite with excellent catalytic activity were prepared by a room-temperature solid-state chemical reaction route. In the present work, the solid-state chemical reaction were expanded to other Ag-based hybrid photocatalysts (such as AgBr@Ag, Ag3CrO4@Ag and Ag3PO4@Ag, etc.), and a general solid synthesis route for these composites were summarized. The obtained Ag particles exhibited lush LSPR nanostructures, and the composition of AgnX@Ag can be easily controlled.
Results

Formation mechanism of composites. The route (I) is described by the following reactions:

\[ \text{Ag}^+ (\text{CH}_3\text{COOAg}) + X^- (\text{NaX}) \rightarrow \text{AgX} + \text{CH}_3\text{COO}^- + \text{Na}^+ (X = \text{Cl}^-, \text{Br}^-) \] (1)

\[ 2\text{Ag}^+ (\text{CH}_3\text{COOAg}) + 2\text{NH}_2\text{OH} \rightarrow 2\text{Ag} + \text{N}_2 + 2\text{H}_2\text{O} + 2\text{H}^+ (\text{CH}_3\text{COOH}) \] (2)

The AgCl and AgBr were formed through the ion-exchange reaction (1) between CH$_3$COOAg and halides (NaCl, NaBr), meanwhile, some Ag$^0$ atoms were generated by redox reaction (2) between Ag$^+$ and low-valent nitrogen atoms in (NH$_2$OH)$_2$H$_2$SO$_4$. The route (II) was designed for the synthesis of feeble-acid insoluble silver salts decorated with Ag-NPs which is summarized from the chemical equations (3)–(5):

\[ \text{nAg}^+ (\text{CH}_3\text{COOAg}) + \text{nX}^- (\text{Na}_n\text{X}) \rightarrow \text{Ag}_n\text{X} + \text{nCH}_3\text{COO}^- + \text{nNa}^+ (X = \text{CrO}_2^{2-}, \text{PO}_4^{3-}, \text{etc.}) \] (3)

\[ \text{Ag}_n\text{X} + \text{nH}^+ (\text{H}_2\text{SO}_4) \rightarrow \text{Ag}_n\text{SO}_4 \text{(slightly soluble)} + \text{H}_2\text{O} \] (4)

\[ \text{nAg}^+ + \text{nNH}_2\text{OH} \rightarrow \text{Ag}_n + \text{n}/2\text{N}_2 + \text{nH}_2\text{O} + \text{nH}^+ (\text{H}_2\text{SO}_4) \] (5)

When (NH$_2$OH)$_2$H$_2$SO$_4$ was added into Ag$_n$X powders obtained from reaction (3), the succeeding process can be conducted along reactions (4) and (5). This can be explained that H$^+$ from (NH$_2$OH)$_2$H$_2$SO$_4$ made equal molar amounts of Ag$^+$ release from the surfaces of Ag$_n$X particles due to the weak acidity of H$_2$O, which is similar to the surface etching. Then these Ag$^+$ were reduced to Ag$^0$ by the low-valent nitrogen atoms in (NH$_2$OH)$_2$H$_2$SO$_4$, causing the in-situ growth of Ag-NPs on the surfaces of Ag$_n$X particles.

Characterization of structure, composition, and microstructures. The XRD patterns of different Ag$_n$X@Ag composites are shown in Fig. 1a. The Prepared Ag particles had the face-centered-cubic structure in accordance with the standard JCPDS 89–3722, coexisting with corresponding Ag$_n$X. In the reaction process, the molar ratio of Ag to Ag$_n$X in the final products could be controlled by the feed ratio of (NH$_2$OH)$_2$H$_2$SO$_4$ to anion \((\text{a} : \text{b} \text{ for (I) or } q: p \text{ for (II)})\). Theoretically, the ratio of Ag/Ag$_n$X should be 2a/b and 2q/p for route (I) and (II), respectively. In addition, similar to our previous work for AgCl@Ag$^0$, the molar ratio of Ag:Ag$_n$X were approximately estimated using the element analysis according to the X-ray energy dispersion spectrum (EDS) of Ag$_3$PO$_4$@Ag, Ag$_2$CrO$_4$@Ag, AgCl@Ag, and AgBr@Ag (see Supplementary data, Fig. S1). The results are close to the theoretical value (2q/p) for Ag$_3$PO$_4$@Ag and Ag$_2$CrO$_4$@Ag, and 2a/b for the other two samples). In order to evaluate the capacity of composition adjustment, a series of AgCl@Ag composites were prepared with different feed ratio of (NH$_2$OH)$_2$H$_2$SO$_4$ to Cl$^-$ \((a: b = 1: 4 \text{ (C-1), 1: 6 \text{ (C-2), 1: 8 \text{ (C-3), 1: 16 \text{ (C-4), respectively). The molar ratios of Ag/AgCl in products were calculated by quantitative analysis of the profile-fitted XRD peaks (Fig. S2). The comparison of theoretical and quantitative calculated ratio of Ag/AgCl is listed in Fig. 1b.}) \)

Figs. 2 and S3 show representative SEM images of Ag$_n$X@Ag composites prepared with room-temperature solid-state chemical reaction. Interestingly, the as-prepared Ag$_n$X@Ag composites possess fine hierarchical structures like jujube cake, indicating that this method is competent to fabricate Ag$_n$X@Ag composite structures in high yields. It can be clearly seen from the enlarged SEM images that the large quasi-spherical or flaky Ag$_n$X particles (ca. from hundred nanometers to micron) were evenly covered by Ag-NPs with a wide range of shapes and broad size distribution (ca. the size range from several to around one hundred nanometers) (Fig. 2). As a whole, Ag-NPs existed in nearly spherical and rodlike outline with different sizes. Specific to the finer morphology, actually, the spherical objects contain oblate or prolate spheroids (marked by the blue circles in the lower picture of panels a, and b in Fig. 2) with various ratio of major to minor axis (R) and polyhedra (red circles). And the rodlike particles contain nanorods (red arrows), nanorices (blue arrows), and other one-dimensional (1D) objects with different aspect ratio (r). Moreover, the distance between adjacent Ag-NPs on the given area is equivalent to or less than the diameter of particle, even becomes dimer or multimer. As shown in Fig. S3a, the Ag-NPs in Ag$_2$CrO$_4$@Ag sample mainly formed spherical objects with small interparticle spacing accompanied by several random aggregates, and some regions approximatively formed a two-dimensional (2D) array of Ag-NPs on Ag$_2$CrO$_4$ matrix. Compared with the other three samples, the surface of AgBr matrix carries with the minimum density of Ag-NPs, and the size distribution of Ag-NPs appears large (the diameter of big particles in the range of 100–300 nm, while most of the particles below 40 nm) (Fig. S3b). Furthermore, in all samples, the Ag-NPs are well loaded on the rough surface of Ag$_n$X particles with two behaviors, adhesion and embedded modes. When the latter
is employed, it is particularly worth noting that the immersion depth in AgnX matrix is different. To sum up, the Ag-NPs in the present AgnX@Ag composites have following features: (i) the broader size distribution; (ii) the variety of shape, especially, the lower symmetric configuration with different R(r); (iii) the embedded Ag-NPs in the AgnX matrix with different immersion depth; and (iv) the small interparticle spacing and random aggregates. In comparison, additionally, the proportion of rodlike and other nonspherical Ag-NPs in AgnX@Ag sample and the size is larger than that of the other three samples. This can be attributed to the increasing orientation growth of Ag-NPs in AgnX@Ag sample because of the gradual production of metallic silver in the surface etching and regrowth process (due to the moderate-intensity acidity of phosphoric acid). And the Ag-NPs in AgnX@Ag sample show a relatively narrow size distribution than the other three samples. This can be explained that the metallic silver were quickly generated by reaction (4) and (5) due to the weak acidity of chromate (compared to the H3PO4), then it adopted instantaneous nucleation growth mode, decreasing the orientation growth.

Attempts have been carried out to observe Ag-NPs by EDS-mapping measurement (under 5 kV accelerating voltage) but it turned out to be unsuccessful (Fig. S4). In accordance with An’s report in 2010 the spatial distribution and domain morphologies of the Ag-NPs is hard to be clearly imaged with EDS mapping because exposing the AgnX@Ag particles to an electron beam with high current density for a long time (for EDS mapping) would constantly reduce part of AgnX to metallic silver.

Finally, in order to study the influence of feed ratio (a:b) on the product morphology, especially on the shape, size and distribution of Ag-NPs, as well as the resulting different photocatalytic performance, we characterize the samples C-1, 3, and 4 with SEM, UV-Vis spectra, and photodecomposition experiments. Compared with the sample C-2, other samples (C-1, 3, and 4) all display hierarchical structures (Fig. S5). However, between them the density and microstructures of Ag-NPs exist more or less difference. Firstly, the density of Ag-NPs on the surface of AgCl particles increased with the increase of the feed ratio a:b (C-1 > C-2 > C-3 > C-4). The AgCl particles surface in C-4 were sparsely modified with a small amount of Ag-NPs, while the surface of AgCl particles in C-1 is covered by dense Ag-NPs, even stacking. Secondly, the Ag-NPs in C-4 consisted mostly of spheres with various grain sizes ranging from several nanometers to 50 nm, while the other three samples have various formations with broad size distributions (from several to one hundred nanometers) or different R(r), including the patterns of sphere (predominate), nonsphere, and aggregation. Furthermore, with the increasing of feed ratio (a:b), considerable large Ag-NPs with a size range of ca. 130–250 nm and the aggregation of nanoparticles were generated gradually. In conclusion, the yield of metallic silver increases with the increase of a:b, resulting in the increase of the density of Ag-NPs on AgCl particle surface, necessarily, as well the appearance of large and nonspherical particles due to the Ostwald and orientation growth.

UV/Vis absorption and photocatalytic performances. In order to evaluate the ability of absorbing light in the work environment, we collected the UV-Vis diffuse reflectance spectra (DRS) of samples in the aqueous suspension. Because the photocatalytic tests were carried out in greater than 400 nm light (filtered irradiation (λ > 400 nm))
and the surface plasmon resonance (SPR) effect of Ag-NPs mostly occurred beyond the wavelength of 300 nm, so we mainly collected and analyzed the DRS at more than 300 nm wavelength of light. Note, the contribution of SPR modes of plasmonic Ag-NPs on the optical absorption of composites and their dependence on particle size, shape, and aggregation state will be discussed latter. Fig. 3a showed that all the samples have strong and broad absorption bands in the visible light region, which can be mainly attributed to the LSPR effects of Ag-NPs, meanwhile, the characteristic absorptions of Ag3PO4, Ag2CrO4, and AgBr also contribute to the visible light absorption of corresponding composites (direct-bandgap/indirect-bandgap of Ag3PO4 and AgBr are 2.43/2.36 eV and 4.28/
2.46 eV respectively, and band gap of Ag2CrO4 is 1.75 eV). To be specific, the Ag3PO4@Ag displayed a high energy intense absorption at ca. 425 nm followed by a tail of strong absorption pattern extending to 800 nm. It can be deduced that the absorption of Ag3PO4 and the LSPR effect of Ag-NPs formed this superimposition spectra, and the absorption edge of Ag3PO4 (ca. 526 nm) was submerged by total spectra. Similarly, the Ag2CrO4@Ag implemented a strong absorption in broad visible region centering at the peak of 615 nm, and coexisting with an obvious absorption shoulder peak at about 360 nm. The AgBr@Ag performed absorption from 400 to 800 nm with a relatively constant output. Moreover, considering the large band gap of AgCl (direct-bandgap/indirect-bandgap = 5.6/3.25 eV), we believe that the visible light absorption of AgCl@Ag is mainly induced by the plasmon resonance of Ag-NPs. In the series of AgCl@Ag products, approximately, the extinction spectrum intensity increased with increasing silver content (but the C-1 and C-2 matched each other) (Fig. 3b). The C-4 DRS spectrum displayed an absorption mound near 370 nm followed with a declined and slightly wavy curve to 800 nm, while other three samples showed absorption in the entire visible region with almost constant intensity. It is worth noting that the C-1 exhibits relatively abundant extinction information in near ultraviolet region (upper illustrations in Fig. 3b).

The photocatalytic activity of the as-prepared catalysts was estimated with the photocatalytic degradation of MO aqueous solution under visible light at room temperature. The relationship between MO-dye decomposition effect and time under visible light irradiation (λ > 400 nm) of Ag3PO4@Ag, Ag2CrO4@Ag, AgCl@Ag, and AgBr@Ag composites are shown in Fig. 3c. It should be noted that these four composites had theoretically equal mole ratio of Ag/AgX. The calculated values of MO degradation rate of Ag3PO4@Ag, Ag2CrO4@Ag, AgCl@Ag, and AgBr@Ag were 0.69, 0.57, 0.52, and 0.41 mg/(min·gcat), respectively. The activities of the latter two samples compare equally or favorably to that of some recently reported corresponding photocatalysts synthesized via other routes. And that of Ag2CrO4@Ag is slightly weaker than the Huang’s report. Moreover, because the photocatalytic measurement of Ag3PO4@Ag was carried out with the irradiation wavelength from 400 nm, we cannot develop a parallel comparison of the capacity to other reports which most of them employed the filtered irradiation with wavelengths starting at 420 nm. To ensure objectivity of comparison, we carried out the control experiments with present Ag3PO4@Ag under the same conditions of others. As shown in Fig. S6, the degradation rate of MO is estimated to be about 0.58 mg/(min·gcat), which is equivalent to that of Ag3PO4@Ag in literature 13 (in that case, Ag3PO4@Ag AAP-2: 0.56 mg/(min·gcat); Ag3PO4@Ag AAP-2: 0.61 mg/(min·gcat)). At the same time, a blank experiment revealed that the degradation of MO dye is negligible, where no photocatalyst is used. In current work, we summarized that the photocatalytic activity of catalysts was increased with the increase of the anions’ charge (PO4\(_{3}^{3-}\) > CrO4\(_{2}^{2-}\) > Cl\(^{-}\) (Br\(^{-}\)). Meanwhile, the photocatalytic activity was also affected by the stability of anions (Cl\(^{-}\) > Br\(^{-}\)). This is consistent with the report by Huang and co-workers.

Another set of catalytic experiments was carried out to evaluate the photocatalytic activity of C-1, 2, 3, and 4 under visible light at room temperature. As is shown in Fig. 3d, the MO-dye decomposition rate increased with the increase of Ag amount. However, the decomposition capacity was increased slightly when metallic silver reached 20 wt% (molar content 25%). AgCl@Ag composites were then selected as the representative to investigate the stability of the AgX@Ag during the recycling photocatalysis experiment. Fig. 3e shows the photocatalytic activities of recycled AgCl@Ag composites on photocatalytic degradation of MO under visible light. Although AgCl@Ag composites have been re-used for five times, MO molecules were still effectively decomposed at the same constant rate as to the original AgCl@Ag composites. It indicates that the AgCl@Ag composites prepared by room-temperature solid-state reaction demonstrate high photocatalytic stability under visible-light irradiation.

**Discussion**

It is well known that the silver nanoparticles exhibit LSPR at visible frequencies, which is well understood as a coherent oscillation of the electrons in the local dielectric environment near the surface of metal nanoparticles (NPs). Theoretically and experimentally, the size and shape of the particle as well as the dielectric function of the surrounding medium determine the frequency and the strength of the resonance. Furthermore, study on the SPR effect of metal nanoparticle shows that the scattering cross section (SCS) of particles, whose scale is the sixth power of its radius, has great contribution to the extinction efficiency, especially for large nanoparticles (as long as the particles are not large enough to exhibit strong retardation effects). The scattering and absorption of a spherical object with arbitrary size have been described exactly by Mie theory. Recently, modern numerical calculation techniques including discrete dipole approximation (DDA) method were developed and applied to study the extinction, absorption, scattering, or other optical properties of nonspherical particles, such as oblate spheroid, rod, triangle, prism, and etc. Wherein, Schatz and coworkers described the dipole and quadrupole plasmon resonance of Ag-NPs with a wide range of sizes, shapes, and dielectric environments, and presented a numerical method for calculating extinction and scattering cross-sections in 2003. Results explicitly manifested that the dipolar SPR, whose frequency is generally in the visible light region (except for the very small particles), is particularly sensitive to the particle size, shape, and aspect ratio (one-dimensional/quasi-one-dimensional (1D/quasi-1D) structure). An universal conclusion is that the dipolar SPR wavelength will obviously shift to the red when the size of spherical object or the R(r) of 1D/quasi-1D structure increased, while the frequency of quadrupole component is relatively weak sensitive to above parameters (i.e. the optical intensity changes rapidly while peak position changes slowly) and it can be “quenched” by particle asymmetry.

In the present work, based on the microstructure of Ag-NPs, the behavior of as-prepared Ag-NPs in the UV-Vis spectra can be supported by corresponding DDA theoretical prediction. Firstly, the plasmon resonance energy and width are inherently blurred in bulk measurements because of the inhomogeneity of silver nanoparticles. Here, the Ag-NPs in each AgX@Ag composites all have variable shapes with a broad size distribution or R(r), such as spheroid, polyhedron, rod, and prism. The dipole plasmon resonances of these variform Ag-NPs were inherently excited in respectively specific wavelength region which mostly fall in the range of visible light region, while the quadrupole plasmon resonances were also excited in the higher frequency region for the large particles and 1D/quasi-1D structure. The congregation of these resonances will span the entire visible region extending to the near UV region. However, these resonance frequencies are superimposed on each other, cannot be distinguished well besides the Ag2CrO4@Ag. Moreover, the embedded mode of Ag-NPs and the small interparticle spacing (cooperative plasmon mode) as well as random aggregates promote the red-shift of the dipole resonance, which in turn increase the absorption and scattering of visible light. Secondly, the SCS of Ag-NPs in Ag3PO4@Ag and Ag2CrO4@Ag are larger than that in other two composites, because the former two had higher surface density of Ag-NPs or larger Ag-NPs under the equal amount of metallic silver. So, the extinction efficiency of Ag3PO4@Ag and Ag2CrO4@Ag will be higher than that in the other two samples. Of course, it does not exclude the contribution of characteristic absorption of Ag3PO4 and Ag2CrO4 in visible region. Furthermore, the small size distribution and small particle spacing of Ag-NPs in Ag2CrO4@Ag make the dipole resonance frequency perform in a relatively narrow long
wavelength region interweaving with the characteristic absorption of Ag₂CrO₄, distinguishing the quadrupole resonance peaks.

In analogy to the above analysis, C-1, C-2, and C-3 exhibit excellent absorption in the near UV and visible light regions stemming from the dipole and quadrupole resonances of a great deal of various Ag-NPs, while the C-4 only exist absorption in the near UV and blue light region arisen from the small amount of Ag-NPs and their simplex spherical shape. The gradual increase of extinction intensity along with the increase of metallic silver can be explained as follow: the increase of metallic silver content results in the increase of Ag-NPs surface density, which in turn increases the total SCS. But, after 20 wt% of metallic silver, the new producing metallic-silver is mainly used for several large particles growing, leading to the phase retardation of incident radiation which partially offset the incremental SPR particle contribution. The extinction characters in near UV of C-1 can be attributed to the quadrupole SPR of the unsocial larger particles.

In the present work, rooted in the lush SPR structures of Ag-NPs and the higher composite structure, the prepared AgₓX@Ag composites showed excellent photocatalytic performances and stability under the visible light irradiation. The Ag-NPs prepared with this method have rich SPR configurations, endowing them with strong ability to capture photon in broad light range (visible), and the absorbed photon would be efficiently decomposed into electron-hole pairs. On the one hand, the LSPR could result in enhancement of the local inner electromagnetic field which helps the separation of generated electrons and holes. Additionally, in an AgₓX@Ag core-shell particle, free electrons in the metallic Ag-NPs are polarized by the AgₓX core, resulting in regions of negative and positive charges in the Ag-NPs that are far from and close to the AgₓX/Ag interface, respectively. The polarization field around the AgₓX core can also force the excited surface electrons in the Ag-NPs further far away from the AgₓX/Ag interface under illumination while the holes diffuse into the AgₓX core, namely, the dipolar character of the Ag-NPs make the absorbed photon more efficiently separate to electron-hole pairs. As a result, the migration of photo-excited electrons away from the AgₓX core prevents the recombination of photo-generated electron-hole pairs and photoreduction of Ag⁺ to Ag, leading to high activity and stability of the composites. The electrons accumulated on the outer surface of the Ag-NPs can be trapped by O₂ in the water solution to form the reactive oxygen species, such as superoxide ions (O₂⁻), while the holes would react with surface hydroxyl groups to form OH radicals. The active species would then degrade the MO.

In the view of excellent SPR structure of Ag-NPs in the AgₓPO₄@Ag, it had stronger SPR effect in visible irradiation than that of other three samples. Therefore, it would possess stronger photocatalytic activity than that of the others. Other photocatalytic ability sequence can be elucidated by the analyses of microstructure and extinction spectra, for example, that the photocatalytic ability of AgCl@Ag increased with increasing metallic silver content can be ascribed to developing trend of content and the SPR structure of Ag-NPs. Furthermore, according to the study of Huang and co-workers, the stability of holes (namely the positive charge centers) determines the activity of photocatalyst, following the rule: the higher stability and higher charged anions lead to the stronger photocatalytic ability. In the present work, better photocatalytic activity of AgₓPO₄@Ag may due to the high charged PO₄³⁻ anion with high stability and stronger deposited electron ability. Moreover, AgCl@Ag showed higher catalytic ability than AgBr@Ag since the Cl⁻ is more stable than Br⁻ (Cl⁻ is not easy to lost electron compared with Br⁻).

In summary, the metalization and oxidation-reduction reactions were successfully designed in solid state to synthesize a series of AgₓX@Ag nanophotocatalysts with high activity at room temperature. The composition of AgₓX@Ag composites could be accurately controlled by regulating the feed ratio of (NH₂OH)₂·H₂SO₄ to anions. The Ag-NPs deposited on AgₓX surfaces have a large number of different shapes and sizes leading to their SPR spectra which cover a wide range of frequencies. And the prepared AgₓX@Ag composites demonstrated high photocatalytic activity and stability under visible light irradiation. The photocatalytic ability of AgₓX@Ag composites was affected by the type and stability of anions. And the high amount and stability of charged anions improve the capacity of photocatalysts. The present work suggested a promising green approach for synthesis of functional materials.

Methods

AgₓX@Ag preparation. The general room-temperature solid-state reaction processes for AgₓX@Ag are illustrated in Fig. 4. It included the route (I) for silver halides@Ag (strong-acid insoluble silver salts) and the route (II) for AgₓX@Ag through room-temperature solid-state reaction process. AgₓX was formed through the ion-exchange reaction of CH₃COOAg and NaₓX, while metallic silver was generated by redox reaction between Ag⁺ and low-valent nitrogen atoms in (NH₂OH)₂·H₂SO₄. Theoretically, the molar ratio of Ag/AgₓX in solution (I) or 2q/p-2q/n in route (II).

Figure 4 | Schematics of recipe for synthesis of AgₓX@Ag through room-temperature solid-state reaction process. AgₓX was formed through the ion-exchange reaction of CH₃COOAg and NaₓX, while metallic silver was generated by redox reaction between Ag⁺ and low-valent nitrogen atoms in (NH₂OH)₂·H₂SO₄. Theoretically, the molar ratio of Ag/AgₓX is 2a/b in route (I) or 2q/(p-2q/n) in route (II).
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