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Introduction

Thin silica shell on Ag₃PO₄ nanoparticles augments stability and photocatalytic reusability[†]

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Semiconductor photocatalysts are promising cost-effective materials for degrading hazardous organic contaminants in water. Ag_3PO_4 is an efficient visible-light photocatalyst for the oxidation of water and dye degradation. The excited Ag_3PO_4 photocatalyst uses a hole to oxidise water or organic contaminants except the electron, which reduces Ag^+ to Ag^0 . In the present study, the inherited disadvantage was overcome by a thin silica shell overcoating on Ag_3PO_4 nanoparticles. The silica-coated Ag_3PO_4 nanoparticles retain the photocatalytic activity even after five cycles of photodegradation, while the bare Ag_3PO_4 nanoparticles show a photocatalytic activity declined to half. The study demonstrates that the thin silica shell enhances the photostability, keeping the photocatalytic activity unaffected, even after several cycles of photodegradation of dyes. XPS analysis showed that the Ag^0 formation on the surface of bare Ag_3PO_4 after five cycles of photodegradation. Electrochemical studies identified that the intermediates, such as OH^* and O_2^- , formed during water oxidation play a crucial role in the photodegradation of dyes. This study can provide insights into the design of core–shell semiconductor nanostructures for reusable photocatalytic applications.

Freshwater aquatics are contaminated by the disposal of various untreated molecules of interest from industries, such as textiles and pesticides.¹⁻⁴ The cost-effective decontamination of organic contaminants in water is urgently needed for the present scenario. Semiconductor photocatalysts have the ability to degrade organic contaminants present in water using solar energy.5-12 Semiconductors with a wide band gap, such as TiO2 and ZnO, are widely utilised for the photodegradation of organic contaminants. However, their application is limited by their UV wavelength absorption.13,14 However, visible light photocatalysts are promising candidates for the photodegradation of organic contaminants in applications outside the lab scenario.15-17 Among them, a Ag₃PO₄ photocatalyst attracts the attention of the scientific community with its capability to produce highly efficient holes for the oxidation of water or organic contaminants under visible light.¹⁸⁻²⁰ Thus far, the Ag₃PO₄ photocatalyst has emerged as a versatile material for the ease of synthesis, usability and its high ability of water oxidation. Besides, capabilities, such as recyclability, photostability, and the ability to degrade all kinds

of organic contaminants, are essential for an ideal photocatalyst. However, one of its non-negotiable disadvantages is its selfreduction of Ag^+ to Ag^0 during the photocatalysis.^{21,22} Such unwanted side reactions decline the efficiency in recycles of photocatalysis and may vary with the kind of molecules. There are various methods to overcome such drawbacks: (i) increasing the surface area by changing the crystallinity, reducing the size and making it porous,²³ (ii) adding ingredients like H₂O₂ to prevent the side reaction or recycling the catalyst,²⁴ and (iii) incorporating other materials to extract electrons and protect the catalyst from self-degradation.²⁵⁻²⁷

Apart from this, some of the recent research studies focus on the coating of an appropriate material onto a semiconductor photocatalyst, which will protect the surface of the semiconductor and subsequently facilitate the adsorption of molecules near the photocatalyst, leading to negotiable loss of photocatalytic efficiency.^{28,29} The present work focuses on designing and synthesising thin silica-coated Ag₃PO₄ nanostructures and studies their reusability for the photocatalytic degradation of methylene blue and rhodamine B dyes in water. The mechanism of photodegradation has been done electrochemically by cyclic voltammetric studies.

Experimental section

Materials

Experiments were all carried out at room temperature. All chemicals were used as received. Tetrahydrofuran $(C_4H_8O$

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99.5% Isochem), acetonitrile (CH₃CN 99.8% Merck), di-sodium hydrogen phosphate (Na₂HPO₄ > 98% Merck), silver nitrate (AgNO₃ 99.8% Nice Chemicals), triethoxy *n*-octyl silane (C₄H₃₂O₃Si > 97% TCI), tetrabutylammonium hexafluorophosphate (C₁₆H₃₆F₆NP > 98% TCI), and acetone ((CH₃)₂CO 99% Isochem) were used for washing purposes. Methylene blue (Nice Chemicals) and rhodamine B (Sigma Aldrich >95%) were used as organic pollutants.

Synthesis of Ag₃PO₄@SiO₂ photocatalysts

Silane-capped Ag_3PO_4 was synthesised by the *in situ* overcoating of silica during the precipitation of Ag_3PO_4 . Then, 300 µL of triethoxy *n*-octyl silane was added to an RB flask containing 0.44 mmol of $AgNO_3$ in 25 mL of tetrahydrofuran, and 2.5 mL of 0.1 M Na_2HPO_4 was added dropwise into the solution. The resulting solution was stirred for 1 hour to ensure complete precipitation. The formation of Ag_3PO_4 was confirmed by the colour change of the solution from colourless to yellow. The synthesised Ag_3PO_4 @SiO₂ photocatalyst was purified by repeated centrifugation and kept in a hot oven at 100 °C for 1 hour. Bare Ag_3PO_4 was also prepared by the same method without triethoxy *n*-octyl silane and purified by repeated centrifugation.

Photocatalytic studies

The photocatalytic activities of Ag₃PO₄@SiO₂ and Ag₃PO₄ were evaluated by the degradation of methylene blue and rhodamine B dyes. First, 0.86 mg of synthesised material is used for 1.6 \times 10⁻⁵ M methylene blue (MB) and rhodamine B (RhB). Photocatalytic degradation was monitored every 10 minutes under 365 nm light of 125 W, and a xenon lamp of 300 W was used for 450 nm light. The bandpass filter was used to transmit a wavelength of 450 nm (from 440 nm to 480 nm) from the xenon lamp. The solution was stirred in the darkness for 30 min to reach the adsorption-desorption equilibrium between the organic molecules and the photocatalyst surface. At illumination intervals, 3 mL reacted solutions were taken out and then analysed using a T90+ UV-Vis spectrophotometer. The degradability of the above pollutants was represented by C/C_0 , where C_0 and C denoted the main absorption peak intensities of the above-mentioned pollutants (rhodamine B at 553 nm and MB at 667 nm) before and after photocatalytic reactions. More than 90% of the dyes were degraded within 30 minutes of irradiation, the remaining dye solution was washed off, and a fresh solution was taken for other recycles. Further TOC analysis of the photodegraded dye solution (first cycle) was carried out to ensure more than 90% conversion, and the results show 92% degradation (ESI Table 1[†]). The used Ag₃PO₄(a)SiO₂ and Ag₃PO₄ nanoparticles were washed with water after each recycling of the material was carried out up to 6 cycles of photodegradation.

Cyclic voltammetric studies

Cyclic voltammetry is deployed for electrochemical studies. Cyclic voltammetry is a three-electrode setup. The glassy carbon working electrode is replaced with FTO, sandwiched by a Ag_{3} - PO_4 @SiO₂-coated glass plate, a Pt counter electrode and an Ag/

AgCl reference electrode. Ag₃PO₄(3)SiO₂ was spin-coated onto a glass plate of dimension 2 cm length and 1 cm breadth. Then, 1 M tetrabutyl ammonium hexafluorophosphate (TBAHFP) in an acetonitrile–10% water mixture was used as a supporting electrolyte. The electrolyte is degassed using N₂ gas before all the experiments, and uniform stirring for 5 minutes has been done before each cyclic voltammetric measurement.

Results and discussion

We synthesised thin silica-coated Ag₃PO₄-based semiconductor nanostructures by a chemical method.30 The lack of solubility of Ag₃PO₄ in polar solvents limits various synthetic possibilities such as incorporation of other materials (other semiconductor or metal nanomaterials) and surface modification like coreshell structures.³¹⁻³⁴ In this case, direct silica overcoating is inappropriate due to the lack of silane loving groups on the surface of Ag₃PO₄ nanostructures. Thus, triethoxy n-octyl silane was chosen as the silane coating agent, which overcoats the in situ formed Ag₃PO₄ nanoparticles. Octyl silane facilitated the anchoring of octyl silane groups on the surface of Ag₃PO₄, where the triethoxy silane group condensed to form a thin silica layer. A basic pH of ~ 10 of Na₂HPO₄ enables the alkaline hydrolysis of octyl silane, resulting in thin silica coating onto the surface of Ag₃PO₄ nanostructures. The formed silica-coated Ag₃PO₄ (Ag₃- $PO_4(aSiO_2)$ is yellow; the unreacted reactants were removed by repeated centrifugation in water. The thin silica shell overcoating enhances the versatility of usage by dispersing in various solvents such as chloroform, tetrahydrofuran and water. The synthesised semiconductor photocatalyst was characterised by the UV-Vis absorption spectrum, which is taken by coating Ag₃PO₄@SiO₂ onto a glass surface, and BaSO₄ coated onto glass was used as the baseline. The absorption spectra displayed in Fig. 1A show an absorption peak at 453 nm, equal to the bandgap (2.36 eV) of Ag₃PO₄. Further, the characteristic peaks at 20°, 29°, 33° and 36° in the PXRD pattern shown in Fig. 1B confirm the crystallinity of Ag₃PO₄@SiO₂ and is found to be similar to the previously reported values.¹⁰ The HR-TEM images of Ag₃PO₄@SiO₂ were recorded by drop casting Ag₃-PO₄@SiO₂ onto a coated Cu grid, as presented in Fig. 1C. The morphological analysis of Fig. 1D reveals the amorphous 2.5 nm silica coated on crystalline Ag_3PO_4 with an average size of 20 \pm 5 nm (ESI Fig. S1A[†]). Further, the EDX spectra of Ag₃PO₄@SiO₂ confirm the presence of elements Si, Ag, P, and O (ESI Fig. S1B^{\dagger}). Purified Ag₃PO₄@SiO₂ is dispersed in distilled water for photocatalytic studies. Methylene blue and rhodamine B were chosen as two different kinds of organic contaminants. Time-dependent absorption spectra were recorded and used to monitor the photocatalytic degradation of dyes.

Photocatalytic activity of Ag₃PO₄@SiO₂

The photocatalytic efficiency of $Ag_3PO_4(@SiO_2 was initially evaluated by the photodegradation of MB (methylene blue) incubated for 30 min to achieve equilibrium of adsorption of dyes on <math>Ag_3PO_4(@SiO_2. Then, it was irradiated with 365 nm light with a power of 125 W, and <math>Ag_3PO_4(@SiO_2 showed a remarkable$

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Fig. 1 (A) Absorption spectra of $Ag_3PO_4@SiO_2$ nanoparticles coated onto a glass. (B) XRD patterns of $Ag_3PO_4@SiO_2$ coated onto a glass surface. (C and D) High-resolution transmission electron microscopic (HRTEM) images of $Ag_3PO_4@SiO_2$. Magnified image of 2.5 nm silicacoated crystalline Ag_3PO_4 nanoparticles (D).

degradation rate of 90% within 20 minutes, which is similar to bare Ag₃PO₄ presented in ESI Fig. S4.[†] Five more cycles of photodegradation were carried out to ensure the recyclability of photocatalysts under 365 nm light having the same power and experimental conditions. For each cycle, 90% completion of photodegradation of MB was ensured by monitoring the UV-vis spectra and correlated with TOC analysis. Unreacted dyes and degradation products were removed by repeated centrifugation. Then, purified Ag₃PO₄(a)SiO₂ nanoparticles were dispersed in 1.6×10^{-5} M of MB solution, and photodegradation was carried out again. The MB concentration was estimated and presented in ESI Fig. S5.† It should be noted that both silica-coated and bare Ag₃PO₄ showed significant photocatalytic degradation of MB even after 6 cycles. The results indicate the photodegradation efficiency of Ag₃PO₄@SiO₂ in parity with bare Ag_3PO_4 . Further, the photocatalytic efficiency of Ag_3PO_4 and Ag₃PO₄@SiO₂ was studied under visible light, where a Xe lamp was used as a light source with a bandpass filter ($\lambda \sim 450$ nm) having a power of 300 W. The difference in the photocatalytic efficiency of Ag₃PO₄ and Ag₃PO₄@SiO₂ was more pronounced in the photodegradation of MB under visible light irradiation, which is presented in Fig. 2A and B respectively. In contrast to the previous experiment, methylene blue showed 2 times enhanced degradation after 4 cycles of photodegradation in Ag₃PO₄@SiO₂ compared to bare Ag₃PO₄. The rate constant was calculated and plotted as a function of number of cycles of photocatalysis by following the Langmuir-Hinshelwood firstorder kinetic model, presented in Fig. 2C and ESI Table 3.† Initially, the rate constant of Ag₃PO₄ is comparable to Ag₃-PO₄@SiO₂. However, the photocatalytic activity of Ag₃PO₄ deteriorates in subsequent cycles, where Ag₃PO₄(a)SiO₂ showed four times enhancement in photodegradation after the 5th cycle (ESI Table 2[†]). TOC analysis was carried out to ensure more than 90% photodegradation (ESI Table 1[†]).



Fig. 2 Photocatalytic degradation of methylene blue (MB) in the presence of (A) Ag_3PO_4 and (B) Ag_3PO_4 @SiO₂ under 450 nm light. (C) Comparison of the rate constant of Ag_3PO_4 (red) and Ag_3PO_4 @SiO₂ (blue) for methylene blue. Photocatalytic degradation of rhodamine (RhB) in the presence of (D) Ag_3PO_4 and (E) Ag_3PO_4 @SiO₂ under 450 nm light. (F) The rate constant comparison of Ag_3PO_4 (red) and Ag_3PO_4 @SiO₂ (blue) for rhodamine B.

The photodegradation studies were extended into other dyes as well, carrying a negative charge, such as rhodamine B. Contrary to methylene blue, the photocatalytic degradation of rhodamine B by Ag_3PO_4 showed a pseudo-first-order kinetics with the increase in cycles, as shown in Fig. 2D and E. Nevertheless, the photocatalytic efficiency of Ag_3PO_4 @SiO₂ remains unaffected by changing the molecule from MB to rhodamine B, and is presented in Fig. 2D–F. Besides, the photocatalytic reusability enhanced when rhodamine B was used as a dye in the presence of Ag_3PO_4 @SiO₂ compared to Ag_3PO_4 . The plot *C*/ $C_0 vs.$ time of Ag_3PO_4 showed a linear plot indicating the reaction that proceeds through pseudo zero order, whereas Ag_3 -PO₄@SiO₂ showed the same kinetics as followed in the MB degradation (ESI Table 4†).

The thin silica prevents direct contact between Ag₃PO₄ and methylene blue, although the amorphous silica layer traps the dye molecules and keeps them in the vicinity of Ag₃PO₄. Thus, the reactive intermediates produced due to the oxidation of water molecules by Ag₃PO₄ react effectively and oxidise methylene blue. The porous nature of thin silica allows the easy penetration of water molecules and hinders the interaction between methylene blue and Ag₃PO₄, which makes the Ag₃PO₄ surface less contaminated.33-36 It should be noted that various other studies showed that the solvent medium³⁵ water plays a significant role in the photodegradation of organic contaminants. It is well documented that in the presence of light, Ag₃PO₄ will react with water molecules to form O₂, O₂^{-•}, OH[•], all of which oxidise organic molecules into CO2 and other inorganic products. Here, excited Ag₃PO₄ follows the same mechanism for the photodegradation of organic molecules. It is expected that SiO₂ prevents direct contact with the molecules. Therefore, the reaction proceeds via the solvent-mediated mechanism. However, the direct contact between photocatalysts and organic contaminants will leave a footprint on the surface of Ag₃PO₄. This may decline the efficiency of photocatalysts in further recycling. Even though Ag₃PO₄ has high photocatalytic efficiency, it has an unavoidable drawback of self-reduction of Ag⁺ on the surface of Ag₃PO₄. The deposition of photodegraded organic contaminants on the surface of Ag_3PO_4 leads to catalytic poisoning. The self-reduction of Ag⁺ to Ag⁰ on the surface of Ag_3PO_4 is initially enhancing, but the photocatalytic processes decrease at later stages.

X-ray photoelectron spectroscopic studies were carried out to analyse the surface contamination of Ag₃PO₄ and Ag₃PO₄@SiO₂ nanostructures. ESI Fig. S7[†] shows the deconvoluted spectra of Ag 3d_{5/2} and Ag 3d_{3/2} peaks of bare Ag₃PO₄ and Ag₃PO₄(a)SiO₂ before photocatalysis to be 368.21 eV (Ag⁺ 3d_{5/2}), 374.10 eV (Ag⁺ 3d_{3/2}) and 369.10 eV (Ag⁰ 3d_{5/2}), 374.81 eV (Ag⁰ 3d_{3/2}) respectively. After 6 cycles of photocatalysis, the peak corresponding to Ag⁰ is more pronounced in bare Ag₃PO₄ than in Ag₃PO₄@SiO₂, and the ratio of peak area of Ag⁰ to Ag⁺ showed a two-time increase in Ag⁰ content in bare Ag₃PO₄ than in Ag₃PO₄@SiO₂. This explains why bare Ag₃PO₄ declined its efficiency of photodegradation after recycles while Ag₃PO₄@SiO₂ retained.³⁷ The XRD pattern of Ag₃PO₄ and Ag₃PO₄@SiO₂ before and after photodegradation agrees with the conclusions (ESI Fig. S8[†]). The HR-TEM images of Ag₃PO₄ and Ag₃PO₄@SiO₂ presented in ESI Fig. S2[†] clearly distinguish the Ag⁰ accumulation on the surface of Ag_3PO_4 rather than Ag_3PO_4 (a)SiO₂.

To evaluate the photocatalytic performance of bare Ag₃PO₄ and Ag₃PO₄@SiO₂, we calculated the photocatalytic degradation efficiency and compared with other works reported in the literature.34-43 The maximum photocatalytic degradation efficiency of bare Ag₃PO₄ obtained after adsorption-desorption of methylene blue shows 1.29 \times 10⁻² mg min⁻¹ mg⁻¹ and Ag_3PO_4 (a)SiO₂ showed a maximum efficiency of 1.45 \times 10⁻² mg min^{-1} mg⁻¹. For rhodamine B, the maximum photocatalytic degradation efficiency of bare Ag₃PO₄ showed $1.62 \times 10^{-2} \text{ mg min}^{-1} \text{ mg}^{-1}$ and Ag_3PO_4@SiO_2 showed an enhanced photocatalytic activity of $2.18 \times 10^{-2} \text{ mg min}^{-1} \text{ mg}^{-1}$ efficiency. The above reported values of degradation efficiency for Ag₃PO₄@SiO₂ are better than those for pure Ag₃PO₄ and the other reported values of methylene blue and rhodamine B.38-43 Further reusability of Ag₃PO₄(a)SiO₂ is well proved in recyclability experiments while retaining the photocatalytic activity even after six cycles of photodegradation of methylene blue and rhodamine B. In the case of Ag₃PO₄(a)SiO₂, the dye molecule gets adsorbed onto the surface of the SiO₂ shell irrespective of charge and it exposes the molecule to reactive intermediates formed in the vicinity of Ag_3PO_4 (ESI Table 2[†]). Considering all these factors, SiO₂-coated Ag₃PO₄ showed better performance, unaffected by the dyes' charges and reusability. Thus, SiO₂ coating will be a better method for making the photocatalyst a versatile and reusable material for the decontamination of water.

Elucidating the mechanism via cyclic voltammetry

Cyclic voltammetric analysis was carried out to elucidate the mechanism and identify the intermediates formed during the experiment. This research gives clear-cut evidence for the mechanism of oxidation of dyes *via* O_2^- , OH[•] and OOH⁻ intermediate formation. A three-electrode setup was used for the study; a glass plate spin coated with Ag₃PO₄@SiO₂ sandwiched with the FTO plate was used as the working electrode, Ag/AgCl as the reference electrode and platinum as the counter electrode. The photocatalytic activity of Ag₃PO₄@SiO₂ and its intermediate formation

were monitored electrochemically *via* the fabricated working electrode. In order to get proper solvation, the working electrode was immersed into electrolytes before sandwiching them (Fig. 3).

The stability of Ag₃PO₄@SiO₂ was confirmed by cycling the modified electrode from a potential range of 1 V to -1 V vs. Ag/ AgCl at different scan rates (ESI Fig. S9[†]). Even after several cycles, the current remains stable, indicating the stability of Ag₃PO₄(a)SiO₂. Cyclic voltammetric studies were conducted in the presence of light and water under deaerated conditions. In the presence of light, Ag₃PO₄@SiO₂ produces electron-hole pairs, which further react with water to form superoxides (O_2^{-1}) , peroxide (HOO⁻) and OH[•]. Fig. 3 shows the cyclic voltammetric response of Ag₃PO₄(a)SiO₂ from a potential range of -1 V to +1 V vs. Ag/AgCl at a scan rate of 0.1 V s⁻¹; it shows two oxidation peaks at 0.32 V and 0.85 V and two reduction peaks at 0.09 V and -0.65 V vs. Ag/AgCl. The oxidation peak at 0.32 V corresponds to the oxidation of super oxides (O_2^{-}) produced as a result of photochemical reactions. On prolonged exposure of light, current response goes on increasing, which indicates the continuous generation of O₂⁻ in the system.^{44,45}

$$Ag_3PO_4 \rightarrow Ag_3PO_4^* + h^+$$
 (photo excitation) (1)

 $H_2O + h^+ + O_2^{-} \rightarrow OOH^- + OH^-$ (photochemical reaction)(2)

$$O_2 \to O_2^- + e^- (0.32 \text{ V}, \text{Ag/AgCl})$$
 (3)

The oxidation peaks at 0.85 V are due to the formation of Ag^+ from metallic silver (Ag^0), which is confirmed by conducting a blank experiment with bare Ag_3PO_4 under the same experimental conditions in the presence and absence of light. During photoexcitation, the recombination of electron-hole results in the decomposition of Ag^+ to Ag^0 and weakens the photocatalytic activity. From the CV analysis, the oxidation peak at 0.85 V appears only in the presence of light, confirming the Ag-to-Ag⁺ oxidation; the peak current increases with time, confirming the photocatalytic generation of Ag. There is no characteristic oxidation peak of Ag^+ observed for the experiments conducted in the absence of light. In the case of Ag_3PO_4 (a)SiO₂, the oxidation peak of Ag^0 emerges only after 30 minutes because the SiO₂ shell inhibits the direct contact of the Ag_3PO_4 surface to the reaction medium (ESI Fig. S11⁺).

 $4Ag_{3}PO_{4} + 6H_{2}O + 12h^{+} + 12e^{-} \rightarrow$ 12Ag + 4H_{3}PO_{4} + 3O_{2} (photochemical reaction) (4)

$$Ag^0 \rightarrow Ag^+ + e^- (0.85 \text{ V}, Ag/AgCl)$$
 (5)

In the reverse scan, the reduction peak at 0.09 V is quasi reversible with the oxidation peak at 0.32 V by a potential difference of 0.23 V. According to the reported work by G. Crompton *et al.*, this peak is due to the reduction of oxygen to super oxide. This super oxide formation is followed by its fast reaction with water producing OH[•] and OOH⁻; this is observed as the reduction peak at -0.65 V. OOH⁻ further reacts with water producing hydrogen peroxide and OH[•] followed by the disproportionation reaction of H₂O₂, which leads to water formation as follows:^{46,47}



Fig. 3 Schematic of $Ag_3PO_4@SiO_2$ sandwiched between the FTO and glass and the mechanism of photodegradation. The set up shows the monitoring of intermediates ((O_2^{-+}), peroxide (HOO^{-}) and OH⁺) formed during the photocatalytic oxidation of water by cyclic voltammetry. Cyclic voltammogram of $Ag_3PO_4@SiO_2$ sandwiched between FTO and the glass plate during the photocatalytic oxidation of water, light irradiated at 450 nm.

$$O_2 + e^- \to O_2^- \tag{6}$$

$$O_2^{-} + H_2O + e^- \rightarrow HOO^- + OH^-$$
 (7)

 $OOH^- + H_2O \rightarrow H_2O_2 + OH^-$ (8)

$$H_2O_2 \to H_2O + \frac{1}{2}O_2 \tag{9}$$

The effect of the sacrificial electron acceptor on the photocatalytic effect was evaluated by experimenting in the presence of AgNO₃ (ESI Fig. S13[†]). In the presence of AgNO₃, the electrons are exported from the conduction band, and Ag⁺ will be reduced to Ag⁰, which is observed as the rise in peak current from 0.4 mA (in the absence of AgNO₃) to 0.8 mA at 0.75 V. The reduction peak current increases with time in the presence of light. No peaks corresponding to the superoxide and peroxide are observed in the absence of light. The above cyclic voltammetric study reveals that light and water are necessary for the photocatalytic generation of intermediates such as OH⁺, O₂⁻⁺ and OOH⁻ and are responsible for the photodegradation of dyes. SiO₂ coating on Ag₃PO₄ gives stability to the photocatalyst, which can be recycled and reused.

Conclusions

Thin silica-coated Ag_3PO_4 was synthesized by *in situ* addition and subsequent condensation of octyl silane during the precipitation of Ag_3PO_4 . The photocatalytic activity of silicacoated Ag_3PO_4 and bare Ag_3PO_4 was studied using methylene blue and rhodamine B as organic contaminants. Thin silica

improves the photostability of Ag₃PO₄ by retaining the photocatalytic efficiency even after six cycles of photodegradation. The photocatalytic efficiency of bare Ag₃PO₄ declined in both dyes after three cycles, and the percentage of photodegradation became half after five cycles of photodegradation. After photodegradation, XPS and HR-TEM analysis of Ag₃PO₄ and Ag₃- PO_4 (a) SiO₂ revealed that the self-reduction of Ag⁺ to Ag⁰ was more predominant in Ag₃PO₄ than in Ag₃PO₄@SiO₂. Photocatalytic generations of such intermediates were monitored electrochemically by a cyclic voltammetric technique. The intermediate formation was confirmed by conducting experiments in the presence and absence of light. It is evident from the study that water and light are indispensable parts for producing intermediate species O2-, OH and OOH, which further results in the photodegradation of dyes. SiO₂-coated Ag₃PO₄ degrades various organic contaminants irrespective of their charge. Thus, SiO_2 coating will be a better method for making the Ag₃PO₄ photocatalyst a versatile and reusable material for the decontamination of water.

Conflicts of interest

The authors declare no competing financial interest.

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