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Ultrafine Ag@AgI nanoparticles on cube single-crystal Ag₃PO₄ (1 0 0): An all-day-active Z-Scheme photocatalyst for environmental purification



Tao Cai^{a,b}, Yutang Liu^{a,b,*}, Longlu Wang^c, Shuqu Zhang^c, Wanyue Dong^{a,b}, Hui Chen^{a,b}, Jianhong Ma^{a,b}, Chengbin Liu^c, Shenglian Luo^c

^a College of Environmental Science and Engineering, Hunan University, Lushan South Road, Yuelu District, Changsha 410082, PR China ^b Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Lushan South Road, Yuelu District, Changsha 410082, PR China ^c State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Lushan South Road, Yuelu District, Changsha 410082, PR China

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ABSTRACT

Exploring and designing an efficient and robust photocatalyst toward the degradation of organic pollutants under nature sunlight irradiation is a challenging research topic. The ability to maintain the photocatalytic activity in the entire daytime will be the ultimate goal for further widespread application of solar energy-driven semiconductor photocatalysis. Here, an all-day-active Z-scheme photocatalytic system is reported by employing Ag@AgI nanoparticles decorated Ag₃PO₄ cubes (C-Ag₃PO₄@Ag@AgI). By coupling the pronounced carrier separation as well as increased stability, the C-Ag₃PO₄@Ag@AgI is capable of performing efficient Rhodamine B (RhB) and bisphenol A (BPA) degradation under sunlight irradiation, and still persist noticeable activity when the light is very weak. The RhB (20 mg/L, 50 mL) can be completely degraded by C-Ag₃PO₄@Ag@AgI (30 mg) within 1 h with the average luminous power of 117.5 mW (3.14 cm²). Dramatically, the as-prepared samples can still maintain photocatalytic activity even in a cloudy day (0.2–6.7 mW). This work has offered a valuable concept of continuous pollutant removal under nature sunlight irradiation in the entire daytime, which may serve as a model system for the wide environment applications, such as the removal of low-level pollutants under weak light irradiation.

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1. Introduction

https://doi.org/10.1016/j.jcis.2018.08.074 0021-9797/© 2018 Elsevier Inc. All rights reserved. Sunlight is a green, abundant, low-cost and renewable nature resource. With increasing concern to the detrimental impacts of human industry activities on the environment, the development

^{*} Corresponding author at: College of Environmental Science and Engineering, Hunan University, Lushan South Road, Yuelu District, Changsha 410082, PR China. *E-mail address*: yt_liu@hnu.edu.cn (Y. Liu).

of effective approaches to harness the solar energy has received significant attention [1,2]. Solar energy-driven semiconductor photocatalysis could produce electron-hole pairs (e^-/h^+) used for redox reactions via absorbing light energy greater than its bandgap energy, which has been considered to be the most potential method to moderate current environment pressure [3–6]. However, the search for an efficient and steady photocatalyst is still a big challenge [7,8]. Especially, how to find and design an all-day-active photocatalyst under the complex and changing climate conditions is a challenging research topic [9]. The ability to maintain photocatalytic activity in the entire daytime has been the ultimate goal for the widespread application of solar energy-driven semiconductor photocatalysis.

Recently, silver orthophosphate (Ag₃PO₄) has sparked extensive interests because of its extremely high efficiency in organic pollutant decomposition under visible light irradiation [10–12]. It can achieve a quantum efficiency of up to 90% at wavelengths around 420 nm [13,14]. Especially, Teng et al. reported that Ag₃PO₄ can still maintain catalytic activity for dye decomposition under weak indoor light irradiation [15,16]. In this regard, Ag₃PO₄ will be a promising material to be employed as an all-day-active photocatalyst. Unfortunately, the reaction time of Rhodamine B (RhB) decomposition needed dozens of hours under such conditions, which limited its practical application. Hence, a vital issue is how to further improve the photocatalytic activity of Ag₃PO₄ under weak light irradiation. One common method to address this issue is to decorate Ag₃PO₄ with plasmonic metal or another semiconductor. Typical examples are Ag/Ag₃PO₄ nanostructure [17], CNT/ Ag₃PO₄ [18] and Ag₃PO₄/CeO₂ hetero-structure [19], in which the introduced component can improve carriers separation rate, leading to enhanced photocatalytic performance. In addition, the exposed crystal facets are closely related to the photocatalytic performance because the photocatalytic reactions are generally take place on the surfaces of catalysts [20,21]. Thus, it inspires us to design a single-crystal Ag₃PO₄ based composite to enhance its photocatalytic activity under weak light irradiation.

Another vital issue that limits the practical application of Ag_3 - PO_4 is severe photocorrosion. Ag_3PO_4 is easily reduced into metal Ag by photogenerated electrons under light irradiation [22–24]. Recently, our group has reported that Ag_3PO_4 @RGO@La, Cr:SrTiO_3 Z-Scheme photocatalyst had excellent anti-photocorrosion performance and catalytic activity [25]. The reason can be attributed to the sufficient interfacial contact between Ag_3PO_4 and RGO and unique Z-Scheme photocatalyst has been the subject of investigations, to the best of our knowledge, cube single-crystal Ag_3PO_4 (100) based Z-Scheme photocatalysts has not been reported. Considering great interests in photocatalytic degradation of contaminates under nature sunlight irradiation, utilizing photocatalyst for environmental remediation under whole daytime and different weather condition can be an interesting idea and strategy.

In this work, we reported that Ag@AgI nanoparticles decorated Ag₃PO₄ cubes (C-Ag₃PO₄@Ag@AgI) can be used as an all-dayactive photocatalyst for the photodegradation of Rhodamine B (RhB) and bisphenol A (BPA). The C-Ag₃PO₄@Ag@AgI sample showed high activity for the degradation of both RhB and BPA under nature sunlight irradiation. In addition, the degradation efficiency of RhB was studied and evaluated in the entire daytime (8:00 a.m. local time \sim 7:00 p.m. local time). The experimental results showed that C-Ag₃PO₄@Ag@AgI was active throughout the day and even under very weak light conditions (0.2-6.7 mW). The effect of different weather on photocatalytic degradation was also studied. Moreover, the photocatalytic degradation and electron transfer mechanism and anti-photocorrosion performance of C-Ag₃PO₄@Ag@AgI were investigated detailly by various control experiments. This study may offer a new paradigm and concept for continuous pollutant removal under nature sunlight irradiation in the whole daytime and open up new opportunities in designing all-day-active photocatalysts.

2. Experimental

2.1. Chemicals

All chemicals used were analytic grade reagents without further purification and purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water (D.I. water) was prepared by ULUPURE purification system and used throughout the experiments.

2.2. Materials synthesis

2.2.1. Preparation of silver phosphate cubes (C-Ag₃PO₄)

The Ag₃PO₄ cubes were prepared by a typical synthesis method, using silver-ammino complex as the silver ions source [26]. Briefly, AgNO₃ (0.3 g, 99.8%) was solved in D.I. water (40 mL). Ammonia aqueous solution (0.1 M) was added dropwise to the above solution until a transparent solution was formed. Then, Na₂HPO₄ aqueous solution (0.15 M, 8 mL) was added into the obtained transparent solution. The as-prepared olivine Ag₃PO₄ cubes were washed with D.I. water several times and dried at 60 °C for 5 h.

2.2.2. Preparation of C-Ag₃PO₄@Ag

The as-prepared Ag₃PO₄ cubes (0.5 g) were added into appropriate aqueous ammonia solution (0.01 M) and stirred for 15 min. Next, glucose ($C_6H_{12}O_6$) solution (0.15 M, 20 mL) was added to the reaction solution and kept stirred for 1.5 h. The precipitates were washed with D.I. water several times and dried at 60 °C for 5 h.

2.2.3. Preparation of C-Ag₃PO₄@Ag@AgI

The obtained C-Ag₃PO₄@Ag (0.5 g) were added into D.I. water and sonicated for 30 min. Then appropriate sodium iodide solutions (0.1 M) was added and keep stirring for 3 h to provide sufficient time for ions-exchange process, in which the theoretical molar ratios of I/P were controlled to be 1%, 5%, and 10%. The actual molar ratios of I/P of as-prepared samples were measured by X-ray photoelectron spectroscopy (XPS) (Table S1). A procedure for the synthesis of C-Ag₃PO₄@Ag@AgI is illustrated in Scheme 1.

2.2.4. Preparation of silver phosphate sphere (S-Ag₃PO₄)

 Ag_3PO_4 sphere was prepared by the direct reaction of $AgNO_3$ and Na_2HPO_4 at room temperature.

2.2.5. Preparation of AgI

Agl was prepared by the direct reaction of $AgNO_3$ and NaI at room temperature.

2.2.6. Preparation of C-Ag₃PO₄@AgI

The obtained C-Ag₃PO₄ (0.5 g) were added into D.I. water and sonicated for 30 min. Then appropriate sodium iodide solutions (0.1 M) was added and keep stirring for 3 h to provide sufficient time for ions-exchange process. The precipitates were washed with D.I. water several times and dried at 60 °C for 5 h.

2.3. Photocatalytic performance measurement

2.3.1. Degradation under natural sunlight

The photodegradation of RhB and BPA using as-prepared samples were performed under natural sunlight irradiation. Typically, 30 mg of as-prepared samples were added into the reaction solution (50 mL, 20 mg/L RhB or BPA) with stirring for 30 min under dark environment to reach an adsorption-desorption equilibrium.



Scheme 1. Schematic illustration of the synthesis procedures of C-Ag₃PO₄@Ag@AgI.

And then, the reaction solution was transferred to out of the window in our laboratory room (Changsha, in China, N28°11'14.26″ E112°57'6.17″). Luminous power was recorded by photometer (PM-MW 2000, S = 3.14 cm^2). During degradation, 1 mL of suspension was taken out at a given interval time and separated through centrifugation (4000 rpm, 10 min).

2.3.2. Degradation under artificial visible light irradiation

The photodegradation of RhB and BPA were also carried out under a 300 W Xe lamp with a cut off filter ($\lambda > 420$ nm) irradiation and other conditions the same as above.

2.4. Characterization and analysis

2.4.1. Characterization

X-ray diffraction (XRD, Rigaku, Smartlab) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, England) were employed to study the crystal structures and chemical composition. The binding energies of the samples were calibrated with respect to the adventitious carbon (C1s) as a reference line at 284.8 eV. The field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) and transmittance electron microscopy (TEM, JEOL, JEM-2100F) were used to observe the morphology. The element composition of the samples was analyzed with the energy dispersive X-ray spectrometry (EDS), which was attached on TEM (JEOL, JEM-2100F). The UV-vis diffuse-reflectance spectra (DRS) were recorded using UV-vis spectrophotometer (Cary 300, Varian). The photoluminescence (PL) spectra were collected on a Hitachi F-7000 fluorescence spectrophotometer. Electron spin resonance (ESR) spectra were obtained on a JES FA200 electron paramagnetic resonance spectrometer. Electrochemical measurements were performed in 0.5 M Na₂SO₄ electrolyte solution using a typical three-electrode configuration. A saturated calomel electrolyte was used as a reference electrode and a Pt coil was used as a counter electrode. The as-prepared photocatalysts thin film on fluorinedoped tin oxide (FTO) was used as the working electrode. The electrochemical response was recorded with a CHI 660C electrochemical analyzer (CHI Inc., USA). TOC test was conducted by TOC analyzer (TOC-VCPH/CPN, Shimadzu).

2.4.2. Analysis

The concentration of RhB was determined by the characteristic optical absorption at 554 nm with a UV–vis spectrophotometer (CARY 300 Conc). The concentration of BPA was analyzed by a high-performance liquid chromatograph (HPLC, Shimadzu LC-20AT). The HPLC analysis was carried out using a phenomenex Luna C-18 column and a SPD-20A UV/Vis detector at 278 nm, with methanol and water (65/35, v/v) as effluent at a flow rate of 0.8 mL/min.

3. Results and discussion

3.1. Structural investigations

Ag@AgI surface-decorated Ag₃PO₄ cubes were presented in this work, of which Ag₃PO₄ cubes with sharp edges and smooth sur-

faces with main diameters about 1 µm (Fig. 1a). The lowresolution SEM image (inset in Fig. 1a) indicated that most of the as-prepared Ag₃PO₄ possessed perfect and regular cube morphology. As shown in Fig. 1b, metallic Ag nanoparticles were formed on the surfaces of the C-Ag₃PO₄ by $C_6H_{12}O_6$ situ reduction process. Then, some large particles appeared on the surface of C-Ag₃PO₄ during the ions-exchange process (Fig. 1c). These surfacedecorated nanoparticles were attributed to the insoluble Ag and AgI, which can prevent the dissolution of Ag₃PO₄ [13]. The XRD pattern, STEM-EDS elemental mapping, EDS pattern, XPS spectra and UV-vis DRS of C-Ag₃PO₄@Ag@AgI also demonstrated that the existence of Ag and AgI, which would be discussed detailly in later. Fig. 1d showed the high-resolution SEM image of C-Ag₃PO₄@Ag@AgI. It can be clearly observed that Ag@AgI nanoparticles uniformly distributed on the surface of Ag₃PO₄ cubes and their dimensions range from 5 to 20 nm. In addition, Ag₃PO₄ spheres have prepared by the direct reaction of AgNO₃ and Na₂-HPO₄ at room temperature. As shown in Fig. S1, all of these samples possessed perfect and sphere morphology with an average diameter of 500 nm.

The structure of the C-Ag₃PO₄@Ag@AgI sample was further studied by high angel annular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS). STEM-EDS elemental mapping of the C-Ag₃PO₄@Ag@AgI confirmed that the Ag components were broadly and denselv dispersed over the whole surface of the sample while the O and P components were sparsely dispersed on the zone of cube (Fig. 2a-d). Moreover, it can be observed that very small amount of I components were distributed on the surface of C-Ag₃PO₄@Ag@AgI (Fig. 2d), indicating the formation of AgI on the surface of Ag₃PO₄ cube (Fig. 2e). These small amounts of elemental I also were demonstrated by EDS pattern (Fig. 2f). It is needs to point out that the high-resolution transmission electron microscopy of Ag₃PO₄ and AgI cannot be provided because the Ag₃PO₄ and AgI crystals are too unstable under irradiation with highenergy electrons [20].

The detailed crystal structures and chemical composition of the samples were analyzed by XRD and XPS. As shown in Fig. 3a, it can be clearly seen that both the C-Ag₃PO₄ and S-Ag₃PO₄ samples possessed a typical body-centered cubic structure (JCPDS NO.06-0505) and no other characteristic diffraction peaks for impurities were observed in the pattern. However, it is noteworthy that the intensity ratio between (110) and (200) peaks for C-Ag₃PO₄ is only about 0.62, remarkably lower than that of S-Ag₃PO₄ (0.74), suggesting that C-Ag₃PO₄ surfaces are dominated by (100) planes [26]. Compared with Ag₃PO₄, AgI had a smaller diffraction peak intensity, which can be assigned as hexagonal β -AgI crystal phase (JCPDS no. 09-0374)[27]. No notably characteristic diffraction peaks of Ag⁰ however, were observed in this pattern, which could be attributed to the relatively low amount and high dispersion of metal Ag. The presence of Ag⁰ component was further confirmed by XPS characterization techniques. Fig. 3b showed the high-resolution XPS spectra of Ag 3d, which could be decomposed into two peaks. Ag 3d5/2 and Ag 3d3/2 are located at 367.29 eV and 373.24 eV respectively, which are attributed to Ag⁺. While the peak located at binding energy of 367.74 and 373.69 eV can be attributed to Ag⁰. As shown



Fig. 1. SEM images of (a) Ag₃PO₄ cubes, (b) C-Ag₃PO₄@Ag, (c) C-Ag₃PO₄@Ag@AgI (5%) and (d) enlarged SEM images of C-Ag₃PO₄@Ag@AgI (5%).



Fig. 2. (a-d) STEM-EDS elemental mapping images analysis for Ag₃PO₄@Ag@AgI (5%) and (e) HAADF-STEM image, (f) EDS pattern.

in Fig. 3c, the XPS survey spectrum of $C-Ag_3PO_4@Ag@AgI$ clearly demonstrated that the existence of Ag, O, P and I, which was consistent with the EDS result. What needs to point out is C 1s peak also

appears in this spectrum, because of the widespread presence of Carbon in air [28]. Above results clearly demonstrated that Ag@AgI surface-decorated Ag_3PO_4 cube have been synthesized successfully.



Fig. 3. (a) XRD pattern of as-prepared samples. (b) High resolution XPS spectrum of Ag 3d. (c) XPS survey spectra of C-Ag₃PO₄@Ag@AgI (5%).

3.2. Photoelectricity properties and band structure determination

The photoelectricity properties of as-prepared samples were measured by UV-vis DRS, PL spectra and EIS Nyquist plots. As shown in Fig. 4a, C-Ag₃PO₄ exhibited excellent absorption with wavelengths shorter than 520 nm. Note that there was a distinct enhanced absorbance form 520 nm to 800 nm for C-Ag₃PO₄@Ag and C-Ag₃PO₄@Ag@AgI composites compared with bare C-Ag₃PO₄, which could be attributed to the plasmon resonance effects of Ag nanoparticles [29,30]. It further verified the existence of Ag nanoparticles in C-Ag₃PO₄@Ag@AgI composite and was consistent with the XPS result. Moreover, the absorption band edge of AgI was about 430 nm and shorter than C-Ag₃PO₄,

indicating its band gap was bigger than C-Ag₃PO₄. Fig. 4b showed the PL spectra of C- Ag₃PO₄, C-Ag₃PO₄@Ag and C-Ag₃PO₄@Ag@AgI. A broad emission peak associated with the interband carrier recombination of Ag₃PO₄ was recorded at 530 nm [31,32]. Compared with C-Ag₃PO₄, both C-Ag₃PO₄@Ag and C-Ag₃PO₄@Ag@AgI exhibited distinctly depressed PL peak, suggesting the recombination of carrier was greatly inhibited. It is worth emphasizing that in the C-Ag₃PO₄@Ag@AgI system, AgI could be regarded as the electron sacrificial agent for Ag₃PO₄ because electrons in Ag₃PO₄ are consumed by the holes of AgI. As a result, it leads to a declining PL peak because the carrier recombination is reduced for Ag₃PO₄ itself, which is also consistent with previous literature [30].



Fig. 4. (a) UV-vis diffuse reflectance spectra and (b) photoluminescence (PL) spectra of as-prepared samples.

Kubelka-Munk plot, XPS valence band spectra and Mott-Schottky plot were used to further get the information of the electronic band structure of as-prepared samples [33]. First, the E_g values of C-Ag₃PO₄ and AgI were calculated by the Kubelka-Munk method. The optical absorption around the band edge of a crystalline semiconductor follows the equation: $\alpha hv = A(hv - E_g)^{n/2}$, in which A, v, α , and E_g are proportionality constant, light frequency, absorption coefficient and band gap, respectively [34]. Note that n = 1 or 4 represent direct or indirect band gap. The value of n was obtained by $\ln(\alpha hv)$ vs $\ln(hv - E_{\alpha})$ plot, in which the approximate E_{α} value of C-Ag₃PO₄ and AgI were 2.3 eV and 2.8 eV, respectively. As shown in Fig. S2(a, b), the straight line slopes of C-Ag₃PO₄ and AgI are about 1, indicating direct band gap. $E_{\rm g}$ values of C-Ag₃PO₄ and AgI were estimated to be 2.4 eV and 2.8 eV by the hv axis intercept of the $(\alpha hv)^{1/2}$ vs hv plot (Fig. S2c). Second, Mott-Schottky method was performed to measure the flat band potential (Fermi energy level. $E_{\rm F}$ [35]. As shown in Fig. S2(d, e), the positive slope of the Mott-Schottky plot for C-Ag₃PO₄ and AgI indicated *n*-type nature and the values of E_F were 0.3 V and -0.26 V vs SCE, respectively. Namely, they were 0.54 V and -0.02 V vs NHE (Normal Hydrogen Electrode). Third, to further explore the band structure, the XPS valence band spectra of samples was measured. The valence band maximum (E_{vb}) of C-Ag₃PO₄ and AgI were 2.4 eV and 2.74 eV, respectively (Fig. S2f). Finally, the conduction band minimum (E_{cb}) was obtained by the equation: $E_g = E_{vb} - E_{cb}$.

3.3. Photocatalytic degradation properties

3.3.1. Under artificial visible light irradiation ($\lambda > 420 \text{ nm}$)

RhB degradation experiment was performed to evaluate the catalytic properties of as-prepared samples under artificial visible

light irradiation. As shown in Fig. 5a, all the samples exhibited obvious photocatalytic performance toward RhB degradation under visible light irradiation. C-Ag₃PO₄@Ag@AgI showed the best performance among them, which can completely degrade 20 mg/L of RhB within only 10 min. Note that under light exposure, RhB hardly undergone degradation within 12 min, which excluded the photodegradation of the dye itself. In addition, C-Ag₃PO₄ showed better degradation activities than S-Ag₃PO₄, which can be ascribed to the metal-like electronic structure and novel atomic configurations of Ag_3PO_4 (100) planes [26]. It is noteworthy that C-Ag₃PO₄@Ag@AgI (5%) shows better catalytic performance compared with C-Ag₃PO₄@AgI, indicating Ag plays a critical role in electronic transmission and the build of Z-scheme photocatalyst. To quantify the photocatalytic performance of different samples, the apparent rate constant of RhB degradation $(k_{RhB, light})$ was calculated with the first-order kinetic equation approximation. The detailed data are provided in Fig. 5b and Table S2, in which C-Ag₃PO₄@Ag@AgI (5%) have the greatest k_{RhB, light} value of 0.44 $(\min^{-1}).$ The prominent catalytic performance of C-Ag₃PO₄@Ag@AgI was ascribed to the excellent redox ability, effective charge separation and plasmon resonance effects. It is needs to point out that the photocatalytic performance is also influenced by the morphology of the sample. Ultrafine Ag@AgI nanoparticles (5–20 nm) has a small size and a large specific surface area, which facilitate to the adsorption of pollutants. As shown in Fig. 5c, the adsorption effect of C-Ag₃PO₄@Ag@AgI on BPA was obviously enhanced compared with C-Ag₃PO₄, thereby better photocatalytic performance (Fig. 5c, d). Moreover, ultrafine Ag@AgI nanoparticles does not block light from entering the interior of material due to the highly dispersion and small size (Fig. 1b-d). Therefore, C-Ag₃PO₄@Ag@AgI also has a satisfactory absorbance



Fig. 5. Time profiles of the photocatalytic degradation of RhB (a) and BPA (c) under visible light irradiation and reaction kinetic curves of RhB (b) and BPA (d). The experimental conditions were [RhB] = 20 mg/L, [BPA] = 20 mg/L, [Cat] = 0.6 g/L, pH = 7, and $\lambda > 420 \text{ nm}$ irradiation.

form 300 nm to 800 nm compared with bare C-Ag₃PO₄ (Fig. 4a). Thus, from the perspective of morphology, this morphology structure is conducive to the photocatalytic reaction. The UV-vis absorption spectra of RhB and HPLC chromatograms of BPA were provided in Fig. S3. To further investigated the degree of mineralization of RhB and BPA, TOC test was carried out. As shown in Fig. S4a, the TOC removal efficiency of RhB with C-Ag₃PO₄@Ag@AgI (45%) was 2 times that of C-Ag₃PO₄@Ag@AgI (22%) and 5 times that of C-Ag₃PO₄ (7.2%). Moreover, C-Ag₃PO₄@Ag@AgI (31%) also exhibited excellent TOC removal efficiency toward BPA compared with C-Ag₃PO₄@Ag (17.2%) and C-Ag₃PO₄ (5.3%) (Fig. S4b). All these results demonstrated that Ag@AgI nanoparticles decorated C- Ag₃PO₄ show enhanced photocatalytic performance.

3.3.2. Under sunlight irradiation

More energy from solar radiation on earth within 1 h than all of the energy consumed by mankind in an entire year [36]. If the solar energy resources can be used efficiently, it will be able to save resources and to relieve the pressure on the environment to a large extent. To embody this concept, RhB photodegradation experiment under nature sunlight irradiation was designed, in which the reaction device was moved to out of the window (Fig. S5). In this experiment, the RhB degradation of various periods during the daytime within 1 h was carried out (from 8:00 a.m. to 7:00 p.m. local time). C-Ag₃PO₄@Ag@AgI as an all-day-active photocatalyst exhibited obvious photocatalytic properties toward RhB degradation of various periods during the whole day (Fig. 6a). Especially from 10:00 a. m. to 2:00 p.m., it showed greatest performance because of strong solar radiation and RhB can be completely degraded within 1 h with the average luminous power of 117.5 mW. Interestingly, C-Ag₃PO₄@Ag@AgI was active throughout the day and even under very weak light conditions (0.2–6.7 mW, 16:00–19:00). The experiment results strongly demonstrate that C-Ag₃PO₄@Ag@AgI can maintain the degradation activity toward RhB in the entire daytime. The change of luminous power during the day was recorded and provided in Fig. 6b. The degradation efficiency within 1 h of RhB of various periods during the whole day was also shown in Fig. 6c. As-prepared samples showed decent degradation efficiency toward RhB throughout the day, especially from 10:00 a.m. to 2:00 p.m., achieving almost 100% degradation efficiency. Interestingly, C-Ag₃PO₄@Ag@AgI still maintained a certain removal rate when the light was very weak (17:00–19:00), indicating an allday-active nature.

To explore the more practical applicability, the degradation of RhB and BPA by C-Ag₃PO₄@Ag@AgI under different climatic conditions was also performed. As shown in Fig. 7(a, b), C-Ag₃PO₄@Ag@AgI showed excellent activity toward both RhB and BPA in a sunny day with an average luminous power of 120 mW. The removal efficiency of C-Ag₃PO₄@Ag@AgI for RhB and BPA within 80 min can reach 100% and 85%, respectively. In addition, under this condition, the C-Ag₃PO₄@Ag@AgI composites showed much better photocatalytic activity for both RhB and BPA than that of C-Ag₃PO₄ alone, which can be ascribed to the excellent redox ability and pronounced charge separation. Importantly, C-Ag₃PO₄@Ag@AgI also exhibited obvious performance toward RhB and BPA degradation in a cloudy day (Fig. 7c and d). The above results reveal that C-Ag₃PO₄@Ag@AgI exhibited strong remove ability for both RhB and BPA irrespective of sunny or cloudy days. It is also demonstrated that the functionality coupling of Ag@AgI and Ag₃PO₄ cubes may offer a new paradigm for the design of a unique, robust and all-day-active photocatalyst.



Fig. 6. (a) Time profiles of the photocatalytic degradation of RhB under sunlight irradiation in an entire day and (b) the changing of luminous power. (c) The degradation efficiency of RhB and the changes of luminous power within 1 h of various periods during the whole day. The experimental conditions were [RhB] = 20 mg/L, [Cat] = 0.6 g/L, pH = 7, under sunlight irradiation. The experiment carried out on April 14, 2017, 8:00 a.m. ~ 7:00 p.m. N28°11′14.26″ E112°57′6.17″.



Fig. 7. Time profiles of the photocatalytic degradation of RhB (a) and BPA (b) under sunlight irradiation in a sunny day. The test is also carried out in a cloudy day (c, d). The experimental conditions were [RhB] = 20 mg/L, [BPA] = 20 mg/L [Cat] = 0.6 g/L, pH = 7, in sunny day and cloudy day.

3.4. Photocatalytic degradation and electron transfer mechanism

The radical trapping experiments were carried out to explore the possible photodegradation mechanism. In this study, the Ethylenediaminetetraacetic acid disodium salt (EDTA), benzoquinone (BQ) and Isopropanol (IPA) were used as the scavengers for h⁺, O_2^- , and OH, respectively. As shown in Fig. 8a, the addition of IPA had no obvious effect on the degradation of RhB and BPA while the introduction of BQ and EDTA obviously inhibits the degradation activity. The experiment results clearly manifested that h⁺ and O_2^- were main active species for the degradation of RhB and BPA in C-Ag₃PO₄@Ag@AgI system. The presence of $O_2^$ was further verified by electron spin resonance (ESR) spectra (Fig. 8b). The above experiment results demonstrated that the photodegradation of RhB and BPA over C-Ag₃PO₄@Ag@AgI composites was mainly dominated by the oxidation action of h⁺ and O_2^- radicals. Hence, probable reactions are:

$$C-Ag_3PO_4@Ag@AgI + hv \rightarrow e^- + h$$

 $e^- + O_2 \rightarrow \cdot O_2^-$

 $\cdot O_2^-$ + RhB or BPA \rightarrow degraded products

h^+ + RhB or BPA \rightarrow degraded products

The above results tell us another key point is this system can produce O_2^- radicals, indicating the Z-scheme mechanism. Assume that the way of carrier transfer between Ag₃PO₄ and AgI is via heterojunction-type mechanism, namely, photogenerated electron in the CB of AgI would transfer to that of Ag₃PO₄, while the holes in the VB of Ag₃PO₄ will transfer to the VB of AgI. As a result, photogenerated electrons in the CB of Ag₃PO₄ (+0.34 V vs. NHE at pH = 7) cannot reduce O₂ into O_2^- (-0.33 V vs NHE, PH = 7) [37], due to the relatively weak reduction ability. If so, it will not match the above experimental results. Based on the above-mentioned analysis, we propose the possible electron transfer mechanism as illustrated in Fig. 8c. After the contact of C-Ag₃PO₄ and Ag@AgI, electrons will transfer from the semiconductor with higher fermi level (E_F) to that with lower one. Namely, electrons would transfer from AgI $(E_{FAgI}$ = -0.02 V) to C-Ag₃PO₄ ($E_{FAg3PO4}$ = 0.54 V) and Ag (E_{FAg} = 0.4 -V) [38] and cause the formation of united E_F (Fig. 8c, right). During this process, an interfacial internal electric field (IEF), with the same direction of electrons transfer [39], is generated at C-Ag₃PO₄/Ag@AgI interface and makes the bands of C-Ag₃PO₄ and AgI bend at the interface. Under light irradiation, both the C-Ag₃PO₄ and the AgI can be excited. The IEF accelerates the electron transfer from CB of C-Ag₃PO₄ to Ag, but it blocks the electron transfer from CB of AgI to Ag due to the role of electric field force. Finally, electrons are accumulated in CB of AgI and reduce O2 into O_2^- through reacting with O_2 , which consistent with the experimental results. In a sum, the way of electron transfer in this system follows Z-scheme mechanism.

3.5. Stability and anti-photocorrosion mechanism

The stability of photocatalyst needs to be considered since this is of important practical significance. The photocatalytic performance of C-Ag₃PO₄@Ag@AgI and C-Ag₃PO₄ were test through multiple cycles removal of RhB under visible light irradiation (Fig. 9a). A visual decrease of performance activity can be observed for C-Ag₃PO₄, in which the photocatalytic activity declines by about 80% after 5 cycles, indicating possible photocorrosion and dissolution issues. However, no obvious loss in the photocatalytic performance of C-Ag₃PO₄@Ag@AgI after 5 cycles can be observed, suggesting better reusability. To further demonstrate the excellent stability of it, the atom content calculated by XPS of C-Ag₃PO₄@Ag@AgI after 5



Fig. 8. (a), The radical-trapping experiments with different scavengers ([RhB] = [BPA] = 20 mg/L, [C-Ag₃PO₄@Ag@AgI (5%)] = 0.6 g/L, [EDTA] = [IPA] = [BQ] = 0.01 M, K_{app} represents the reaction rate constant). (b), DMPO spin-trapping ESR spectra for DMPO- O_2^- over C-Ag₃PO₄@Ag@AgI (5%) in methanol dispersions. (c), the band configuration of as-prepared samples and Z-scheme electrons transfer mechanism.



Fig. 9. (a), Repetition tests of photocatalytic degradation of RhB in the suspension of C-Ag₃PO₄ and C-Ag₃PO₄@Ag@AgI. SEM images of (b) C-Ag₃PO₄ and (c) C-Ag₃PO₄@Ag@AgI (5%) after RhB degradation experiments. (d) Anti-photocorrosion mechanism of C-Ag₃PO₄@Ag@AgI.

cycles were also provided in Table S3. There were no obvious changes in the atom content of as-prepared samples. Moreover, the morphologies of both C-Ag₃PO₄ and C-Ag₃PO₄@Ag@AgI after reaction were also investigated. As shown in Fig. 9(b, c), it can be clearly observed that the C-Ag₃PO₄ crystals were almost completely destroyed and decomposed into small and irregular fragments due to solubility and photocorrosion. Amazingly, all the C-Ag₃PO₄@Ag@AgI crystals kept their original cube morphology and no obvious morphology or crystalline structure changes could be observed. The above experimental results demonstrated that C-Ag₃PO₄ becomes more robust when decorated with Ag@AgI nanoparticles, resulting from the inhibition of photocorrosion. Based on the above analysis and our previous studies [25], we proposed the anti-photocorrosion mechanism as illustrated in Fig. 9d. Photogenerated electrons in Ag₃PO₄ will transfer to the Ag nanoparticles rapidly and recombine with the photogenerated holes from AgI, which effectively reduces the chance of contact between the electron and Ag⁺ ions, thereby inhibiting the photocorrosion. More importantly, since electrons are consumed timely by holes from AgI via Ag nanoparticles, photogenerated holes accumulated on VB of Ag₃PO₄ will make Ag₃PO₄ to be a rich-hole region, which can suppress the photo-reduction of Ag₃PO₄ (photocorrosion). Thus, a hole-protection anti-photocorrosion mechanism was proposed by our group. In addition, what needs to point out is that the insoluble Agl nanoparticles ($K_{sp} = 8.3 \times 10^{-17}$) could effectively protect the slight soluble C-Ag₃PO₄ ($K_{sp} = 1.4 \times 10^{-16}$) from dissolution in aqueous solutions, which may also slightly enhance its stabilities during the reaction process.

4. Conclusions

In conclusion, the use of C-Ag₃PO₄@Ag@AgI as an all-day-active photocatalyst for the degradation of RhB and BPA under sunlight irradiation has been proved. The as-prepared C-Ag₃PO₄@Ag@AgI maintained the degradation activity toward RhB in the entire daytime (8:00 a.m. \sim 7:00 p.m.), especially from 10:00 a.m. to 2:00 p. m., achieving almost 100% degradation efficiency. In addition, it exhibited strong remove ability for both RhB and BPA irrespective of sunny or cloudy days. The excellent catalytic activity could be account for the following reasons. First, the Z-scheme architectures can promote charge separation and form a hole-rich region on the surfaces of C-Ag₃PO₄, which boosts carrier utilization and prevent photocorrosion. Second, the decoration of Ag@AgI nanoparticles can prevent the dissolution of the Ag₃PO₄, leading to better stability. Third, Ag₃PO₄ cubes with metal-like electronic structure ((100) facets) are capable of performing efficient photocatalytic reaction. This work offer a new paradigm and concept of continuous pollutant remove under nature environment throughout the day. Further studies of the proposed model may find more suitable applications, such as the remove of low-level pollutants in a cloudy day.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.08.074.

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