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Article

Decorating Ag/AgCl on UiO-66-NH₂: Synergy between Ag plasmons and heterostructure for the realization of efficient visible light photocatalysis

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ABSTRACT

UiO-66-NH₂, as typical visible light responsive Zr-based metal-organic frameworks (MOFs), has attracted great interest in recent years. However, rapid combination of the photoinduced carriers limits its further application. Here, we designed a facile precipitation-photoinduced method to post-synthetically decorate Ag/AgCl on the surface of UiO-66-NH₂ and form a heterostructure. Metallic Ag can not only transmit electrons between UiO-66-NH₂ and AgCl but also absorb visible light, because of the surface plasmon resonance (SPR) effect. The rhodamine B photodegradation rate of UiO-66-NH₂/Ag/AgCl (16.2 wt.% Ag) is about 10 and 4 times those of UiO-66-NH₂ and Ag/AgCl, respectively. The SPR effect of Ag NPs and the formation of a heterostructure synergistically increase the absorbability of visible light, accelerate the separation of photoinduced charges, and promote the formation of superoxide radicals. We expect that our work could provide a new viewpoint for constructing efficient MOF-based photocatalytic systems.

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1. Introduction

With rapid industrial development and consumption of fossil fuels, environmental pollution has become an overwhelming problem all over the world [1,2]. Synthetic dyes are widely used in tanning, plastics, paints, cosmetics, and textile industries [3–5]. Dye residues in wastewater can cause serious environment pollution, even at low concentrations [6,7]. Hence, it is essential to degrade dye residues into non-hazardous products [8,9]. In this context, photodegradation, which utilizes the inexhaustible solar energy to decompose dyes, is efficient and environmentally friendly [10,11]. Many kinds of heterojunction photocatalysts have been reported to exhibit high activities in

various fields of photocatalysis [12–16], but the low solar energy conversion efficiency limits their further application [17–19]. Up to now, developing efficient photocatalysts with a high visible light response has been a great challenge for researchers.

Metal-organic frameworks (MOFs), composed of metal-oxo clusters and organic linkers, have received increasing attention in recent years [20]. Because of their large surface areas, well-ordered porous structures, and tunable organic linkers or metal clusters [21], they have been applied in numerous fields [22–25]. In recent years, several kinds of MOFs have been proved to behave as semiconductors for the photodegradation of dyes [26–28]. Exploring MOFs as novel photocatalysts has

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attracted the attention of researchers [29,30]; the organic linkers of MOFs can act as antennas to harvest light and subsequently activate the metal sites via ligand-to-metal cluster charge transitions [31]. UiO-66 is a typical water-tolerant Zr-containing MOF that can only absorb ultraviolet (UV) light because of the large band gap, which greatly reduces the utilization of solar energy. The band gap energy of UiO-66 can be partly changed by substituting the organic linkers with amino group (UiO-66-NH₂) [32]. The photoabsorption edge of UiO-66-NH₂ shifts from the UV to the visible light region. The insufficient light absorbability and short lifetimes of carriers limit the practicability of UiO-66-NH₂ under solar irradiation [33]. Many strategies have therefore been used to modify UiO-66-NH₂, such as loading with metal nanoparticles, combining with semiconductors, and decorating with organic linkers or metal centers [33].

Recently, as a representative of significant plasmonic photocatalysts, Ag/AgCl composites have attracted great interest because of their strong absorption in the visible light region, which results from the surface plasmon resonance (SPR) effect of Ag [34–37]. Combining other semiconductors with Ag/AgCl is a common method to take advantage of the Ag SPR effect; examples include Ag@AgCl/BiVO₄ [38], Ag/AgCl/SrTiO₃ [39], Ag/AgCl/TiO₂ [40], and WO₃/Ag/AgCl [41]. The combination of Ag/AgCl and MOFs is a possible way to overcome the drawbacks of the latter in photocatalysis, but, presently, few reports exist in this subject, and, especially, the visible light photocatalytic performance need to be improved [42,43].

In this study, we synthesized UiO-66-NH₂/Ag/AgCl catalysts by post-synthetic modification to construct novel visible light responsive heterostructure photocatalysts with Ag SPR effect. The photocatalytic activity of the UiO-66-NH₂/Ag/AgCl composite was investigated by degrading a rhodamine B (RhB) solution under visible light. The formed UiO-66-NH₂/Ag/AgCl composites improve the absorption ability of visible light and the separation efficiency of the light-generated carriers. The UiO-66-NH₂/Ag/AgCl samples display significantly improved photodegradation activity and good stability. In particular, UiO-66-NH₂/Ag/AgCl with 16.2% Ag loading displays the highest degradation rate, which is about 10 times and 4 times those of pristine UiO-66-NH₂ and Ag/AgCl, respectively. We discover that the synergy between the Ag SPR and the heterostructure is the main reason for the highly improved activity. Moreover, we clarify the migration path of the photoinduced charges and the main reactive species in RhB photodegradation.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. UiO-66

UiO-66 was prepared by a modified method [44]. 0.167 g ZrCl₄, 0.125 g terephthalic acid (H₂BDC), and 3.5 mL acetic acid were dissolved in 50 mL *N,N*-Dimethylformamide (DMF) in a 100 mL glass beaker while stirring. Then, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and placed in an oven at 120 °C for a day. The resulting UiO-66

sample was collected, washed three times with DMF, and immersed in methanol for 3 d; the methanol was replaced every 24 h. Finally, UiO-66 was activated by removing the solvent under vacuum for 12 h at 60 °C.

2.1.2. UiO-66-NH₂

UiO-66-NH₂ was synthesized by using a modified method [45]. In a typical process, 0.0811 g ZrCl₄ (0.348 mmol) and 0.0471 g 2-aminoterephthalate acid (0.26 mmol) were ultrasonically dissolved in 60 mL DMF in a 100 mL glass beaker. Then, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. After cooling to room temperature naturally, the sample was collected by centrifugation and then washed with DMF and methanol three times. Finally, the sample was dried at 60 °C for 12 h under vacuum.

2.1.3. UiO-66-NH₂/Ag/AgCl

UiO-66-NH₂/Ag/AgCl composites were synthesized via a facile ultrasound-assisted precipitation-photoreduction method. 0.2 g UiO-66-NH₂ was added to 100 mL deionized water, and the resulting mixture was ultrasonicated for 0.5 h. Then, a certain amount of 0.1 mol/L AgNO₃ solution (1.0, 2.0, 3.0, and 4.0 mL) was added dropwise to the suspension with mechanical stirring. After stirring for 10 min, the resulting mixture was ultrasonicated for 20 min. Subsequently, an excess amount of 0.10 mol/L HCl solution was added to the mixture under stirring. After stirring for another 10 min in darkness, the above mixture was irradiated with an UV lamp for 0.5 h, and a fraction of the Ag⁺ on AgCl/UiO-66-NH₂ was reduced to Ag⁰. The sample was filtrated and washed with deionized water three times. Finally, the powder was dried under vacuum at 60 °C for 12 h. The amount of the AgNO₃ solution was 1.0 mL, and the mass ratio of Ag to UiO-66-NH₂ was 5.4%; we named this composite UiO-66-NH₂/Ag/AgCl (5.4 wt.%), which was abbreviated as UAA-5.4. Similarly, the other three samples with 10.8 wt.%, 16.2 wt.%, and 21.6 wt.% Ag loadings were named UAA-10.8, UAA-16.2, and UAA-21.6, respectively. The Ag/AgCl sample was synthesized by the same method as described above, but without the addition of UiO-66-NH₂ powder.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Focus diffractometer using Cu K_α as the radiation source ($\lambda = 1.5418 \text{ \AA}$) at a scanning speed of 5°/min and 2 θ range 5°–80°. All the UiO-66-NH₂/Ag/AgCl samples were investigated at a scanning speed of 0.5°/min in the 2 θ range 37.5°–39.5°.

The scanning electron microscopy (SEM) images of the samples were obtained by using a SIGMA HD scanning electron microscope. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the samples were obtained by using a JEOL Model JEM-2100 F electron microscope.

The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples were recorded on a PerkinElmer Lambda

750S UV-vis spectrophotometer equipped with an integrating sphere.

X-ray photoelectron spectroscopy (XPS) was carried out on a PHI-1600 ESCA spectrometer using Mg $K\alpha$ ($h\nu = 1253.6$ eV) excitation source. The binding energies were calibrated by using the C 1s peak at 284.6 eV.

Photoluminescence (PL) measurements were conducted by using a Horiba Jobin Yvon Fluorolog PL spectrometer with an excitation wavelength of 400 nm at room temperature.

The transient-state fluorescence spectra were recorded on a Fluorolog-3 fluorescence spectrometer that was monitored at 460 nm and excited at 400 nm.

Total organic carbon (TOC) analysis was performed on a Shimadzu TOC-VCPH analyzer.

2.3. Photoelectrochemical measurements

Photoelectrochemical analysis was performed by using a CHI 6043E electrochemistry work station (Chenhua Instrument) that employed the standard three-electrode system: Ag/AgCl acted as the reference electrode, Pt foil acted as the counter electrode, and 0.5 mol/L Na_2SO_4 aqueous solution served as the electrolyte. A 300 W Xe lamp (Ceaulight) coupled with an AM 1.5 G solar power system (Ceaulight) was used as the light source. The samples were painted on photoanodes by drop-coating method. In a typical process, 4 mg of the sample was dispersed in 500 μL aqueous ethanol solution (100 μL ethanol and 400 μL deionized water), and 3 μL Naflon was added to the above solution, before it was ultrasonically treated to form a homogeneous suspension. Furthermore, the working electrodes were obtained by dropping 40 μL of the above suspension onto 1 cm^2 of F-doped tin oxide glass; afterward, the electrodes were dried at room temperature for 12 h. Chronoamperometry tests were performed at 0.8 V. The transient photocurrent responses of the samples were obtained under inconsecutive irradiation at 0.8 V. Electrochemical impedance spectroscopy (EIS) was performed at the open-circuit potential in the frequency range 0.01 to 10^5 Hz. Mott-Schottky plots were collected at a frequency of 1000 Hz with a bias potential that ranged from 1.0 to -1.0 V (vs. Ag/AgCl).

2.4. Photocatalytic activity

The photocatalytic activities of all the samples were evaluated for the degradation of RhB, which is a representative model of dye degradation. In all the experiments, a 300 W Xe lamp with a 400 nm cutoff filter was used as the light source. 100 mL RhB (5 mg/L) and 40 mg photocatalyst were added to a photoreactor. Before light irradiation, the above suspension was stirred in total darkness for 0.5 h to realize absorption and desorption equilibrium between the photocatalyst and RhB. 4 mL of the suspension was sampled every 10 min and the retained powder was removed by centrifugation. Then, a liquid supernatant was used to measure the concentration of RhB through UV-vis spectrophotometry at 553 nm.

2.5. Reactive species trapping experiments

Reactive species trapping experiments were performed by adding different scavengers. The entire scavenger is 0.01 mol/L RhB solution, and the other conditions were consistent with those of the photocatalytic activity experiments. Ammonium oxalate (AO) is a photoinduced hole (h^+) scavenger, *p*-benzoquinone (BZQ) is a superoxide radical ($\bullet\text{O}_2^-$) scavenger, and *tert*-butyl alcohol (TBA) is a hydroxyl radical ($\bullet\text{OH}$) scavenger.

3. Results and discussion

3.1. Morphology and physical properties

Fig. 1a shows the XRD patterns of the samples. The locations of the diffraction peaks of UiO-66 and UiO-66-NH₂ are in agreement with those reported in the literature [46,47], which suggests that we successfully synthesized the skeleton of UiO-66. For Ag/AgCl, the diffraction peaks located at 27.83°, 32.24°, 46.23°, 54.83°, and 57.48° correspond to the (111), (200), (220), (311), and (222) planes of AgCl (JCPDS no. 31-1238), respectively. In Fig. 1b, the peak located at 38.3° is assigned to the (111) crystal plane of metallic Ag (JCPDS no. 04-0783). All the UiO-66-NH₂/Ag/AgCl samples contain both the UiO-66-NH₂ and Ag/AgCl phases. However, the intensities of the diffraction peaks of UiO-66-NH₂ in the UiO-66-NH₂/Ag/AgCl samples decrease, compared with those of pure UiO-66-NH₂. This is possibly due to the coverage of Ag/AgCl on the surface of the UiO-66-NH₂ particles, which affects the crystallinity of the substrate. The XRD results indicate that Ag/AgCl is formed and successfully loaded onto the UiO-66-NH₂ surface without changing the cage construction of the MOFs.

Fig. 2a–c display the SEM images of UiO-66, UiO-66-NH₂, and UAA-16.2. All of them exhibit an octahedral shape. The average diameter of the UiO-66 particles is about 300 nm, whereas the average diameters of the UiO-66-NH₂ and UiO-66-NH₂/Ag/AgCl nanocrystals are about 100 nm. We can clearly observe that pristine UiO-66 and UiO-66-NH₂ crystals have a smooth surface and sharp edges, whereas UAA-16.2 displays a relatively rough

Fig. 1. (a) XRD patterns and (b) magnified patterns of the $2\theta = 38^\circ$ – 39° region of the different samples, obtained at a low scanning velocity.

Fig. 2. SEM images of (a) UiO-66, (b) UiO-66-NH₂, and (c) UAA-16.2, and (d) elemental mapping images of UAA-16.2.

surface and obtuse edges because of the coverage of Ag/AgCl NPs on them. Fig. 2d shows the elemental mapping image of UAA-16.2. It confirms the successful deposition of Ag and Cl elements on the surface of UiO-66-NH₂.

Fig. 3a and 3b show the TEM images of UiO-66 and UiO-66-NH₂, respectively. The morphologies of UiO-66 and UiO-66-NH₂ are octahedral, which agrees with the SEM results. Fig. 3c and 3d show the TEM and HRTEM images of UAA-16.2, respectively. After loading with Ag/AgCl, the morphology became indistinct, and particles were observed on the surface of UiO-66-NH₂. From Fig. 3d, we determine lattice spacings of 0.320 and 0.236 nm, which correspond to the (111) plane of AgCl and (111) plane of Ag, respectively. These findings also confirm the formation of a heterostructure and the existence of Ag/AgCl on UAA-16.2. By combining the XRD, SEM, and TEM results, we demonstrate the successful construction of

Fig. 3. TEM images of (a) UiO-66, (b) UiO-66-NH₂, and (c) UAA-16.2, and (d) HRTEM image of UAA-16.2.

UiO-66-NH₂/Ag/AgCl composites without destroying the structures of the MOFs.

Fig. 4a–d present the XPS patterns of the as-prepared samples. Fig. 4a displays the survey XPS patterns of UiO-66, UiO-66-NH₂, and UAA-16.2, which confirm that the main ingredient elements are Zr, Ag, O, C, and Cl. Fig. 4b shows the Zr 3d spectra of UiO-66, UiO-66-NH₂, and UAA-16.2. The Zr 3d binding energy (B.E.) spectra contain two peaks at 183.0 and 185.4 eV, which are ascribed to Zr 3d_{5/2} and Zr 3d_{3/2}, respectively [48]. Fig. 4c shows the Cl 2p spectra of UAA-16.2. The B.E. peaks at 198.3 and 200.4 eV are assigned to Cl 2p_{3/2} and Cl 2p_{1/2}, respectively, and are close to those of Cl[−] [49]. Fig. 4d presents the Ag 3d spectra of the UiO-66-NH₂/Ag/AgCl catalysts. The B.E. peaks at 368.1 and 374.2 eV are consistent with the binding energies of Ag 3d_{5/2} and Ag 3d_{3/2}. Furthermore, the spectra can be divided into two groups at about 367.9/373.9 eV and 368.9/374.8 eV, which correspond to Ag⁺ and Ag⁰, respectively [50]. The XPS results of Ag 3d and Cl 2p reveal the existence of Ag nanoparticles and the fabrication of the Ag/AgCl structure, which are in line with the XRD, SEM, and TEM results. In addition, based on the peak areas of Ag⁰ and Ag⁺ obtained from Fig. 4d, we calculated the mass percentages of Ag⁰ in UiO-66-NH₂/Ag/AgCl, which are listed in Table 1. Apparently, the amount of metallic Ag NPs kept increasing with the addition of Ag.

3.2. Optical properties and band structures

Fig. 5a shows the UV-vis DRS of the samples. UiO-66 exhibits a distinct absorption edge at about 350 nm. It suggests that UiO-66 can only absorb UV light. UiO-66-NH₂ shows an absorption edge at 440 nm, which indicates that amino modification leads to a shift in the absorption wavelength of UiO-66 [32,33]. Compared with that of pristine UiO-66-NH₂, the UiO-66-NH₂/Ag/AgCl samples display stronger absorbances across the entire visible light region (400–800 nm). In addition, the absorption intensity improves in the visible light region as the Ag content increases. The absorption intensity of the UiO-66-NH₂/Ag/AgCl composites improves remarkably, which is attributed to the existence of Ag/AgCl NPs. We amplified the UV-vis DRS of the UiO-66-NH₂/Ag/AgCl samples in the region 400–500 nm (Fig. 5b) and observed that they exhibited an absorption peak at about 425 nm. It can be ascribed to the SPR effect of the metallic Ag NPs present in the samples [51]. According to Kubelka-Munk band gap estimation theory [52], we calculated the band gap energies (E_g) of the samples. Fig. 5c presents the E_g of UiO-66, UiO-66-NH₂, and UAA-16.2. UiO-66 has a wide band gap of approximately 3.83 eV, which is similar to that reported previously [53]. Compared with that of UiO-66, the E_g of UiO-66-NH₂ (2.85 eV) greatly decreases [54]. The decrease in the E_g is associated with the decoration of the amino substituent and nonbonding oxygen near the metalloid cluster [55]. The E_g of UAA-16.2 is about 2.82 eV, and the other UiO-66-NH₂/Ag/AgCl samples display similar E_g values (Fig. S1). Therefore, we conclude that Ag/AgCl mainly improves the absorption intensity, rather than changing the position of the absorption edges.

Fig. 4. (a) Survey, (b) Zr 3d, (c) Cl 2p, and (d) Ag 3d XPS spectra of the samples.

Fig. 5d shows the VB XPS patterns of UiO-66, UiO-66-NH₂, and UAA-16.2. Comparing with the pattern of UiO-66, the relative positions of the valence bands obviously shift in the direction of lower energy for UiO-66-NH₂ and UAA-16.2, due to the amino modification. Fig. S2 displays the Mott-Schottky plot of UiO-66-NH₂. Clearly, the UiO-66-NH₂ sample is an n-type semiconductor with a positive slope. The flat band potential (E_{fb}) is determined to be -0.70 V (vs. Ag/AgCl). The E_{fb} we measured was converted to the normal hydrogen electrode (NHE) potential through the following equation [12]:

$$E_{fb}(\text{vs. NHE}) = E_{fb}(\text{pH}=0, \text{vs. Ag/AgCl}) + E_{AgCl} + 0.059 \times \text{pH} \quad (1)$$

where E_{AgCl} is 0.197 V and the pH value is approximately 6.8 .

Table 1

Relative peak areas of Ag⁰ and Ag⁺ and mass percentages of Ag⁰.

Sample	Peak area of Ag ⁺	Peak area of Ag ⁰	Ag ⁰ /Ag (%)	Ag ⁰ /sample (wt.%)
UAA-5.4	3087.4	2058.3	40.0	2.2
UAA-10.8	4977.8	1783.4	26.4	2.9
UAA-16.2	8408.3	2980.9	26.2	4.2
UAA-21.6	8696.5	3672.4	29.7	6.4

Therefore, the E_{fb} (vs. NHE) of UiO-66-NH₂ is -0.10 V. Since UiO-66-NH₂ is an n-type semiconductor, its E_{fb} (vs. NHE) is 0.3 V below the conduction band (CB) energy level, which is considered to be -0.4 V. According to the equation the VB energy level of UiO-66-NH₂ should be 2.46 V.

$$E_{VB} = E_{CB} + E_g \quad (2)$$

3.3. Photocatalytic performance

Fig. 6a shows the photocatalytic activities of the samples. The photocatalytic properties of the samples were evaluated by degrading the RhB aqueous solution under visible light irradiation. Fig. S3 reveals that UAA-16.2 barely degraded RhB in the absence of visible light irradiation. It indicates that the degradation process is light-driven, and not adsorption-driven. Fig. 6b displays the peak intensities corresponding to the UV-vis light absorption related to RhB degradation for different visible light exposure durations. The main absorption peak at 553 nm keeps decreasing in intensity until it disappears, and no new absorption peaks appear, which indicates that RhB has indeed degraded.

Fig. 5. (a) Full UV-vis DRS and (b) UV-vis DRS corresponding to the range 400–500 nm; (c) Kubelka-Munk transformed UV-vis DRS and (d) valence band (VB) XPS spectra of the samples.

In Fig. 6a, pristine UiO-66, UiO-66-NH₂, and Ag/AgCl reveal low photocatalytic activities toward the degradation of RhB. The UiO-66-NH₂/Ag/AgCl samples exhibit higher photocatalytic activities than the pristine samples, which should be attributed to the formation of heterostructures. With increasing Ag content, the photocatalytic activities of the UiO-66-NH₂/Ag/AgCl samples reveal volcano-type variations. UAA-16.2 exhibits the highest photocatalytic efficiency, and 99% of RhB (100 mL, 5 mg/L) is degraded within 50 min. UAA-21.6 displays a lower photocatalytic efficiency than UAA-16.2, probably because a large amount of the Ag/AgCl particles agglomerate on the surface of UiO-66-NH₂ (Fig. S4). In Fig. S4, it is obvious that the Ag/AgCl particles are more highly dispersed on UAA-16.2 than on UAA-21.6. The low dispersion of Ag/AgCl on the surface of UiO-66-NH₂ results in weak interaction between the substrate and Ag/AgCl, which is undesirable for the formation of a heterostructure [56]. It lowers the separation efficiency of the photoinduced carriers, and subsequently decreases the photocatalytic activity of UAA-21.6. Therefore, the appropriate content and dispersion of Ag/AgCl result in effective synergy between the Ag SPR and the heterostructure, which greatly improves the photocatalytic activities of the UiO-66-NH₂/Ag/AgCl samples. Comparing with the results obtained from previous reports (Table S1), we find that the photocatalytic performances obtained in this study are superior under similar reaction conditions. To identify the degree of mineralization of RhB, we performed TOC analysis of the RhB solution for different periods of visible light irradiation, and the results are shown in Fig. S5. It

is obvious that the TOC value decreases gradually, and the removal efficiency of TOC is about 37% after 4 h of visible light irradiation. It takes longer for UiO-66-NH₂/Ag/AgCl to photodegrade RhB to inorganic substances, because the mineralization of RhB involves several steps and decoloration is only one of them. If the irradiation time is sufficient, UiO-66-NH₂/Ag/AgCl can photodegrade RhB completely.

In order to understand the reaction kinetics of the photodegradation process, in Fig. 6c, we calculated the kinetic plots based on the pseudo-first-order model:

$$\ln(C_0/C) = k_{app} t \quad (3)$$

in which C_0 is the original concentration of RhB (mg/L), C is the RhB concentration at different reaction times (mg/L), k_{app} is the apparent reaction rate constant, and t is the reaction time. As shown in Fig. 6c, there is a good linear correlation between $\ln(C_0/C)$ and the reaction time, which indicates that the degradation of RhB follows first-order kinetics. The trend of k_{app} in Fig. 6c is consistent with that of the photocatalytic activity (Fig. 6a). Among the samples, UAA-16.2 exhibits the largest k_{app} value of 0.045 min⁻¹, which is about 10 times that of UiO-66-NH₂ and 4 times that of Ag/AgCl (Table S2). In order to evaluate the recyclability and stability of the photocatalysts, the photodegradation of RhB over UAA-16.2 was repeated three times, as shown in Fig. 6d. The photocatalytic degradation rate was maintained at a high value after the three cycles. The slight decrease could be attributed to mass loss of the sample during the recycling processes. Furthermore, the XRD patterns of the fresh and used UAA-16.2 are displayed in Fig. S6. The used

Fig. 6. (a) Photocatalytic degradation of RhB over the samples under visible light irradiation; (b) Time-dependent UV-vis absorption spectra for the degradation of RhB over UAA-16.2; (c) Kinetic data corresponding to the equation $\ln(C_0/C) = k_{app} t$; (d) RhB photodegradation stability of UAA-16.2.

UAA-16.2 displays a similar XRD pattern as the fresh UAA-16.2, which proves that Ag/AgCl is stable in the composite UiO-66-NH₂/Ag/AgCl. Both the stability and XRD results indicate that the UiO-66-NH₂/Ag/AgCl samples exhibit high photocatalytic efficiency and good stability, which are helpful for their further applications.

3.4. Photoelectronic performance and charge carrier separation

Fig. 7a and 7b show the photoelectrochemical results of the samples. The increased photocurrent densities indicate the improved electrical conductivities of the photocatalysts [57]. As displayed in Fig. 7a, the UiO-66-NH₂/Ag/AgCl samples exhibit higher photocurrent densities than pristine UiO-66 and UiO-66-NH₂. It is in agreement with the results of RhB photodegradation presented in Fig. 6a. Fig. 7b displays the EIS results that were used to study the electrochemical behavior of the semiconductors, especially the charge separation efficiencies [58]. The UiO-66-NH₂/Ag/AgCl samples reveal smaller arcs in the Nyquist plots, compared to those of UiO-66 and UiO-66-NH₂, which suggests that the former exhibits lower charge-transfer resistances and more efficient charge separation. UAA-16.2 displays the smallest arc radius, which is indicative of its strongest resistance to charge recombination. Furthermore, the EIS results are in line with those obtained for RhB photodegradation.

Fig. 8 displays the PL emission spectra of the samples ob-

tained at the excitation wavelength of 400 nm. We reduced the peak intensity of UiO-66-NH₂ by one-third to see the results more clearly. The PL emission spectra have been widely used to investigate the efficiencies of trapping, migration, and transfer of the charge carriers of semiconductor materials [59]. The UiO-66-NH₂/Ag/AgCl samples exhibit remarkably weakened PL emission spectra, compared with that of UiO-66-NH₂, which indicates that the existence of Ag/AgCl can effectively inhibit the recombination of the photoinduced electrons and holes. UAA-16.2 reveals the lowest PL intensity, which suggests that its efficiency of separation of the photoinduced carriers is the highest among the samples. Generally, the lower the PL intensity, the higher is the efficiency of separation of the photoinduced carriers and the better is the photocatalytic activity of the sample [60]. The PL intensity results are in accordance with the photocatalytic degradation performances observed in Fig. 6a.

We also measured the lifetimes of the excited charge carriers in UiO-66-NH₂ and UAA-16.2, and the PL decay curves are shown in Fig. S7. The lifetimes of UiO-66-NH₂ and UAA-16.2 were calculated by fitting the transient-state fluorescence decay curves, and the results are displayed in Table S3. The average lifetimes of UiO-66-NH₂ and UAA-16.2 are 1.18 and 0.90 ns, respectively. The shorter lifetime in UAA-16.2 suggests that the photoinduced electrons transfer faster from UiO-66-NH₂ to Ag/AgCl, compared with the case of UiO-66-NH₂. The fast transfer suppresses the recombination of electron-hole pairs and improves the photocatalytic activity.

Fig. 7. (a) Transient photocurrent responses and (b) EIS Nyquist plots of the samples, obtained under visible light irradiation.

According to the photoelectronic performance and transient-state fluorescence results, the photoinduced electrons in UAA-16.2 can transfer fast. The PL results prove that the recombination of the photoinduced electrons and holes in UAA-16.2 is effectively suppressed. Therefore, the photoinduced electrons and holes can be separated efficiently.

3.5. Proposed mechanism and discussion

Fig. 8. PL emission spectra of the samples.

To better understand the mechanism of the photocatalytic degradation, we designed reactive species trapping experiments by using different scavengers to identify the main reactive species. BZQ, AO, and TBA are scavengers of $\bullet\text{O}_2^-$, h^+ , and $\bullet\text{OH}$, respectively. In Fig. 9a, the addition of BZQ and AO lowers the photocatalytic activity, with the sequence being BZQ > AO. On the other hand, addition of TBA has little influence on the photocatalytic activity. Thus, we propose that $\bullet\text{O}_2^-$ is the main reactive species, while $\bullet\text{OH}$ has little impact on the reaction. In order to confirm the migration path of the photoinduced electrons, we loaded Pt onto UAA-16.2 by photodeposition. Fig. 9b displays the HRTEM image of the Pt-loaded UAA-16.2 sample. We observed that almost all the Pt NPs attached to AgCl in Fig. 9b and Fig. S8, indicating that the photoinduced electrons are enriched on AgCl. As a result, the enriched electrons on AgCl can react with O₂ to form $\bullet\text{O}_2^-$, which is the main reactive species in the photocatalytic degradation.

Under visible light irradiation, the photoinduced electrons and holes of pure UiO-66-NH₂ rapidly recombine (Fig. 7 and 8), which significantly decreases its photocatalytic activity (Fig. 6a). The CB and VB energy levels of AgCl are about -0.06 and 3.20 eV (vs. NHE), respectively [51]. AgCl cannot be excited by visible light because of the large band gap (about 3.26 eV).

Fig. 9. (a) Results of trapping experiments of the reactive species during the photocatalytic reaction, and (b) HRTEM image of Pt-loaded UAA-16.2.

Fig. 10. Schematic illustration of UiO-66-NH₂/Ag/AgCl and the proposed mechanism of RhB photodegradation over UiO-66-NH₂/Ag/AgCl under visible light irradiation.

On the basis of the characterization results and the photocatalytic activity data, we propose a reasonable mechanism in Fig. 10 for RhB photodegradation over the UiO-66-NH₂/Ag/AgCl samples. The formed UiO-66-NH₂/Ag/AgCl heterostructure generates a large amount of interfaces at the location where they contact, which provides plenty of active sites for dye degradation. Moreover, the Ag NPs formed on the surface of AgCl/UiO-66-NH₂ significantly enhance the absorption of visible light because of the SPR effect. The synergy between the heterostructure and the Ag SPR greatly improves the photocatalytic activity.

In the UiO-66-NH₂/Ag/AgCl system, UiO-66-NH₂ absorbs visible light and generates photoinduced electrons and holes. The Ag NPs not only behave as an electron mediator but also can be excited by visible light to generate electrons and holes because of the SPR effect. A large number of electrons will be stored in the lowest unoccupied orbital of Ag, which then increases its Fermi energy level [61,62]. The additional photoinduced electrons will transfer to the CB of AgCl to equilibrate the Fermi energy level of Ag. Thereafter, a relatively high concentration of electrons is observed on the surface of AgCl, which then migrate to the photocatalyst surface to react with O₂ in the RhB solution to form •O₂⁻ ((O₂/•O₂⁻) = -0.04 eV vs. NHE). The Ag SPR effect promotes the formation of •O₂⁻, according to the reactive species trapping experiments. The generated •O₂⁻ species will then oxidize organic pollutants like RhB. Moreover, the aggregation of electrons on the CB of AgCl makes it an electron-rich region, which can protect the AgCl from photooxidation. Meanwhile, the photoinduced electrons in the CB of UiO-66-NH₂ transfer to the Ag NPs to recombine with the photoinduced holes generated by the Ag SPR effect. Additionally, the photoinduced holes of UiO-66-NH₂ remaining in the VB can also oxidize organic pollutants.

The synergy between the Ag SPR and the heterostructure for the UiO-66-NH₂/Ag/AgCl system greatly promotes the separation of photoinduced charges and the ability to absorb visible light, and thus overcomes the disadvantages of pristine UiO-66-NH₂ and Ag/AgCl. Accordingly, this system exhibits a significantly improved photocatalytic activity.

4. Conclusions

We successfully constructed a visible light responsive UiO-66-NH₂/Ag/AgCl heterostructure by a precipitation-photoreduction method. The UiO-66-NH₂/Ag/AgCl heterostructure exhibits a significantly higher photocatalytic activity for the degradation of aqueous RhB solution under visible light irradiation than pristine UiO-66-NH₂ and Ag/AgCl. The formation of the heterostructure can greatly suppress the recombination of the photoinduced carriers, which increases the number of carriers exhibiting strong redox ability. The Ag NPs in the heterostructure system not only behave as an electron mediator but also absorb visible light because of SPR effect. In the UiO-66-NH₂/Ag/AgCl system, a relatively high amount of •O₂⁻ is formed due to the electrons generated by the Ag SPR, which improves the photocatalytic activity. The significantly improved photocatalytic activity should be ascribed to the synergy between the heterostructure and the Ag SPR. The synthesized photocatalysts also exhibit good stability and recyclability in the photodegradation process of RhB. We expect that the UiO-66-NH₂/Ag/AgCl photocatalysts can offer a viewpoint for understanding the migration of charge carriers and provide new ideas for the design of novel post-synthetic modified MOF photocatalysts.

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Graphical Abstract

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Decorating Ag/AgCl on UiO-66-NH₂: Synergy between Ag plasmons and heterostructure for the realization of efficient visible light photocatalysis

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Ag/AgCl plasmons were decorated on UiO-66-NH₂ to enhance the visible light absorbability, and the heterostructure suppresses the rapid recombination of the photoinduced carriers. The synergy between the heterostructure and the Ag plasmons greatly improves the visible light photocatalytic activity.

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UiO-66-NH₂表面修饰Ag/AgCl: 利用等离子态银和异质结的协同作用实现高效可见光催化

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摘要: 人工合成染料广泛应用于制革、涂料、化妆品等行业, 是工业废水中的常见污染物。染料残留物即使浓度较低也可以对环境和生物造成严重危害, 因此在排放前将工业废水中的染料降解为无毒无害物质十分必要。光催化为降解有机污染物提供了一个利用太阳能且无二次污染的途径。UiO-66-NH₂是具有可见光吸收性能的金属-有机骨架化合物(MOFs), 近年来引起了光催化领域研究人员的广泛关注。但吸光能力不足和载流子的快速复合限制了它在光催化领域的进一步应用。

本文通过沉淀-光沉积法制备了一系列不同银含量的UiO-66-NH₂/Ag/AgCl复合物, 通过XRD、SEM、TEM及XPS等手段对该体系进行了表征。结果表明, UiO-66-NH₂表面成功负载了Ag/AgCl, 形成了异质结, 并且没有改变MOFs的骨架结构。UV-vis结果表明, UiO-66-NH₂/Ag/AgCl结构中的Ag具有表面等离子体共振效应(SPR)。随后, 通过在可见光条件下降解罗丹明B测试了UiO-66-NH₂/Ag/AgCl系列样品的光催化性能, 其中Ag含量为16.2 wt.%的UiO-66-NH₂/Ag/AgCl表现出最高的光降解速率, 分别是UiO-66-NH₂和Ag/AgCl的10倍和4倍。我们认为, Ag的SPR效应增强了复合物吸收可见光的能力, 异质结的形成加速了光生电子和空穴的分离, 二者的协同作用极大地提高了光降解活性。通过活性物种俘获实验确定了在该体系的光降解反应过程中超氧自由基($\cdot\text{O}_2^-$)是主要活性物种。此外, 通过对电子传输路径的研究, 结果发现Ag的SPR效应加剧了光生电子的产生, 有利于 $\cdot\text{O}_2^-$ 的形成。实验还发现含有过量Ag的UiO-66-NH₂/Ag/AgCl样品的光降解效率有一定程度的下降, 通过对样品形貌的考察, 推测过量Ag会造成Ag/AgCl颗粒团聚, 降低UiO-66-NH₂和Ag/AgCl之间的作用力, 不利于异质结的形成, 进而影响光降解活性。

总之, 本文通过UiO-66-NH₂与Ag/AgCl的结合, 克服了其各自的缺陷, 提升了可见光吸收能力和载流子分离效率, 大幅度改善了光降解性能, 并且对该体系的反应机理做了一定程度的研究。希望本研究可以为MOFs材料光催化体系的构建提供有价值的参考。

关键词: UiO-66-NH₂; Ag/AgCl; 异质结; 可见光催化; 超氧自由基

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