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High-effective photocatalytic properties and interfacial transfer efficiencies of charge carriers for the novel Ag$_2$CO$_3$/AgX heterojunctions achieved by surface modification

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The novel Ag$_2$CO$_3$/AgX heterojunctions are achieved from the surface modification of Ag$_2$CO$_3$ with AgX (X = Cl, Br and I) nanoparticles by a facilely efficient ion-exchange method, which distinctly enhance degradation activity for typical RhB, MB, and MO dyes compared with Ag$_2$CO$_3$. The formation of heterostructure is evidenced by XRD, SEM, EDS, XPS and UV-vis DRS analyses, which indicates the bonding interaction between Ag$_2$CO$_3$ and AgX reduces the transfer potential barrier of charge carriers on their interface and extends visible light harvest at 480-640 nm. Photocurrent responses and PL spectra demonstrate Ag$_2$CO$_3$/AgX heterojunctions can effectively separate electron-hole pairs and suppress their recombination. The dye sensitization effect indicates that the effective electronic injection from RhB to heterojunction is in favor of improving photocatalytic ability. The possible transferred and separated behaviors of electron-hole pairs and photocatalytic mechanisms are illustrated in detail.

Introduction

During the past decades, photocatalysis as a “green” technique has been extensively researched in the field of wastewater treatment because most kinds of pollutants can be degraded completely by semiconductor photocatalysts under the visible light. The plenty of efforts have been made to explore high-efficiency photocatalysts for the decomposition of organic contaminants. However, to search new photocatalysts with high catalytic activity and research the transfer and separation behaviors of charge carriers still possess a big challenge so far.

It is well known that the generation of electron-hole pairs upon light irradiation promotes the formation of powerful oxidative activated species on the photocatalyst surface to decompose organic pollutants. The most photocatalysts, owing to so fast recombination rate of electron-hole pairs on the surface, are restricted in industrial applications. Therefore, inhibiting the recombination of internal charge carriers is essential for improving the net charge transfer and separation efficiency of photocatalyst. For this purpose, the variously effective strategies have been successfully explored and developed, such as controlling doped-defect, loading noble metal and constructing heterostructure etc. In consequence, tailoring photocatalyst properties by fabricating designed structure is indispensable to improving transfer and separation efficiency of charge carriers. It has demonstrated that hybridized two semiconductors, bringing about construction of heterostructure, can greatly decrease recombination probability of electron-hole pairs and increase lifetime. For instance, TiO$_2$/ITO/SWCNTs and Cu$_2$O/TiO$_2$ show the improved photoelectrochemical activity as well as g-C$_3$N$_4$/BiPO$_4$ and SnO$_2$/TiO$_2$ also exhibit the enhanced photocatalytic ability, which ascribes to the efficient transfer and separation of charge carriers in heterojunctions.

It is the heterostructure that dominates some behaviors of charge carriers, such as the transportation direction, separation distance and recombination rate and so on. Therefore, rational designing heterojunction with rapid transfer and separation efficiency and studying effect of heterostructure on the behavior of charge carriers are important and desired for the exploitation of high-effective photocatalysts. Although there have been some reports about discussion for the transfer behavior of charge carriers in heterojunctions, the better comprehending the transfer, separation, and recombination process of electron-hole pairs still possesses an important significance to probe into the intrinsic reasons of the enhanced photocatalytic activity. As a target, we design and synthesize heterojunction using a simple method and further investigate their transferred and separated behavior of charge carriers.

The reported Ag$_2$PO$_4$ and Ag$_2$CO$_3$ photocatalysts have high-efficiency degradation ability for multiformic dyes, but they easily take place photocorrosion under visible irradiation. However, when the silver phosphate surface is modified with silver halide to construct AgX/Ag$_2$PO$_4$ heterojunction, it not only improves photocatalytic ability but also increases the stability of samples. Meanwhile, the various photocatalysts modified by silver halide also
attract attentions of the most researchers. Such as Ag/AgX/GO,\textsuperscript{17} Ag/AgX/BiOX,\textsuperscript{18} Ag/AgX/Ag\textsubscript{2}O\textsubscript{3},\textsuperscript{19} Ag/AgX/gC\textsubscript{3}N\textsubscript{4},\textsuperscript{20} Ag/AgX/Bi\textsubscript{2}O\textsubscript{3} and so forth all exhibit improved photocatalytic ability.

To our knowledge, no researches on the composite Ag\textsubscript{2}CO\textsubscript{3}/AgX photocatalysts have been reported. In this work, the unique Ag\textsubscript{2}CO\textsubscript{3}/AgX heterojunctions achieved by modifying silver carbonate surface with silver halide nanoparticles are prepared with a facilely ion-exchange method. These heterojunctions exhibit distinctly enhanced degradation ability for the typical RhB, MB and MO dyes. The possible transferred and separated behaviors of charge carriers and photocatalytic mechanisms are discussed in depth.

Experimental

Preparation and Characterization. The Ag\textsubscript{2}CO\textsubscript{3} samples were prepared by our previous reported method.\textsuperscript{27} The Ag\textsubscript{2}CO\textsubscript{3}/AgX heterojunctions were prepared by ion-exchange method. As-prepared Ag\textsubscript{2}CO\textsubscript{3} samples (1 g) were put into the beaker with 30 ml H\textsubscript{2}O. After ultrasonic dispersion 30 min, suspensions were quickly added to the KX (X = Cl, Br and I) solutions (30 ml, 10 mmol L\textsuperscript{-1}), and then aged 4 h. The precipitations were washed in turn with secondary distilled water and absolute ethanol to dissolve any unreacted raw materials. Lastly, the Ag\textsubscript{2}CO\textsubscript{3}/AgX heterostructure products were blow-dried using blower under atmosphere at room temperature.

The phases of the Ag\textsubscript{2}CO\textsubscript{3} and Ag\textsubscript{2}CO\textsubscript{3}/AgX samples were characterized by powder X-ray diffractometer (XRD, Rigaku D/max-2000) equipped with a Cu-K\textalpha radiation at a scanning rate of 5° min\textsuperscript{-1} in the 20 range of 10 - 90°. X-ray tube voltage and current were set at 45 kV and 50 mA, respectively. The morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM, FEI QUANTA 200F). X-ray photoelectron spectroscopy (XPS) analysis was measured on an American electronics physical H5700ESCA system with X-ray photoelectron spectroscopy using Al K\textalpha (1486.6 eV) monochromatic X-ray radiation. The peak positions were corrected against the C 1s peak (284.6 eV). The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples were recorded on a UV-vis spectrophotometer using Al K\textalpha (1486.6 eV) monochromatic X-ray radiation. The peak positions were corrected against the C 1s peak (284.6 eV).

Results and discussion

Fig. 1 XRD patterns of Ag\textsubscript{2}CO\textsubscript{3}/AgX samples.

Fig. 2 FESEM images and EDS spectra (insert) of Ag\textsubscript{2}CO\textsubscript{3} (a) and Ag\textsubscript{2}CO\textsubscript{3}/AgX (Cl (b), Br(c) and I (d)) samples.

The characteristic peaks appearing at each XRD pattern in Fig. 1 are well indexed to Ag\textsubscript{2}CO\textsubscript{3} and AgX (X = Cl, Br and I), which demonstrates the as-prepared samples are composed of Ag\textsubscript{2}CO\textsubscript{3} and AgX, respectively. The metal Ag or other
characteristic peaks are not detected. All the sharp and intense diffraction peaks reveal the samples have the high crystallinity. According to FESEM image in Fig. 2(a), Ag$_2$CO$_3$ sample displays smooth surface. By comparison, as shown the FESEM images in Fig. 2(b-d), the appearances of Ag$_2$CO$_3$/AgX samples change into obviously rough morphologies owing to the Ag$_2$CO$_3$ surface covered by abundant AgX nanoparticles, which is evidenced by the high-magnification FESEM images of Ag$_2$CO$_3$/AgX samples (see Fig. S1 in the ESI†). In addition, the EDS spectra of all the samples (the insert of Fig. 2(a-d) display the Ag$_2$CO$_3$/AgX samples contain Cl, Br and I elements, respectively. All above results indicate that the Ag$_2$CO$_3$/AgX heterojunctions are constructed via the surface modification of Ag$_2$CO$_3$ with AgX nanoparticles.

Fig. 3 High-resolution XPS spectra of Ag$_2$CO$_3$ and Ag$_2$CO$_3$/AgX samples.

XPS spectra are employed to gain a better insight into the surface state and interaction characteristics between Ag$_2$CO$_3$ and AgX nanoparticles in heterojunctions. The total XPS spectra of Ag$_2$CO$_3$/AgX heterojunctions (see Fig. S2 in the ESI†) display the different binding energy peaks are assigned to Ag 3d, Ag 3p, O 1s, C 1s, Cl 2p (a), Br 3d (b) and I 3d (c) states, and to Ag and O auger features, respectively. From the high-resolution XPS spectra of Ag$_2$CO$_3$/AgX heterojunctions in Fig. 3, the wide and asymmetric shapes of C 1s and O 1s spectra indicate they have different chemical states. The peaks at 284.6 eV and 288-289 eV in Fig. 3(a) are due to C element in Ag$_2$CO$_3$ and hydrocarbon contaminants, respectively; The peak at 530.6 eV and shoulder peak at the high binding energy in Fig. 3(b) belong to O 1s state of Ag$_2$CO$_3$ and adsorbed hydroxyl species, respectively. Moreover, the XPS spectra of Ag 3d in Fig. 3(c) are attribute to the Ag 3d$_{5/2}$ and 3d$_{3/2}$ states at 367.9 eV and 374.0 eV, respectively. Contrary to C 1s and O 1s, the shape of no-broadening and symmetric peaks for Ag 3d XPS spectra indicates that Ag may only possess one chemical state. In other words, no metal Ag generates on the Ag$_2$CO$_3$/AgX heterojunctions surface. Fig. 3(d) exhibits the obvious emission peaks deriving from 2p$_3$ and 2p$_1$ of Cl (197.9 and 199.5 eV), 3d$_{5/2}$ and 3d$_{3/2}$ of Br (68.4 and 69.7 eV) as well as 3d$_{3}$ and 3d$_{5}$ of I (621.0 and 632.5 eV), respectively, which is consistent with the results of EDS spectra. It is noticed that the peaks of O in Ag$_2$CO$_3$/AgX (X = Cl, Br and I) relative to Ag$_2$CO$_3$ shift 0.6, 0.8 and 1.1 eV toward the high binding energy, respectively, which demonstrates bonding effects between Ag$^+$ and CO$_3^{2-}$ on the Ag$_2$CO$_3$ surface are enhanced. This shift phenomenon may result from connection between Ag$_2$CO$_3$ and AgX by bonding interaction on their interface, because the shift of binding energy likely arises from bonding interaction and electron transfer among semiconductors. Similarly, the peaks of Ag 3d$_{5/2}$ in Ag$_2$CO$_3$/AgX (X = Cl, Br and I) also shift 0.2, 0.3 and 0.7 eV to the high binding energy, respectively, which further indicates bonding interaction on the interface between Ag$_2$CO$_3$ and AgX.

Fig. 4 UV-vis DRS spectra of Ag$_2$CO$_3$, AgX and Ag$_2$CO$_3$/AgX samples.

Fig. 5 Dynamic curves and plots of ln(c$_0$/c) versus time (insert) of RhB solutions over Ag$_2$CO$_3$ and Ag$_2$CO$_3$/AgX samples.

The light harvest and heterostructure information are connected with the absorption variation before and after formation of the heterojunction. The UV-vis DRS spectra of Ag$_2$CO$_3$, AgX and Ag$_2$CO$_3$/AgX samples in Fig. 4 indicate that...
all samples except for AgCl exhibit strong visible light absorption. The changes of absorption edge of may result from optical characteristics of AgX themselves on the Ag$_2$CO$_3$ surface. More remarkably, compared with Ag$_2$CO$_3$ and AgX, absorption intensities of Ag$_2$CO$_3$/AgX heterojunctsions are all interesting enhancement at 480-640 nm. Some reports believe that this absorption region may arise from Ag surface plasmon resonance effect, but it is eliminated at present experiments because of no Ag generation on the sample surface evidenced in XRD and XPS analyses. Furthermore, the bonding interaction can effectively decrease contact barrier and strengthen electronic coupling of tow semiconductors, thus resulting in the improved absorption of heterojunctsions at long wavelength. Therefore, the absorption at 480-640 nm may be due to the electronic coupling effect on the interface between Ag$_2$CO$_3$ and AgX nanoparticles.

![Absorbance and color variations of RhB solutions over Ag$_2$CO$_3$/AgX (X = Cl (a), Br (b) and I (c)) samples.](Image)

The photocatalytic activity of samples is evaluated by degradation of RhB solution. When KX solutions are added to 30 ml Ag$_2$CO$_3$/AgX samples exhibit the higher degradation activity (see Fig. S3 in the ESI†). The specific surface area of 1.739, 2.055 and 1.816 m$^2$ g$^{-1}$ for Ag$_2$CO$_3$/AgX (X = Cl, Br and I) samples are almost twice that of Ag$_2$CO$_3$ (0.914 m$^2$ g$^{-1}$), which may be due to the abundant AgX nanoparticles on the Ag$_2$CO$_3$ surface. It suggests that the specific surface area has an effect on the improved degradation activity of Ag$_2$CO$_3$/AgX heterojunctsions.

![Photocurrent responses of Ag$_2$CO$_3$ and Ag$_2$CO$_3$/AgX photoelectrodes under visible light with $\lambda \geq 400$ nm and different illumination conditions (insert).](Image)

The magnitude of the photocurrent represents the charge collection efficiency of the electrode surface, and indirectly indicates the separated efficiency of electron-hole pairs. From the insert of Fig. 7, all photoelectrodes are prompt in generating photocurrent under visible and UV-visible light. Ag$_2$CO$_3$/AgX photoelectrodes yield the greater photocurrent than Ag$_2$CO$_3$ photoelectrode under visible light in Fig. 7. In order to explore the improved photocurrent, the relative band positions of Ag$_2$CO$_3$ and AgX (X = Cl, Br and I) are calculated (see Table S1 in the ESI†). The external electric field and the effectively interfacial bonding interaction between Ag$_2$CO$_3$ and AgX may result in the lower contact barrier, which is in favor of the transfer of charge carriers. In Ag$_2$CO$_3$/AgCl heterojunction, the transfer of charge carriers on the interface is thermodynamically
promoted owing to the suitable band position of Ag$_2$CO$_3$ ($E_{	ext{CB}} = 0.29$ eV and $E_{\text{VB}} = 2.75$ eV) and AgCl ($E_{	ext{CB}} = 0.06$ eV and $E_{\text{VB}} = 3.31$ eV). Electrons and holes can migrate from the CB and VB of AgCl to that of Ag$_2$CO$_3$ under external electric field, respectively. The result leads to increasing charge carrier concentrations in CB and VB of Ag$_2$CO$_3$, which improves photocurrent intensity. However, because the broad band gap of AgCl cannot absorb visible light, no redundant photogenerated charge carriers are produced. The lower carrier concentrations of AgCl at the room temperature only bring about the less extent enhancement of photocurrent. Furthermore, when the Ag$_2$CO$_3$ surface is modified by AgBr(AgI) nanoparticles, because of better matching energy band position (AgBr: $E_{\text{CB}} = 0.04$ eV and $E_{\text{VB}} = 2.64$ eV, AgI: $E_{\text{CB}} = -0.42$ eV and $E_{\text{VB}} = 2.38$ eV), the electrons and holes migrate from the CB of AgBr(AgI) and VB of Ag$_2$CO$_3$ to the CB of Ag$_2$CO$_3$ and VB of AgBr(AgI), respectively. It increases the amount of net charge carriers and improves their separated efficiency. In addition, the narrow band gap of AgBr with 2.6 eV and AgI with 2.8 eV can harvest visible light to produce the much photogenerated charge carriers. Thus, the more intense photocurrent responses are produced in Ag$_2$CO$_3$/AgBr(AgI) heterojunctions.

Fig. 8 PL spectra of Ag$_2$CO$_3$ and AgX/Ag$_2$CO$_3$ samples ($\lambda_{\text{ex}} = 350$ nm).

Furthermore, the photoluminescent (PL) spectra can be regarded as an effective approach to comprehend the separated capacity of charge carriers. The obvious fluorescence quenching takes place in the PL spectra of Ag$_2$CO$_3$/AgX heterojunctions compared with that of Ag$_2$CO$_3$ in Fig. 8. Unlike photocurrent responses, the holes of AgCl cannot transfer to the VB of Ag$_2$CO$_3$ after attaining equilibrium at the interface because of no external electric field. In addition, AgCl is not excited under the exceeding 315 nm (3.25 eV). Consequently, the light absorption efficiency of Ag$_2$CO$_3$ decreases owing to the shield effect resulting from surface AgCl nanoparticles, which may be responsible for PL reduction of Ag$_2$CO$_3$/AgCl heterojunctions. By contrast, the quenching extent of Ag$_2$CO$_3$/AgBr(AgI) heterojunctions exhibits more conspicuous than Ag$_2$CO$_3$/AgCl, which may ascribe the interfacial transfer of charge carriers between Ag$_2$CO$_3$ and AgBr(AgI). Using excitation wavelength of 350 nm (2.93 eV), AgBr and AgI are also excited besides Ag$_2$CO$_3$. Thus electrons transfer from CB of AgBr(AgI) to that of Ag$_2$CO$_3$ as well as holes transfer from VB of Ag$_2$CO$_3$ to that of AgBr(AgI), giving rise to the recombination rate decrease thus resulting in the more obvious PL quenching. We deduce that one important reason of the enhanced photocatalytic ability for the Ag$_2$CO$_3$/AgX heterojunctions may originate from the increase of net charge carrier quantities and improvement of their transferred and separated efficiency.

Fig. 9 Dynamic curves of RhB solutions over Ag$_2$CO$_3$ and AgX/Ag$_2$CO$_3$ under the different monochromatic wavelength

The silver halide exhibits dye sensitization effect to some extent, which is usually little considered at previously photocatalytic researches. Therefore, the interaction of dyes and Ag$_2$CO$_3$/AgX heterojunctions should be indispensably taken into account to investigate charge carrier transfer process. The monochromatic wavelength irradiation method is usually applied to identify existence of dye sensitization effect according to the different absorption regions of RhB (500-580 nm) and catalysts (< 500 nm). As shown in Fig. 9(a), performing monochromatic wavelength with 420 nm to excite the Ag$_2$CO$_3$ sample, the degradation efficiency of RhB reaches approximately 100% after 90 min. In contrast, when monochromatic wavelength with 550 nm is used to excite RhB molecules, the result exhibits that the approximate 5% of RhB is degraded within 90 min, which is the same as decomposition extent without any photocatalysts. No occurring dye sensitization effect demonstrates the transfer of electrons between RhB and Ag$_2$CO$_3$ is insignificant and neglectful. However, in Fig. 9 (b-d), upon exciting Ag$_2$CO$_3$/AgX (X = Cl, Br and I) heterojunctions by monochromatic wavelength with 420 nm, approximate 100% of RhB molecules are decomposed within 90, 70 and 80 min, respectively. In comparison, the distinct removal rates of 10%, 20% and 40% for RhB are still
achieved, even only exciting RhB molecules employing monochromatic wavelength with 550 nm. It indicates that the dye sensitization effects occur in surface AgX nanoparticles because of eliminating interaction between RhB and Ag₂CO₃. The energy level of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of RhB are -1.0 eV and 1.1 eV, respectively. AgX can act as an effective electron acceptor due to their lower CB potential. The photoexcited electrons in LUMO of RhB will preferentially transfer to the CB of AgX, leading to the increased aggregation of electron quantities, and then immediately migrate to the CB of Ag₂CO₃ to generate the abundant activated species participating in photocatalytic reaction. Therefore, the other reason of the photocatalytic enhancement for RhB degradation may be attributed to the dye sensitization effect.

It is noticed that the dye sensitization effect displays more and more intense in sequence from AgCl/AgX, AgBr/AgX and AgI/AgX. The potential energy difference between the CB of AgX and the LUMO of RhB provides the thermodynamic requirement for dye sensitization effect occurring but cannot determine the sensitized extent. At present experimental results, the dye sensitization effect may be controlled by the transferred and separated efficiency of charge carriers for AgX/AgX heterojunctions. The lower VB position of AgCl cannot accept photogenerated holes from Ag₂CO₃ in AgCl/AgX heterojunction, and its suitable CB position may merely serve as a medium of electron transfer from RhB to Ag₂CO₃. The lower electronic transfer efficiency results in low-level dye sensitization effect. In contrast, the CB and VB of AgBr can serve as electrons donor and holes acceptor, respectively, owing to their matching position with Ag₂CO₃, which enhances the transferred and separated efficiency of charge carriers. Therefore, this can induce the rapidly electronic transfer from RhB to the CB of AgBr, leading to the more obvious dye sensitization effect. Moreover, besides the matching band position in AgCl/AgCl heterojunction, the higher CB and VB position of AgI than AgBr relative to Ag₂CO₃ may be in favor of accelerating electronic transfer and separation, which further improves the extent of dye sensitization effect.

Based on above analysis results, Fig. 10 exhibits the schematic transfer and separation behaviors of charge carriers and photocatalytic mechanisms of RhB over AgX/AgX heterojunctions. For purpose of further verifying improved transfer and separation efficiency of charge carriers and photocatalytic activity, the degradations of typical MB and MO dyes are also carried out. Dynamic curves and absorbency variations of MB and MO solutions under visible light are carried out, respectively (see Fig. S7-S8 in the ESIT†). AgX/AgX (X = Cl, Br and I) heterojunctions exhibit enhanced photocatalytic ability for MB decomposition in Fig. S7(a). Consuming 25, 15 and 20 min for removal MB are distinctly reduction compared with AgCl (30 min). Even though the relative stable azo dye MO servers as degraded target molecule in Fig. S8(a), it is still decomposed by Ag₂CO₃/AgBr(AgI) heterojunctions within 10 min, except degradation time over AgCl is equal to AgX (20 min). Furthermore, as shown in Fig. S7(b-d) and Fig. S8(b-d), no shifting of the maximum absorption peak and vanishing absorbance of ultraviolet region at 250-380 nm for MB and MO solutions further prove that dye molecules are degraded completely. Here the improved degradation ability further affords credible evidence for the improved transfer and separation efficiency of charge carriers owing to construction of AgX/AgX heterojunctions by the surface modification of AgX nanoparticles.

Conclusions

In summary, the novel AgX/AgX heterojunctions are achieved from the surface modification of AgX nanoparticles with a facilely efficient ion-exchange method, which improve the photocatalytic activity and stability for RhB, MB and MO dyes degradation compared with AgCl. The bonding interaction between AgCl and AgX reduces the contact potential barrier of the interface which is in favor of transfer and separation of charge carriers. The dye sensitization effect increases accumulations of net electron quantities in heterojunctions, which results in generating the more activated
species. This work provides a simple preferred method for improving photocatalytic activity and stability of photocatalyst by surface modification of semiconductor nanoparticles.

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Notes and references


Graphical Abstract

Ag₂CO₃/AgX heterojunctions are achieved from the surface modification of Ag₂CO₃ with AgX nanoparticles, which improve the photocatalytic activity and stability for dyes degradation.