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Article

Thermo-responsive functionalized PNIPAM@Ag/Ag₃PO₄/CN-heterostructure photocatalyst with switchable photocatalytic activity

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ABSTRACT

It is extremely important for photocatalysts to exhibit intelligent responsiveness to their environment. Herein, a poly *N*-isopropyl acrylamide (PNIPAM)-modified Ag/Ag₃PO₄-20/CN hybrid material with excellent convertible photocatalytic activity is prepared. PNIPAM has good hydrophilicity below the lower critical solution temperature (LCST); this increases the capacity of the photocatalyst for adsorbing tetracycline (TC) molecules. In addition, the PNIPAM-modified Ag/Ag₃PO₄-20/CN can prevent the loss of Ag₃PO₄. The dispersity is improved by loading g-C₃N₄ nanosheets (CN) for enhancing the efficiency of photocatalytic activity. Furthermore, a Z-scheme heterostructure is formed between CN and Ag₃PO₄, accelerating the separation efficiency of the holes and electrons. Ag nanoparticles can be used as electron-shuttle mediators, and electrons receiving more energy are transferred via the localized surface plasmon resonance (LSPR) effect. Furthermore, the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst exhibits an excellent degradation rate for the degradation of TC when the temperature is lower than the LCST. The photoluminescence spectra and photocurrent curves prove that the carrier-separation efficiency of PNIPAM@Ag/Ag₃PO₄-20/CN is higher than those of Ag/Ag₃PO₄/CN and CN. The main active species of ·O₂⁻ and h⁺ are detected to reveal the plausible mechanism of the PNIPAM@Ag/Ag₃PO₄-20/CN hybrid material system. This work provides a way to develop intelligent materials for switchable photocatalytic applications.

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1. Introduction

During the extensive course of development of silver salt semiconductor photocatalysts, silver phosphate (Ag₃PO₄) receives tremendous attention. Ag₃PO₄ can improve the electron transmission because it possesses the d-state wave function, which has the properties of high delocalization and isotropic

distribution [1]. Ag₃PO₄ has strong oxidation capacity, which can be attributed to the suitable valence band position allowing to generate numerous holes. Further, its narrow band gap (2.5 eV) provides it with excellent visible-light absorption capability. Moreover, Ag₃PO₄ has the advantages of photosensitivity, easy preparation, and non-toxicity. Heretofore, Ag₃PO₄ is considered as an ideal material for photocatalytic activity in pho-

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photocatalytic degradation. Recently, some Ag_3PO_4 adorned semiconductor systematic photocatalysts have been considered. Li's group [2] obtained a $\text{Ag}_2\text{WO}_4/\text{Ag}_3\text{PO}_4$ hetero-structure, which exhibited a highly efficient mineralization of bisphenol A under simulated solar light. Pang et al. [3] demonstrated that Ag_3PO_4 could completely degrade rhodamine B (RhB) after 36 h and the degradation rate of RhB by Ag_3PO_4 polypods (0.08099 h^{-1}) was 46 times than that by *N*-doped TiO_2 (0.00173 h^{-1}). Further, $\text{Ag}_3\text{PO}_4/\text{AgI}$ prepared by an in situ anion-exchange method showed efficient electron transfer rate and good stability [4]. However, Ag_3PO_4 particles easily agglomerate, inhibiting the electron transport during photocatalytic degradation. The strategy of introducing semiconductor materials as supports, with the properties of facile synthesis and low cost, can be considered to improve the activity of photocatalysts [5].

As one kind of support material, graphitic carbon nitride (*g*- C_3N_4), has rich resources, excellent optical properties, and recyclable characteristics. Besides, *g*- C_3N_4 nanosheets (CNs) provide numerous surface reactive sites because of their high specific surface area [6,7]. Moreover, CNs have a shorter transfer/diffusion distance than *g*- C_3N_4 , reducing the recombination probability of the photo-generated charge carriers. CN, as a supporter, is an ideal material to solve the uncontrolled aggregation problems [8–10]. To date, many studies have shown that the Z-scheme heterostructure can improve the performance of photocatalysts. Zhu et al. [11] synthesized ZnO/CeO_2 , a direct Z-scheme heterostructure, which displayed a high degradation rate of RhB. The Z-scheme *g*- $\text{C}_3\text{N}_4/\text{Bi}_4\text{NbO}_8\text{Cl}$ heterostructure, which was prepared by You's group, solved the issues of high redox potentials and low charge separation efficiency [12]. Further, an efficient visible-light-driven photoelectrical-converted Z-scheme $\text{CdTe-Bi}_2\text{S}_3$ heterostructure was synthesized by Liu et al. [13]. Considering the certainty that a Z-scheme heterostructure reduces the carrier recombination rate, the $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ composite catalyst belongs to this type [14,15]. Therefore, the strategy of introducing CN-dispersed Ag_3PO_4 and forming heterostructures has been considered as a favorable approach.

Noble-metal-modified semiconductor photocatalysts for wastewater treatment have attracted widespread attention. They serve as positively contributed, producing the localized surface plasmon resonance (LSPR) effect, for the process of visible-light-driven photocatalysis [16,17]. When the photon energy is consistent with the resonance energy of its oscillation, the catalyst can produce the LSPR effect, causing excellent free electron mobility. The LSPR effect can be triggered through the combination of Ag and semiconductors. Hence, Ag-modified semiconductors are extensively researched [18,19]. For example, Jeong et al. [20] acquired a Ag/BiVO_4 composite whose SPR effect enhanced photocatalytic water splitting. Shen's group [21] synthesized a green Ag-TiO_2 catalyst with excellent performance for removing dyes and oxidizing desulfurization. A novel three-dimensional $\text{Ag}/\text{AgBr}/\text{BiVO}_4$ photocatalyst successfully prepared by Wei's group exhibited excellent photocatalytic performance [22]. Therefore, an $\text{Ag}/\text{Ag}_3\text{PO}_4$ complex can improve the absorption range of visible light and speed up the electronic transmission rate.

Poly *N*-isopropyl acrylamide (PNIPAM), as a thermo-responsive polymer, has reversible hydrophilic-to-hydrophobic conversion around the lower critical solution temperature (LCST) (32°C) [23–25]. With temperature decrease, the hydrophilicity of PNIPAM is increased, showing changes from shrinking agglomeration to a stretching swelling status [26,27]. Therefore, constructing a temperature-sensitive composite photocatalytic material can effectively utilize the temperature of the reaction system to achieve the regulation of the photocatalytic degradation process. PNIPAM also serves as a protective layer, preventing the loss of photosensitive materials.

Herein, a temperature-sensitive responsive Z-scheme $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4/\text{CN}$ heterostructure was prepared by precipitation and emulsion polymerization methods to photodegrade tetracycline (TC) under visible light. Interestingly, with the $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4/\text{CN}$ composite a responsive control of temperature was achieved. Moreover, the $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4/\text{CN}$ composite prevented the loss of Ag_3PO_4 and increased the adsorption capacity for the TC molecules. The photocatalytic activity of the Z-scheme $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4/\text{CN}$ heterostructure was measured by the degradation of TC. Furthermore, a strong interfacial interaction between CN and Ag_3PO_4 promoted rapid migration of the electron-hole pairs. These results showed that $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4/\text{CN}$ realized the reversible conversion property at different temperatures and remarkably improved the photocatalytic degradation performance of the photocatalyst.

2. Experimental

2.1. Preparation of the samples

2.1.1. Synthesis of CN and $\text{Ag}/\text{Ag}_3\text{PO}_4/\text{CN}$ photocatalysts

$\text{Ag}/\text{Ag}_3\text{PO}_4/\text{CN}$ photocatalyst was synthesized by the chemical precipitation method. Specifically, cyanuric acid and melamine in a molar ratio of 1:1 were mixed in 120 mL of ethanol. Then, the mixture was calcinated at a high temperature (550°C) with a heating rate of $2.3^\circ\text{C}/\text{min}$ for 8 h. CN was obtained by a simple one-step method. Moreover, 0.4 g of yellow products were dispersed in 150 mL water and sonicated for 1 h to achieve uniform solution. Approximately 0.073 g of Na_3PO_4 was dispersed in 40 mL water and stirred for 30 min. After that, 2.9 mL of 0.1 mol/L AgNO_3 solution was added dropwise under an ultrasonic procedure for 3 h. Additionally, the reactant was irradiated for 20 min by a 250-W UV lamp to produce a part of Ag. Lastly, the reactant was transferred to a 100-mL reactor and heated to 150°C for 12 h. The final product was centrifuged for several times by water and ethanol and then vacuum dried at 60°C for 12 h. The resulting product is called as $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-10}/\text{CN}$. Furthermore, different mass ratios of the composite photocatalysts were obtained by adding different amounts of Na_3PO_4 and AgNO_3 , respectively. These are referred as $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-10}/\text{CN}$, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-15}/\text{CN}$, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-25}/\text{CN}$, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-30}/\text{CN}$, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-40}/\text{CN}$, and $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-50}/\text{CN}$.

2.1.2. Preparation of $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$

photocatalysts

In a distinctive procedure, the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst was synthesized by the emulsion polymerization method. Here, 0.5 g of the Ag/Ag₃PO₄-20/CN complex was dispersed into 60 mL of ethanol and 10 mL of 3-(trimethoxysilyl) propyl methacrylate (MPS) with magnetic stirring, using a water bath to maintain a constant temperature (50 °C) under nitrogen (N₂) atmosphere. When the reaction was completed, the product was centrifuged and dried, and is named as Ag/Ag₃PO₄-20/CN. After that, 0.2 g of *N*-isopropylacrylamide (NIPAM) and 0.03 g of *N,N'*-methyl-enebis (acrylamide) (MBA) were mixed into 50 mL of water by sonication. Then 0.2 g of the surface-modified Ag/Ag₃PO₄-20/CN was added. Ammonium persulphate ((NH₄)₂S₂O₈) was added as an initiator at 60 °C for 12 h in the presence of N₂. Lastly, PNIPAM@Ag/Ag₃PO₄-20/CN was washed a few times with water and ethyl alcohol. Finally, the products were dried under vacuum at 60 °C for 12 h.

2.2. Characterization

The crystalline properties were characterized by the powder X-ray diffraction (XRD model MAC Science, Japan) with Ni-filtrated Cu K_α radiation. The scan range of 2θ was 10°–80° at a scan rate of 5°/min. The elements on the surface of photocatalysis and surface electronic states were measured on X-ray photoelectron spectroscopy (XPS) by thermo ESCALAB 250X (America) electron spectrometer. The morphology of as-prepared samples and energy dispersive spectrometer (EDS) images were observed by scanning electronic microscopy (SEM) on an S-4800 field emission. The transmission electron microscopies (TEM) of as-prepared samples were obtained on JEM-2010 electron microscope with accelerating voltage of 200kV. Fourier transforms infrared (FT-IR) spectra of the samples were recorded with KBr pellets with a Bruker Vertex 70 spectrometer from 4000–500 cm⁻¹. Raman spectra were measured on a confocal laser micro-Raman spectrometer (Thermo Fischer DXR, USA). Specific surface area was detected by the Brunauer-Emmett-Teller (BET) technique (Tristar II 3020) from the N₂ adsorption isotherm, the pore size distribution was determined by desorption isotherm using the Barrett-Joiner-Halenda (BJH) method. UV-Vis diffuse reflectance spectra (DRS) of the samples were obtained from an UV-2450 using BaSO₄ as a reflectance standard. The diffuse reflectance spectra (DRS) of the catalysts were performed in the range of 250–850 nm using a UV-Vis spectrophotometer (UV-2450; Shimadzu, Japan) equipped with an integrating sphere. Transient photocurrent response used Na₂SO₄ solution (0.5 mol/L) as a supporting electrolyte in the voltage of 0.5 V. Electrochemical impedance spectroscopy (EIS) analysis were measured by using a CHI 760E electrochemical workstation. The photoluminescence (PL) spectra were detected on a F4500 (Hitachi, Japan) photoluminescence detector. Thermogravimetric analysis (TGA) of the samples was conducted by a Diamond TG/DTA Instrument (STA 449C Jupiter, Netzsch, Germany). Angle meter was investigated using an optical contact angle-measuring device (KSV, CM200, Finland). The active species of ·OH and ·O₂⁻ radicals were verified with 5,5-dimethyl-1-pyrroline *N*-oxide

(DMPO) at room temperature by electron spin resonance (ESR) (Bruker A300, Germany) experiment.

2.3. Photocatalytic performance tests

In this work, TC was used to analyze the performance of the samples at different temperatures. Briefly, 50 mg of the photocatalyst was dissolved in 100 mL of TC solution with a concentration of 20 mg/L, and a constant temperature was maintained by passing it through condensed circulating water. The solution was reacted for 30 min first in the dark until it reached an adsorption/desorption balance and then under visible light by a 250-W Xenon arc lamp through a filter for 2 h. A sample was collected every 15 min and was immediately centrifuged and filtered through the filter. Finally, the filtrate was detected by UV-vis spectrophotometry, exhibiting a maximum absorption peak at 357 nm. The degradation rate could be calculated as follows:

$$\text{Degradation efficiency} = (1 - C_t/C_0) \times 100\%, \quad (1)$$

where C_t means the remaining concentration after irradiation and C_0 represents the initial concentration of the TC solution.

3. Results and discussion

3.1. Adsorption experiments

3.1.1. Adsorption capacity analysis

In order to further prove that PNIPAM has the ability of improving the adsorption properties of Ag/Ag₃PO₄-20/CN, we conducted adsorption experiments for the removal of TC, which are shown in Fig. 1. In detail, 50 mg of each sample was dissolved in 100 mL of the TC solution having a concentration of 20 mg/L, in a 250-mL flask. The adsorption experiment was carried out for 90 min, and the target solution was collected every 10 min. The concentration of the TC solution was tested by UV-Vis spectrophotometry. The removal efficiency and adsorption capacity were calculated by the following formulas (Eqs. (2) and (3)):

$$\text{Removal efficiency} = (1 - C_t/C_0) \times 100\% \quad (2)$$

$$Q_e = (C_0 - C_e) \times V/W \quad (3)$$

where Q_e (mg/g) is called the adsorption amount reaching adsorption equilibrium, and C_e (mg/L) and V (mL) are the equilibrium concentration and solution volume, respectively. The initial concentration and the concentration of any time t of TC are C_0 and C_t , respectively. In addition, W (mg) is the quality of the photocatalyst involved in the reaction [28]. We can find that the removal efficiency is high in the first 10 min and then gradually decreases. The removal efficiencies of Ag/Ag₃PO₄-20/CN and PNIPAM@Ag/Ag₃PO₄-20/CN for TC are 25.27% and 32.65%, respectively. In addition, the adsorption ability of PNIPAM@Ag/Ag₃PO₄-20/CN ($Q_e = 13.059$ mg/g) is improved compared to Ag/Ag₃PO₄-20/CN (10.1084 mg/g).

3.1.2. Adsorption kinetics

In order to further study the kinetic properties, the pseudo-first-order kinetic (FOK) model and pseudo-second-order kinetic (SOK) model were used to fit the adsorption data. Table

Fig. 1. The TC removal efficiency (A) and adsorption capability (B) of Ag/Ag₃PO₄-20/CN and PNIPAM@Ag/Ag₃PO₄-20/CN.

1 shows the corresponding parameters. The kinetic curves of Ag/Ag₃PO₄-20/CN and PNIPAM@Ag/Ag₃PO₄-20/CN quickly reach equilibrium within 30 min, as shown in Fig. 2A. This phenomenon is attributed to the fact that the adsorption on the outer surface of the sample can quickly reach saturation. The correlation coefficients of Ag/Ag₃PO₄-20/CN and PNIPAM@Ag/Ag₃PO₄-20/CN are presented in Table 1. PNIPAM@Ag/Ag₃PO₄-20/CN exhibits SOK during the adsorption process, for which the correlation coefficient (0.9986) is greater than that for FOK (0.9967). Furthermore, PNIPAM@Ag/Ag₃PO₄-20/CN shows a higher value of K_2 than Ag/Ag₃PO₄-20/CN, indicating that PNIPAM@Ag/Ag₃PO₄-20/CN has excellent adsorption capacity, which agrees with the experimental results. The kinetic adsorption data are used to better research the kinetic properties of the adsorption process by the intra-particle diffusion model, as displayed in Fig. 2B. The related fitting parameters of the intra-particle diffusion

model are listed in Table 2. According to the intra-particle diffusion model, the fitted line has three curves, which present a multi-linear relationship. This indicates that the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst adsorption process has multiple rate control steps and its slope gradually decreases. The process is mainly divided into the following three steps. Firstly, the TC molecules rapidly diffuse from the original solution to the catalyst surface. Second, the TC molecules on the surface of the adsorbent diffuse into the channel. Finally, the adsorption tends to reach equilibrium [29].

3.2. Photocatalytic activity test

The photocatalytic activities of the as-obtained samples were verified by photodegrading TC. Prior to the photocatalytic tests, the prepared samples underwent adsorption reactions for 30 min under dark conditions. Fig. 3A shows the activities of

Table 1
The kinetic parameters of the FOK and SOK models.

Material	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	$Q_{e,c \text{ exp}} \text{ (mg/g)}$	$K_1 \times 10^{-3} \text{ (L/min)}$	R^2	$Q_{e,c \text{ exp}} \text{ (mg/g)}$	$K_2 \text{ (L/min)}$	R^2
Ag/Ag ₃ PO ₄ -20/CN	10.1852	7.426	0.993	10.2786	0.7958	0.9967
PNIPAM@Ag/Ag ₃ PO ₄ -20/CN	12.9041	6.782	0.9869	13.4298	0.2922	0.9986

Fig. 2. The adsorption kinetic models of TC on (A) Ag/Ag₃PO₄-20/CN and PNIPAM@Ag/Ag₃PO₄-20/CN and (B) the fitting of the intra-particle diffusion model.

Table 2

Parameters of the intra-particle diffusion model.

C_0 (mg/L)	K_1	C_1	K_2	C_2	K_3	C_3
20	1.8501	1.982	0.3527	10.0467	0.2332	10.9389

different mass ratio samples (Ag/Ag₃PO₄-10/CN, Ag/Ag₃PO₄-15/CN, Ag/Ag₃PO₄-20/CN, Ag/Ag₃PO₄-25/CN, Ag/Ag₃PO₄-30/CN, Ag/Ag₃PO₄-40/CN, and Ag/Ag₃PO₄-50/CN). We find that the different mass ratio Ag/Ag₃PO₄/CN photocatalysts have different photocatalytic activities: 64.36%, 77.27%, 84.82%, 79.93%, 76.63%, 66.27%, and 61.70%, respectively. When Ag₃PO₄ is above about 20%, it caused a reduced photocatalytic activity, which can be attributed to the additional Ag₃PO₄ granules being adhered to the surface of CN, inhibiting the contact with the contaminants in the photocatalyst system [30]. It is noteworthy that Ag/Ag₃PO₄-20/CN exhibits excellent catalytic performance. Moreover, PNIPAM@Ag/Ag₃PO₄-20/CN (88.96%) exhibits a much higher activity than Ag/Ag₃PO₄-20/CN, as displayed in Fig. 3C. This demonstrates that PNIPAM accelerates the electron transport rate and increases the photocatalytic performance. The corresponding first-order linear dynamic curves between $\ln(C_0/C_t)$ and the time are presented in Figs. 3B and 3D. The rate constants (k) for the as-prepared samples are obtained from the slope. Clearly, the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst exhibits the highest k value (0.0207 min⁻¹), which is 7.14 and 1.05 times higher than those of CN (0.0029 min⁻¹) and Ag/Ag₃PO₄-20/CN (0.0198 min⁻¹), respectively. Therefore, the photocatalytic property of PNIPAM@Ag/Ag₃PO₄-20/CN presents a comparatively more excellent performance for the photodegradation of TC.

In order to test the temperature-sensitive properties of the synthesized samples, we tested the degradation of TC at dif-

ferent temperatures. Figure 3E shows that the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst achieves thermo-response below and above the LCST values. The photocatalytic degradation rates (88.96%, 82.42%, 76.54%, 69.97%, 65.87%, and 56.73%) are displayed in Fig. 3E. They indicate that the degradation efficiency is reduced with increasing ambient temperature. Therefore, intermolecular hydrogen bonds are formed between the amide groups and water molecules at a low temperature, so that a stable hydrated structure is formed around the hydrophobic group of the macromolecule. Further, the polymer molecular chain swells in water and stretches into a hydrophilic form, when the random coil state releases the Ag/Ag₃PO₄-20/CN photocatalyst. When $T > \text{LCST}$, the hydrogen bonds between the amide groups and water molecules are replaced by the intramolecular hydrogen bonds formed between the C=O and -N-H in the amide group. Thus, the hydration structure is destroyed, resulting in a rapid collapse of the polymer chain, which curls into a hydrophobic tight ball. Therefore, the catalyst is so packaged that it is difficult to be in contact with the contaminants, reducing the catalytic activity. Furthermore, the UV absorption peak intensity of TC at 357 nm is significantly reduced and has a certain positional shift, as presented in Fig. 3F. This demonstrates that the TC pollutant is degraded into other small molecular substances. Therefore, PNIPAM@Ag/Ag₃PO₄-20/CN achieves controllability to the surrounding environment and has excellent photocatalytic degradation ability [31].

In order to evaluate the mineralization ability of the as-prepared photocatalyst for contaminants during photocatalytic degradation, the total organic carbon (TOC) test results are presented in Fig. 4. It can be seen that only 37.21% and 47.63% TOC are removed using pure CN and

Fig. 3. (A) Different mass ratio Ag/Ag₃PO₄/CN, (C) CN, Ag/Ag₃PO₄-20/CN, PNIPAM@Ag/Ag₃PO₄-20/CN, and (E) PNIPAM@Ag/Ag₃PO₄-20/CN under different temperature conditions for the photocatalytic degradation TC; (B,D) the pseudo-first-order reaction kinetics and (F) absorbance variations for TC degradation.

Fig. 4. TOC removal ratio of TC ($C_0 = 20$ mg/L) over CN, Ag/Ag₃PO₄-20/CN, and PNIPAM@Ag/Ag₃PO₄-20/CN performing direct photolysis under visible-light irradiation.

Ag/Ag₃PO₄-20/CN, respectively. However, the removal rate of TOC reaches up to 69.24% within 120 min using PNIPAM@Ag/Ag₃PO₄-20/CN. This indicates that the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst has a higher mineralization efficiency for TC photodegradation than CN and Ag/Ag₃PO₄-20/CN [32].

3.3. Stability

It is well comprehended that the stability of a material is an important basis for evaluating the quality and further application of the photocatalyst. The PNIPAM@Ag/Ag₃PO₄-20/CN and Ag/Ag₃PO₄-20/CN composites were tested by four recycling experiments, which are shown in Fig. 5A. The degradation efficiency of Ag/Ag₃PO₄-20/CN decreases slightly after four cycles of the degradation of TC. It is worth noting that the stability of the PNIPAM@Ag/Ag₃PO₄-20/CN composite is significantly enhanced comparing to that of Ag/Ag₃PO₄-20/CN. This indicates that the introduction of PNIPAM can effectively inhibit the photo-etching and deactivation of Ag₃PO₄. To the further research the stability of PNIPAM@Ag/Ag₃PO₄-20/CN, the X-ray diffraction (XRD) patterns of PNIPAM@Ag/Ag₃PO₄-20/CN for

the degradation of TC before and after the four recycling experiments are displayed in Fig. 5B. The characteristic diffraction peak position and crystal structure of PNIPAM@Ag/Ag₃PO₄-20/CN show little change, indicating good stability when PNIPAM is added as a photoactive protective layer on the surface of Ag/Ag₃PO₄-20/CN.

3.4. Effect of temperature on wettability of composite system

In order to prove that the PNIPAM@Ag/Ag₃PO₄-20/CN material exhibits different hydrophilic and hydrophobic properties after phase transformation at different temperatures, the contact angle test is presented in Fig. 6. It shows photographs of the contact angles when the surface of PNIPAM@Ag/Ag₃PO₄-20/CN is in contact with a water droplet within 8 s at 25 and 45 °C in the same plane. At 25 °C, the shape of the water droplet on the surface of PNIPAM@Ag/Ag₃PO₄-20/CN gradually becomes flat with increasing time, as displayed in Fig. 6A. In addition, the contact angle value of the PNIPAM@Ag/Ag₃PO₄-20/CN surface gradually decreases from 69.0° to 31.3°, which indicates that the composite presents a hydrophilic state in Fig. 6B. Furthermore, Ag/Ag₃PO₄-20/CN is released to participate in the degradation reaction, because PNIPAM exhibits a diastole state at 25 °C. The shape of the water droplet on the surface of PNIPAM@Ag/Ag₃PO₄-20/CN hardly changes within 8 s with increasing time, at 45 °C. PNIPAM tightly covers the catalyst so that PNIPAM@Ag/Ag₃PO₄-20/CN exhibits a contracted state [33,34]. The above results prove that PNIPAM@Ag/Ag₃PO₄-20/CN achieves controllability of degradation at different temperatures.

3.5. Effect of temperature on dispersibility of composite system in water

In order to further observe the dispersion of the PNIPAM@Ag/Ag₃PO₄-20/CN system in the process of a reversible temperature change from 20 to 45 °C in water, we conducted a corresponding test as shown in Fig. 7. At 25 °C, PNIPAM@Ag/Ag₃PO₄-20/CN is dispersed in water to form a

Fig. 5. (A) Cycling experiments for the photocatalytic degradation of TC by Ag/Ag₃PO₄-20/CN and PNIPAM@Ag/Ag₃PO₄-20/CN; (B) XRD patterns of PNIPAM@Ag/Ag₃PO₄-20/CN before and after the photocatalytic degradation of TC.

Fig. 6. Photographs of the shape of a water droplet on the surface of the PNIPAM@Ag/Ag₃PO₄-20/CN composite at different temperatures (A) 20 °C and (B) 45 °C in 8 s.

homogeneous solution, showing good dispersibility in water. With temperature increase, as shown in Fig. 7(b–e), PNIPAM@Ag/Ag₃PO₄-20/CN begins to aggregate and finally agglomerates to precipitate at the bottom of the bottle. As shown in Fig. 7(g–j), PNIPAM@Ag/Ag₃PO₄-20/CN changes from its aggregated state to the original dispersion solution as the temperature is lowered. This indicates that the as-prepared catalyst has a temperature-sensitive function [35,36].

Fig. 7. Photographs of the PNIPAM@Ag/Ag₃PO₄-20/CN composite dispersed in water at different temperatures.

3.6. Compositional and structural information

The typical XRD diffraction patterns of the as-prepared composites are exhibited in Fig. 8. The notable peaks located at 20.9°, 29.7°, 33.4°, 36.6°, 47.6°, 52.7°, 54.9°, 57.3°, 61.7°, 70.1°, and 72.2° are indexed to the (110), (200), (210), (211), (310), (222), (320), (321), (400), (420), and (421) crystal planes of Ag₃PO₄ (PDF = 43-0542), respectively [37,38]. Notably, four distinct peaks are detected, appearing at 38.1°, 44.3°, 64.2°, and 77.5° in the composite, which are indexed to the Ag (111), (200), (220), and (311) planes, respectively [39]. The diffractive peaks at 12.9° and 27.8° are attributed to the (100) and (002) planes of CN owing to the layer stacking factor [40]. This indicates that CN, Ag₃PO₄, PNIPAM@Ag/Ag₃PO₄-20/CN, and the different mass ratios of Ag/Ag₃PO₄/CN are successfully prepared. No diffraction peaks are observed in Ag/Ag₃PO₄-10/CN because of the low content of Ag₃PO₄. When PNIPAM is added, there are no significant changes in the shapes of the peaks of the Ag/Ag₃PO₄-20/CN composite, indicating that PNIPAM does not change the peak structure of the complex [41].

In order to further detect the surface element compositions and electronic states of the as-prepared photocatalysts, the results of the X-ray photoelectron spectroscopy (XPS) are ex-

Fig. 8. The XRD patterns of different mass ratios of Ag/Ag₃PO₄/CN (A) and the (B) as-prepared CN, Ag/Ag₃PO₄-20/CN, Ag₃PO₄, and PNIPAM@Ag/Ag₃PO₄-20/CN photocatalysts.

Fig. 9. XPS spectra of (A) survey, (B) C 1s, (C) N 1s, (D) Ag 3d, (E) O 1s, and (F) P 2p.

hibited in Fig. 9. The survey spectrum (Fig. 9A) verifies that the PNIPAM@Ag/Ag₃PO₄-20/CN samples contain C, N, Ag, P, and O elements, which is in accordance with the XRD results. As shown in Fig. 9B, the C 1s spectrum includes three peaks at approximately 283.7, 287.2, and 397.9 eV, which are attributed to the binding energies of C=C, C-N, and N=C-N, respectively [42,43]. In Fig. 9C, the N 1s spectrum can be fitted into four peaks located at 397.9, 399.3, 400.3, and 403.6 eV, which are ascribed to the bonds of C=N-C, N-C₃, and N-H and π excitation [44,45]. In Figs. 9D and F, we note that the peaks of PNIPAM@Ag/Ag₃PO₄-20/CN and Ag/Ag₃PO₄-20/CN have a slight shift toward a higher binding energy than those of Ag₃PO₄. This indicates that there is an interaction between Ag₃PO₄ and CN [46,47] and that the Ag element has been suc-

cessfully prepared. Moreover, the binding energy peaks at 530.2 and 532.1 eV are in good accordance with the O 1s state, and they are assigned to the Ag-O and -OH group, respectively [48,49]. The XPS results further verify that the PNIPAM@Ag/Ag₃PO₄-20/CN heterostructure is obtained.

3.7. Morphology analyses

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed to determine the morphology, and the results are presented in Figs. 10 and 11. The SEM images of CN are displayed in Fig. 10A and 10B. It can be seen that uniform ultra-thin carbon nitride nanosheets are synthesized. Further, Ag₃PO₄ granules are clearly exhibited on

Fig. 10. Morphology of CN (A, B), Ag/Ag₃PO₄-20/CN (C), and PNIPAM@Ag/Ag₃PO₄-20/CN (D, E) and EDX analysis (F) of PNIPAM@Ag/Ag₃PO₄-20/CN.

Fig. 11. TEM images of CN (A), Ag/Ag₃PO₄-20/CN (B), and PNIPAM@Ag/Ag₃PO₄-20/CN (C) and elemental mapping (D) of the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst.

the surface of CN. As shown in Figs. 10D and 10E, PNIPAM@Ag/Ag₃PO₄-20/CN presents a blurred surface compared to the Ag/Ag₃PO₄-20/CN surface, which shows that PNIPAM is successfully covering the surface of Ag/Ag₃PO₄-20/CN. It is noticeable that the elements of C, N, Ag, P, and O are discovered in the energy-dispersive X-ray (EDX) analysis of the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst. Fig. 11A exhibits that the CN morphology has a wrinkled lamellar structure and is almost transparent. Moreover, the black Ag₃PO₄ particles of the as-prepared Ag/Ag₃PO₄-20/CN display excellent dispersion in Fig. 11B. It is easy to find that there exists a layer of a substance, like a fog, on the surface of the CN and Ag/Ag₃PO₄ particles. This indicates that Ag/Ag₃PO₄-20/CN is successfully modified by PNIPAM. The distributions of C, N, Ag, P, and O in the mapping images of PNIPAM@Ag/Ag₃PO₄-20/CN further confirm that the as-prepared materials are synthesized.

3.8. Fourier transform infrared spectra and Raman spectra

The Fourier transform infrared (FTIR) spectra of CN, Ag₃PO₄, PNIPAM, Ag/Ag₃PO₄-20/CN, and PNIPAM@Ag/Ag₃PO₄-20/CN are displayed in Fig. 12. The typical peaks at 810, 1100–1750, and 3100–3400 cm⁻¹ are attributed to the characteristic respiratory peak of the tri-s-triazine units, telescopic vibration of the C–N heterocycles, and N–H groups, respectively [50]. For the Ag₃PO₄ sample, the two peaks at 1045 and 843 cm⁻¹ correspond to the P–O stretching oscillation in PO₄³⁻ [48,51]. The position at around 3150 cm⁻¹, marked with a dotted line, is the N–H symmetric stretching peak of CN [52]. We can see that the PNIPAM@Ag/Ag₃PO₄-20/CN material has a new peak of PNIPAM at 2976 cm⁻¹, indicating that Ag/Ag₃PO₄-20/CN is successfully modified by PNIPAM. To further research the structural compositions of the as-prepared materials, the Raman spectra are presented in Fig. 13. For Ag₃PO₄, the Raman peaks at 558 and 913 cm⁻¹ correspond to the oscillation of PO₄³⁻ [38]. The Raman spectrum of CN is dominated by the vibrational modes of C–N at the vibration absorption peaks of 1158, 1232, 1475, and 1649 cm⁻¹ [53,54]. We have found that the Ag/Ag₃PO₄-20/CN composite contains the peaks of C–N and PO₄³⁻, which indicate that Ag₃PO₄ and CN coexist in the composites. In the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst, all the peaks are shifted to a low wavenumber, indicating that Ag/Ag₃PO₄-20/CN is modified by PNIPAM [55].

3.9. Brunauer-Emmett-Teller surface area measurements

The specific surface area is an influential factor for enhancing photocatalytic activity, because a large specific surface area has more surface-active sites. The adsorption-desorption characteristics of N₂ are presented in Fig. 14. The adsorption-desorption isotherms are type IV with a hysteresis loop [56,57]. The Brunauer-Emmett-Teller (BET) surface area of CN is 91.0253 m²/g, as presented in Table 3. In comparison, the

Fig. 12. FT-IR spectra of CN, Ag₃PO₄, PNIPAM, Ag/Ag₃PO₄-20/CN, and PNIPAM@Ag/Ag₃PO₄-20/CN.

Fig. 13. Raman spectra of Ag_3PO_4 , CN, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$.

BET area of $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ is lowered to $74.9156 \text{ m}^2/\text{g}$, which is to the loading of Ag_3PO_4 particles on the CN surface. Moreover, $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ has a larger surface area ($83.9404 \text{ m}^2/\text{g}$) than the $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ photocatalyst. This indicates that PNIPAM can effectively increase the specific surface area of $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$. At the same time, the photocatalytic activity of $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ is higher than that of $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$. The results show that one of the factors affecting the photocatalytic activity is the surface area of the photocatalyst.

3.10. UV-vis diffuse reflection spectroscopy analysis

The light absorption property and energy band characteristics of Ag_3PO_4 , $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$,

Fig. 14. N_2 adsorption-desorption isotherms of CN, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$.

Table 3

BET surface area of CN, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$.

Sample	BET surface area (m^2/g)
CN	91.0253
$\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$	74.9156
$\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$	83.9404

and CN were analyzed by UV-vis diffuse reflection spectroscopy (DRS). Ag_3PO_4 and CN exhibit a distinct absorption edge at the positions of 521 and 473 nm, as presented in Fig. 15A [58]. In comparison to the spectra of $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, they exhibit a slight red shift, implying that the ability of the response to visible light is improved [59]. Ag_3PO_4 and CN can form a heterostructure, which can easily generate electrons and holes to improve the light absorption capacity. Moreover, the band gap energy (E_g) of Ag_3PO_4 and CN is evaluated using the following equation:

$$\alpha(h\nu) = A(h\nu - E_g)^{n/2} \quad (4)$$

where α , ν , h , A , and E_g denote the absorption coefficient, the light frequency, Planck's constant, a constant, and the band gap energy, respectively [60]. Further, n for both Ag_3PO_4 and CN is 1 [61,62]. The E_g values are computed by Eq. (4), and those of Ag_3PO_4 and CN are 2.38 and 2.62 eV, respectively. The E_g values are also given in Fig. 15B.

3.11. Photoelectrochemical properties analysis

To investigate the photoelectrochemical performances of the as-obtained materials, the transient photocurrent response and electrochemical impedance spectroscopy (EIS) results are presented in Fig. 16. Rapid and stable photocurrent responses of CN, Ag_3PO_4 , $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ are detected under visible-light illumination. Importantly, the photocurrent responses of the $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ composites are much higher than those of the pure CN and Ag_3PO_4 . This indicates that a heterostructure is formed between CN and Ag_3PO_4 , which accelerates the electron transport and improves the separation efficiency of the electrons and holes [63,64]. Meanwhile, $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ exhibits a higher photocurrent response than $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, revealing that PNIPAM efficaciously elevates the electron and hole separation and transfer. In addition, the EIS are presented in Fig. 16B. The arc radius of $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ is the smallest among those of CN, Ag_3PO_4 , and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, indicating that $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ has a relatively

Fig. 15. (A) UV-Vis DRS of Ag_3PO_4 , $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$, $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$, and CN; (B) The plots of $(\alpha h\nu)^2$ versus $h\nu$ of Ag_3PO_4 and CN.

Fig. 16. Transient photocurrent response (A) and EIS (B) of the CN, Ag_3PO_4 , $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$, and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$ samples.

higher surface reaction rate [65,66]. Therefore, $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$ possesses a high charge separation efficiency after the addition of PNIPAM.

3.12. Photoluminescence spectra

To research the catalytic efficiencies of the photocatalysts, we studied the photoluminescence (PL) spectra and the free recombination of the photoinduced electrons and holes in each

Fig. 17. PL spectra of the CN, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$, and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$ samples.

sample by PL spectroscopy [41]. The samples were excited at 360 nm. Fig. 17 shows the PL spectra of the CN, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$, and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$ samples, and the CN exhibits that the strongest emission peak is located at 467 nm. This is attributed to the high recombination rates of the carriers in CN. In addition, the PL intensity of $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$ is remarkably lower than that of $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$, illustrating that the recombination rate of $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$ is smaller than that of $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$. This indicates that the catalyst extends the life of the charge carrier and reduces the electron-hole pair binding rate after the introduction of PNIPAM [67]. Therefore, the PL results illustrate that the Z-scheme $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$ heterostructure can remarkably improve the charge transfer and the photocatalytic performance in the process of photocatalytic degradation [68,69].

3.13. Thermogravimetric analysis

To reveal the thermal stability of the as-prepared materials, thermogravimetric (TG) analysis was performed. The temperature detection range was from room temperature to 800 °C at a heating rate of 10 °C/min. The TG thermograms for CN, Ag_3PO_4 , PNIPAM, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$, and $\text{PNIPAM@Ag}/\text{Ag}_3\text{PO}_4\text{-20/CN}$ are clearly displayed in Fig. 18. It is clear that CN undergoes a weight loss in the range of normal temperature to

Fig. 18. TG thermograms for heating CN, Ag_3PO_4 , PNIPAM, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, and $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$.

100 °C. The loss of mass corresponds to the quantity of water, and it is caused by the adsorption of a small amount of water vapor from the outside of the material. Furthermore, CN becomes unstable when the heat temperature is above 530 °C, whereas heating to 690 °C does not yield any residue of the material being observed [70]. In addition, Ag_3PO_4 has a weight loss after 500 °C, probably caused by the presence of residual compounds in the sample [71]. For PNIPAM, there are three weightless stages. The weight loss phase before 100 °C may be owing to the sample removing water and organic solvents. When the temperature is in the range of 200 to 500 °C, the molecular chain in PNIPAM will dehydrogenate as the temperature increases, during which stage, the dopant will be released. When the temperature continues to rise to 400 °C, the molecular chain of PNIPAM will break and decompose [72]. This phenomenon will lead to serious weight loss in the thermogravimetric analysis curve of PNIPAM [73,74]. Furthermore, $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ has more residue than $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ at 694 °C, indicating that the $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ composite has high thermal stability.

3.14. Mechanism

Fig. 19. Trapping experiments of the photocatalytic degradation of TC by $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$.

3.14.1. Trapping experiment and ESR experiment analysis

To ascertain the active species in the degradation process, holes, $\cdot\text{O}_2^-$, and $\cdot\text{OH}$ active species were trapped by ethylenediamine tetraacetic acid disodium salt (EDTA-2Na), ascorbic acid, and isopropyl alcohol (IPA), respectively. When ascorbic acid was added, the degradation rate of TC significantly decreased (20.96%), compared to that without scavengers (88.96%) (Fig. 19). Therefore, the $\cdot\text{O}_2^-$ radicals play a major role in the degradation process. In contrast, the degradation rate (62.11%) of TC is slightly lower with the addition of IPA, indicating that the $\cdot\text{OH}$ radicals also participate in the degradation reaction. When EDTA-2Na is added, the degradation rate of TC is also significantly decreased (36.61%). Therefore, holes are also the main active species. ESR is further performed to explore the active species in a reaction. As can be seen from Fig. 19, no ESR signals are observed in the sample under dark conditions. For CN, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, and $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, the characteristic peaks of $\cdot\text{O}_2^-$ radicals are noted in Fig. 20A. Furthermore, the $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ sample displays the strongest intensities, compared to those of CN and $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$. This reveals that more $\cdot\text{O}_2^-$ radicals are produced in $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$. Concurrently, Fig. 20B reveals that the $\cdot\text{OH}$ signals of the $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ complex also exhibit a stronger

Fig. 20. ESR spectra for CN, $\text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$, and $\text{PNIPAM}@ \text{Ag}/\text{Ag}_3\text{PO}_4\text{-20}/\text{CN}$ (A) in methanol dispersion for $\text{DMPO}-\cdot\text{O}_2^-$ and (B) in aqueous dispersion for $\text{DMPO}-\cdot\text{OH}$.

intensity than those of CN and Ag/Ag₃PO₄-20/CN, indicating that the PNIPAM@Ag/Ag₃PO₄-20/CN complex has the ability to generate numerous ·OH radicals. Consequently, ·O₂⁻ and ·OH play a significant role in the photocatalytic degradation process.

3.14.2. Possible mechanism

PNIPAM, as a thermo-sensitive polymer, has the property of hydrophilic–hydrophobic reversible conversion near the LCST temperature. At low temperatures, the hydrophilicity of PNIPAM is enhanced. Moreover, its morphology changes from a shrinking agglomeration to a stretch swelling. Therefore, the Ag/Ag₃PO₄-20/CN catalyst is released and the PNIPAM@Ag/Ag₃PO₄-20/CN composite achieves temperature controllability. Moreover, the PNIPAM surface can improve the adsorption of the TC molecules. The band gaps of CN and Ag₃PO₄ are 2.62 eV and 2.38 eV, respectively, which are presented in Fig. 15B. In addition, the conduction band (CB) positions of CN and Ag₃PO₄ are detected by the Mott-Schottky technology in Fig. 21. Thus, the valence band (VB) position of CN and Ag₃PO₄ can be calculated by Eq. (5):

$$E_{VB} = E_{CB} + E_g \quad (5)$$

where E_g , E_{VB} , and E_{CB} are the band gap of the semiconductor, VB energy, and CB energy, respectively. The values of E_{CB} are -1.11 and 0.31 eV for CN and Ag₃PO₄, respectively. Therefore, the E_{VB} values of CN and Ag₃PO₄ are 1.51 and 2.69 eV, respectively. The calculated results are consistent with the result of the XPS VB spectra presented in Fig. 20. Based on the analyses of the above results, the possible mechanism of the photocata-

lytic TC degradation reaction over PNIPAM@Ag/Ag₃PO₄-20/CN is proposed in Fig. 22. When PNIPAM@Ag/Ag₃PO₄-20/CN is illuminated by visible light, CN and Ag₃PO₄ are excited and electrons are transferred from the CB to the VB. Moreover, the holes remain in the VB of CN and Ag₃PO₄. If a hole is transferred from the VB of Ag₃PO₄ to CN, it will not oxidize OH⁻ to produce ·OH. This is because the VB position of CN is 1.51 eV, which has a lower value than the standard oxidation–reduction potential of OH⁻/·OH (1.99 eV) [75]. Moreover, the electrons in the CB of Ag₃PO₄ cannot reduce O₂ to generate ·O₂⁻ because the CB potential of Ag₃PO₄ (0.31 eV) is lower than the standard redox potential of O₂/·O₂⁻ (-0.33 eV) [76]. Therefore, the Z-scheme Ag/Ag₃PO₄-20/CN heterostructure must be prepared because ·O₂⁻ and ·OH are discovered by the ESR spin-trap technique and trapping experiments. The electrons in the CB of Ag₃PO₄ and holes in the VB of CN recombine in the inner heterostructure. Therefore, the separation efficiency of the electrons and holes is increased in the CB of CN and in the VB of Ag₃PO₄. Meanwhile, Ag nanoparticles (NPs) can be used as electron transport receptors, accelerating the electron transfer from the CB of Ag₃PO₄ to the VB of CN. Meanwhile, electrons receive more energy to transfer by the LSPR effect from the Ag NPs to CN across the barrier. Further, the O₂ captures the electrons of the Ag NPs, producing ·O₂⁻ radicals. Then, the electrons in the CB of CN are trapped, resulting in the O₂ forming ·O₂⁻ radicals to oxidize TC to CO₂ and H₂O. Simultaneously, the holes in the VB of Ag₃PO₄ reduce H₂O into ·OH radicals and act on TC. Moreover, the holes can directly reduce TC, forming CO₂ and H₂O.

Fig. 21. The Mott-Schottky mechanism of (A) CN, (B) Ag₃PO₄ at various frequencies, and XPS valence band spectra of (C) CN, (D) Ag₃PO₄.

Fig. 22. Proposed mechanism of the temperature-sensitive PNIPAM@Ag/Ag₃PO₄-20/CN complex photocatalytic degradation of TC.

4. Conclusions

In summary, an intelligent controllable Z-scheme PNIPAM@Ag/Ag₃PO₄/CN heterostructure is successfully fabricated by precipitation and emulsion polymerization methods, and it has an efficient and enhanced photocatalytic activity relative to those of Ag/Ag₃PO₄/CN, CN and Ag₃PO₄. The photocatalytic degradation rate at 25 °C (88.96%) is significantly higher than that at 45 °C (56.73%). This indicates that the PNIPAM@Ag/Ag₃PO₄/CN catalyst changes from a contracted state to a relaxed state and Ag/Ag₃PO₄/CN is released when $T < LCST$. Moreover, at 25 °C, the contact angle value of the PNIPAM@Ag/Ag₃PO₄/CN surface decreases from 69.0° to 31.3°, which indicates that the composite is in a hydrophilic state. The shape of the water droplets on the surface of PNIPAM@Ag/Ag₃PO₄-20/CN hardly changes within 8 s with increasing time at 45 °C. Remarkably, the PNIPAM@Ag/Ag₃PO₄-20/CN photocatalyst exhibits the highest k value (0.0207 min⁻¹), which is 7.14 and 1.05 times that of CN (0.0029 min⁻¹) and Ag/Ag₃PO₄-20/CN (0.0198 min⁻¹), respectively. The excellent photocatalytic activity can be attributed to the Ag NPs and Z-scheme heterostructure, which enhance the separation efficiency of the charge carriers. The current work achieves controllability to the surrounding environment and creates conditions for the uncontrollability of the environment during the degradation process.

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Graphical Abstract

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Thermo-responsive functionalized PNIPAM@Ag/Ag₃PO₄/CN-heterostructure photocatalyst with switchable photocatalytic activity

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The PNIPAM@Ag/Ag₃PO₄/CN photocatalyst exhibits a response to the degradation process under ambient temperature. The Z-scheme heterostructure and plasma resonance effect of the Ag nanoparticles achieve effective separation of the electrons and holes under visible-light irradiation.

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热响应型PNIPAM@Ag/Ag₃PO₄/CN复合光催化剂的制备及性能

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摘要: 近年来, 在银盐半导体光催化剂的研究过程中, Ag₃PO₄由于具有各向同性分布、强氧化性和优异的可见光吸收能力等优点, 引起了人们的广泛关注。Ag₃PO₄在反应过程中生成的Ag纳米颗粒会产生等离子体共振效应, 对可见光驱动的光催化过程起积极作用。但是, 在催化剂制备过程中Ag₃PO₄颗粒容易发生团聚, 这限制了光催化降解过程中催化剂的反应活性。片状g-C₃N₄具有较大的比表面积, 可对Ag₃PO₄颗粒起到良好的分散作用, 并为反应提供更多活性位点。此外, g-C₃N₄与Ag₃PO₄能够形成Z-型异质结, 提高电子与空穴的分离效率。

在光催化降解污染物过程中, 周围环境对催化剂性能具有显著影响, 构建对环境具有响应性的光催化剂, 实现环境调控光解过程对于理解光催化降解机理具有重要意义。聚N-异丙基丙烯酰胺(PNIPAM)是一种温度响应型聚合物, 在LCST (32 °C)附近具有可逆的亲水性至疏水性转化。随着温度降低, PNIPAM亲水性增加, 显示出从收缩团聚到拉伸溶胀状态的变化。PNIPAM还可以用作保护层包裹在Ag₃PO₄颗粒表面, 防止Ag₃PO₄颗粒在反应过程的损失。

本文采用沉淀法和乳液聚合合法合成了热响应型PNIPAM@Ag/Ag₃PO₄/CN复合光催化剂, 并以20 mg·L⁻¹四环素(TC)作为目标污染物探究其对温度可逆转换的光催化性能。通过X射线衍射(XRD)、X射线光电子能谱(XPS)、扫描电镜(SEM)、透射电镜(TEM)、荧光(PL)、接触角测试等一系列表征对该催化剂的结构特征、微观形貌、光学性能和亲疏水性进行了分析。由XRD可知, Ag/Ag₃PO₄/CN复合物和PNIPAM@Ag/Ag₃PO₄/CN具有相同的衍射峰强度和位置, 表明PNIPAM未影响Ag/Ag₃PO₄/CN复合物的晶型结构。XPS结果表明, 复合材料含有Ag, P, O, C和N。由SEM和TEM可知, PNIPAM已将Ag/Ag₃PO₄/CN复合物成功包裹。接触角测试表明, PNIPAM@Ag/Ag₃PO₄/CN在25 °C表现出亲水性, 在45 °C呈现疏水性。光催化性能测试结果进一步表明, PNIPAM@Ag/Ag₃PO₄/CN实现了在不同温度下的光催化可逆转换性能: 25 °C时照射120 min, TC降解效率可达88.96%; 45 °C时照射120 min, TC降解效率是56.73%。此外, 对催化剂进行了循环实验, 经过4次循环后催化剂仍具有优异的光催化降解性能, 表明所制备的催化剂具有良好的稳定性。

为了进一步研究PNIPAM@Ag/Ag₃PO₄/CN光催化剂的光催化机理, 用抗坏血酸、乙二醇四乙酸和异丙醇进行了自由基捕获实验。结果表明, 超氧自由基和羟基自由基在降解TC过程中起主要作用。通过价带谱测试和带隙计算出材料的价带位置, 计算出的导带位置与莫特肖基曲线测试结果一致。最后, 对可能的机理进行了分析。总之, PNIPAM@Ag/Ag₃PO₄/CN光催化剂不仅实现了对降解过程不同温度的响应性, 还可防止Ag₃PO₄颗粒团聚和光腐蚀, 提高了电子-空穴对的传输速率。这为环境响应型复合光催化剂的制备提供了一种策略。

关键词: 智能响应性; 片状g-C₃N₄; Ag₃PO₄; Ag; 聚N-异丙基丙烯酰胺

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