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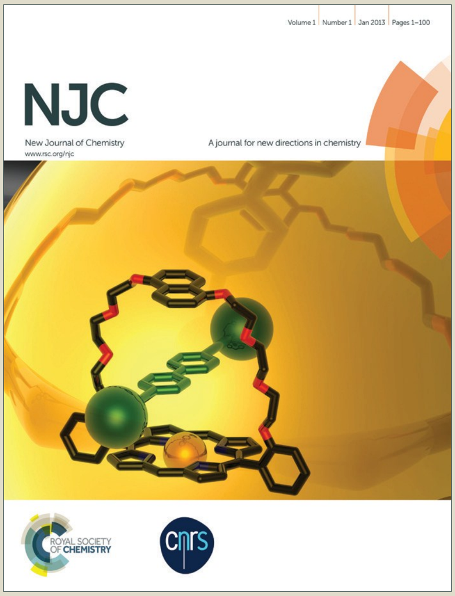

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The in-situ growth of Ag/AgCl on the surface of CNT and the effect of CNT to the photoactivity of the composite

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The CNT/Ag/AgCl was fabricated by a facile solvothermal method. The introduced carbon nanotube (CNT) was both in the interior and surface of the Ag/AgCl. The composites were characterized by X-ray diffraction (XRD), scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS), UV-vis absorption spectra, photoluminescence (PL), electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS). The photocatalytic ability of the Ag/AgCl and CNT/Ag/AgCl was valued by degrading the methyl orange (MO) dye, the results showed that the photocatalytic ability of CNT/Ag/AgCl (with trace carbon nanotube content) is much higher than that of the pure Ag/AgCl. The photoactivity of the composite is mainly depending on the addition carbon nanotube amount. The SEM-EDS results suggest that the carbon nanotube and the Ag/AgCl combined well and the carbon nanotube dispersed well in the whole place (both the interior and surface) of the Ag/AgCl particles. The formation process of CNT/Ag/AgCl is also proposed. The EIS result indicates that the CNT/Ag/AgCl has much lower resistance than that of the Ag/AgCl. The addition carbon nanotube is good for the electron transfer in the CNT/Ag/AgCl system. Especially, the carbon nanotube in the interior of the composite can transfer the electrons generated in the interior of the Ag/AgCl to its surface, which can solve the problem of the high electron-hole recombination in Ag/AgCl system. Therefore, the photoactivity of Ag/AgCl can be enhanced. A possible reaction mechanism is also proposed.

1. Introduction

The development of the modern society has attached the environmental pollution. The photocatalysts has attracted the public's attention because of its potential applications in water splitting and solving the environmental pollutant problems [1]. The traditional photocatalysts (such as TiO_2 and ZnO) possess many advantages, such as strong oxidizing power, thermal and chemical stability, nontoxic and cheap. Therefore, they have been widely investigated [2-5]. However, they also suffer the high recombination rate of photogenerated electron-hole pairs and weak visible light absorption ability, which greatly inhibit their practical applications. Therefore, the preparations of new active photocatalysts (which possess efficient visible-light-driven ability) have attracted much attention.

In the past decades, the visible-light response plasmonic photocatalysts, which possess surface plasmon resonance (SPR) property, have obtained much attention because of their excellent performance in pollutants decomposition [6-9]. Generally, the plasmonic photocatalysts contain noble-metal (such as Ag, Au and Pt) and semiconductor (such as Ag/AgCl, Ag/AgBr etc.). Huang et al. has reported that the Ag/AgCl [10] and Ag/AgBr [11] possess high photoactivity and stability in recycle experiments. Wang et al. [12] prepared different metallic Ag amount on the surface of Ag/AgCl, and they found that the metallic Ag affected the photostability and photocatalytic activity of Ag/AgCl. Many relevant works have been reported and the photocatalyst exhibited high activity [13-17]. However, the pure Ag/AgX photocatalyst still suffer the high recombination of electron-hole pairs. In order to solve the problem of Ag/AgX and fully display its high photoactivity. Ag/AgX was dispersed on cheaper supporting materials (including active and inactive materials): Huang et al. [18] prepared $Ag/AgBr/WO_3•3H_2O$ composite through an ion-exchange method. This photocatalyst could degrade methylene blue solution efficiently under visible light irradiation. Li et al. [19, 20] utilized g-C_3N_4 as an active supporting material as well as the template to fabricate Ag/AgCl/g-C_3N_4 and Ag/AgBr/g-C_3N_4 with small Ag/AgX particles anchored on g-C_3N_4 surface. The synergistic effect between the two materials enhanced the photoactivity of the composite. Yu et al. [21] prepared Ag/AgCl/TiO_2 by depositing AgCl nanoparticles into TiO_2 nanotubes, and then reducing some AgCl particles to Ag^0 species. The particle size is about 20 nm. The composite showed higher capability in decomposing MO than TiO_2. They also synthesized Ag@AgCl immobilized on titanate nanowire films, and the composites showed enhanced activity in degrading MO, RhB and phenol. The reactive species were also discussed [22]. Cui et al. [23]

prepared Ag/AgCl intercalated $K_4Nb_6O_{17}$ composite, and the composites showed enhancing activity in degrading Rhodamine B. They also prepared quantum dots Ag@AgCl decorated on the surface of flower-like Bi_2WO_6. The composite can degrade Rhodamine B and phenol efficiently [24]. Besides, many relevant works have been reported, such as AgCl/Al_2O_3[25], Ag/AgCl/ZnO[26], Ag-AgCl-TiO_2/rectorite [27], Ag/AgCl/SiO_2[28], Ag/AgBr/ZnO[29], Ag/AgBr/TiO_2[30] and so on. When Ag/AgX was dispersed on these materials, their sizes become much smaller and the amount of active sites increased. Moreover, the Ag/AgX with small size is beneficial for the separated electrons transfer to the surface of the catalyst and leads to the low recombination of the electron-hole pairs [31]. In all, these properties lead to the enhanced photoactivity of the composite and can reduce the consuming of noble-metal. However, these works all need high content of the substrate to supply enough surface area to anchor the Ag/AgX particles.

In addition, Ag/AgX can be modified by carbon materials (with relative small content) which can transfer electrons faster and more efficient. A lot of relevant works have been published. Quan et al. [32] fabricated Ag@AgCl/RGO composites by a deposition-precipitation reaction and followed by photoreduction. The Ag@AgCl/RGO showed enhanced photoactivity than that of pure Ag/AgCl in degrading RhB. The GO content played an important role in determining the activity. Our previous work (CNT/Ag/AgBr [33]) showed that pure CNT has no activity in degrading the MO, but it can transfer the photogenerated electrons in Ag/AgBr efficiently and enhance the activity of Ag/AgBr in degrading the MO dye. However, introducing superfluous CNT will cover the surface of the composite and affect the light absorption of Ag/AgBr, hence leads to the decreasing activity of the composite. Furthermore, many relevant works have been reported, such as Ag/AgCl/rGO [34], Ag/AgBr/GO [35] and so on. These works showed that the introduced carbon materials can transfer the electrons effectively and enhance the photoactivity of the composite. The composite also showed stable activity. In addition, CNT is a chemically inert material and can be functionalized with group (such as –COOH), which is facile to bind to target ions or nanoparticles [36]. Besides, it is much cheaper than graphene. So, it is widely investigated by the researchers [37-39].

Based on the above analysis, the combination of CNT and Ag/AgCl may take full advantage of CNT and Ag/AgCl. The introduced CNT can probably act as the electron capture and efficiently separate the photogenerated electron-hole pairs in the composite, and enhance the photoactivity of the composite. An et al. [40] prepared AgX (Cl, Br, I) on the surface of CNT in the form of nanoparticles. The composite showed enhancing photoactivity in degrading the 2,4,6-tribromophenol and the antibacterial ability. But the content of CNT used in this work was as high as about half mass content of the composite. The CNT was used as supporting material in this work. As far as we know, few works about the preparation and photocatalytic properties of the CNT/Ag/AgCl composite with small amount CNT to modify the Ag/AgCl has been reported until now.

In this work, a novel CNT/Ag/AgCl composite with trace CNT content (0.1 % - 5 %) was prepared by a one-step solvothermal method. The morphology of the composites was investigated by SEM, and the results indicated that the introduced CNT was both in the interior and the surface of the Ag/AgCl. The CNT played an important role in the formation process and a possible formation process was proposed. The trace amount CNT can significantly enhance the photoactivity of the composite in decomposing Methyl orange (MO) dye. The role of CNT in the composite was analysed based on the Photoluminescence (PL) and Electrochemical impedance spectroscopy (EIS) results. The introduced CNT can transfer the electrons efficiently. Especially, the CNT in the interior of the composite can transfer the electrons generated in the interior of the particles to the surface, which is beneficial for solving the problem of high electron-hole pair recombination rate in the pure Ag/AgCl. This work may supply a new insight in preparing CNT doping in the interior of the materials. It may expand the CNT application in many other areas.

2. Experimental

2.1 Preparation of the Ag/AgCl and CNT/Ag/AgCl photocatalysts

All chemicals were of analytical grade and used without further purification. Ag/AgCl and CNT/Ag/AgCl were prepared by a typical solvothermal method. As an example, 0.1 % CNT/Ag/AgCl was prepared in the follow process: first, CNT dispersed in ethylene glycol (EG) was prepared (named as solution A). 9 mL solution A (which contains 0.225 mg CNT) was added into a 100 mL beaker, and then was diluted to 90 mL by EG (named as solution B). After that, 0.2250 g of $AgNO_3$ was added into the solution B and stirred for 20 min (solution C). Then, solution C was transferred into five 25 mL Teflon-lined stainless steel autoclaves. Next, 1 mL NaCl EG solution (0.0154 g/mL) was added into each autoclave under vigorous stirring. At last, the Teflon-lined stainless steel autoclaves were maintained at 120℃ for 24 h. After the solvothermal reaction, the precipitate was washed with deionized water and ethanol several times and was dried at 60℃ (the mass ratio of the introduced CNT to $AgNO_3$ was 0.1 wt. %, and the sample was named as 0.1 % CNT/Ag/AgCl). The pure Ag/AgCl was prepared with the similar method without the addition of CNT solution. The other mass ratios of CNT/Ag/AgCl were obtained by adding different volume of solution A (Among them, 5 % CNT/Ag/AgCl was prepared by using a higher concentration of CNT EG solution).

2.2 Characterization

X-ray powder diffraction (XRD) analysis was studied on a Bruker D8 diffractometer with Cu-Kα radiation (λ = 1.54 Å) in the 2θ range of 10º-80º. The field-emission scanning electron microscopy (SEM) analysis were carried on a field-emission scanning electron microscope (JEOL JSM-7001F) equipped with an energy-dispersive X-ray spectroscope (EDS) running at an acceleration voltage of 10 kV. Photoluminescence (PL) spectra of the catalyst were tested on the QuantaMaster & TimeMaster Spectrofluorometer, QuantaMaster^{TM} 40 (Photon Technology International, Inc.). The UV-vis absorption spectra (in the diffuse reflectance spectra mode) of the samples in solid state were obtained on a UV-vis spectrophotometer (UV-2450, Shimadzu Corporation, Japan). X-ray photoemission spectroscopy (XPS) was measured on a PHI5300 with a monochromatic Mg Kα source. Electrochemical impedance spectroscopy (EIS) was carried on an electrochemical workstation (CHI660B, CHI Shanghai, Inc.).

2.3 Photocatalytic experiments

The application of the prepared composites for the degradation of organic dye Methyl Orange (MO) was researched under visible-light irradiation at 30℃. In a typical procedure, a 0.0700 g amount photocatalyst was dispersed in 70 mL MO solution (10 mg/L). The solution was first stirred for 0.5 h in the dark to ensure the adsorption/desorption equilibrium between the photocatalysts and the pollutant, and then light up the lamp (300 W Xe arc lamp equipped with an ultraviolet cut filter to provide visible light with $\lambda \geq 400$ nm) to start irradiation. The mixed solution was sampled in certain intervals and centrifuged, and the above liquid was then monitored by UV-vis spectroscopy at 463 nm. The degradation process of 4-CP (10 mg/L) is similar to the above operation.

3. Results and discussion

CNT modified Ag/AgCl particles were prepared by a facile one-pot solvothermal method. The structure, morphology, optical absorption performance and elemental composition were characterized and the possible formation process was proposed. The MO dye and 4-chlorophenol (4-CP) was used as the model pollutants to test the photoactivity of the CNT/Ag/AgCl composites under visible light irradiation. Because the introduced CNT both in the interior and surface of Ag/AgCl, it can transfer the photogenerated electrons efficiently and enhance the photoactivity of the composites.

3.1. Structure, morphology and thermal property

The structure of the samples was investigated by XRD, and the results are shown in Fig. 1. The peaks at 2θ= 27.8°, 32.2°, 46.3°, 54.8°, 57.6°, 67.4°, 74.4° and 76.7°, which are marked with "◆", are assigned to the (111), (200), (220), (311), (222), (400), (331) and (420) planes of cubic phase AgCl crystal (JCPDS cards no. 31-1238). The peak of Ag and CNT is not obvious in the XRD of the composite, which may be due to the small amount of Ag and the low intensity of CNT [33] (the existence of them can be confirmed in the following parts). The morphologies of Ag/AgCl and the CNT/Ag/AgCl composites with different CNT content were observed by SEM (as shown in Fig. 2 a-i). It can be seen that the Ag/AgCl is mainly in the form of particles with relative smooth surface, and the size is about several micrometers (as shown in Fig. 2 a and b). The particle size of the composite does not change obviously, but the surface of the sample becomes unsmooth after CNT was introduced in the Ag/AgCl sample. Moreover, there are some holes can be seen in the particles' surface (as shown in the red circles in Fig. 2 c) and small amount of CNT was observed on the surface of the samples (as shown in Fig. 2 d, the blue circles). When the CNT amount in the preparation process was raised to 0.5 %, the "hole" on the surface of the particles becomes more obvious (as shown in Fig. 2 e, the red circles). It is clear that the CNT covered on the surface of the catalyst and in the "hole" place with good distribution (as shown in Fig. 2 f, the blue circles). When the CNT content further increased to 1 %, many "holes" can be observed on the surface of the particles (as shown in Fig. 2 g, the red circles). Besides, it is clear that the CNT can be seen everywhere on the surface of the catalyst (Fig. 2 h). When the CNT amount increased to 5 %, the "hole" on the surface of the particles is also obvious (as shown in Fig. 2 i, the red circles). It can also be seen that not only the surface of the Ag/AgCl was covered by CNT, but also the superfluous CNT agglomerate together (as shown in Fig. 2 i, the blue circles). This may not beneficial for the photoactivity of the catalyst. The corresponding EDS results of the samples are showed in Fig. 2 j. It can be seen that the intensity of the C peak gradually increased, which indicates the CNT content gradually increased [33]. They are in good agreement with the SEM results. Besides, all of the samples consist of Ag and Cl elements. In all, the SEM-EDS results indicate that the CNT played an important role in the formation of the "hole".

In order to test the exact CNT content in the 5 % CNT/Ag/AgCl, the TG and DTA of the pure Ag/AgCl and 5 % CNT/Ag/AgCl samples were investigated. The results are shown in Fig. 3 A and B. As shown in Fig. 3 A, it is clear that the Ag/AgCl almost has no weight loss below 650℃. The endothermic peak occurs at around 455℃ may ascribed to the phase change of Ag/AgCl. As shown in Fig. 3 B, it is clear that the 5% CNT/Ag/AgCl not only has the endothermic peak at about 454℃, but also has an extra exothermic peak at about 488℃. The extra peak at about 488℃ may be ascribed to the CNT reacted with O_2 and the weight loss about 4.9% is due to the loss of CNT. The TG results indicate that the CNT content in the 5 % CNT/Ag/AgCl composite is about 4.9%, which is close the theoretical value.

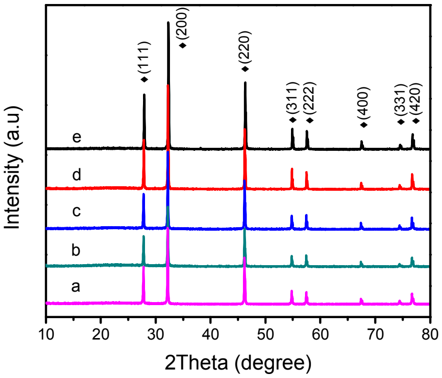
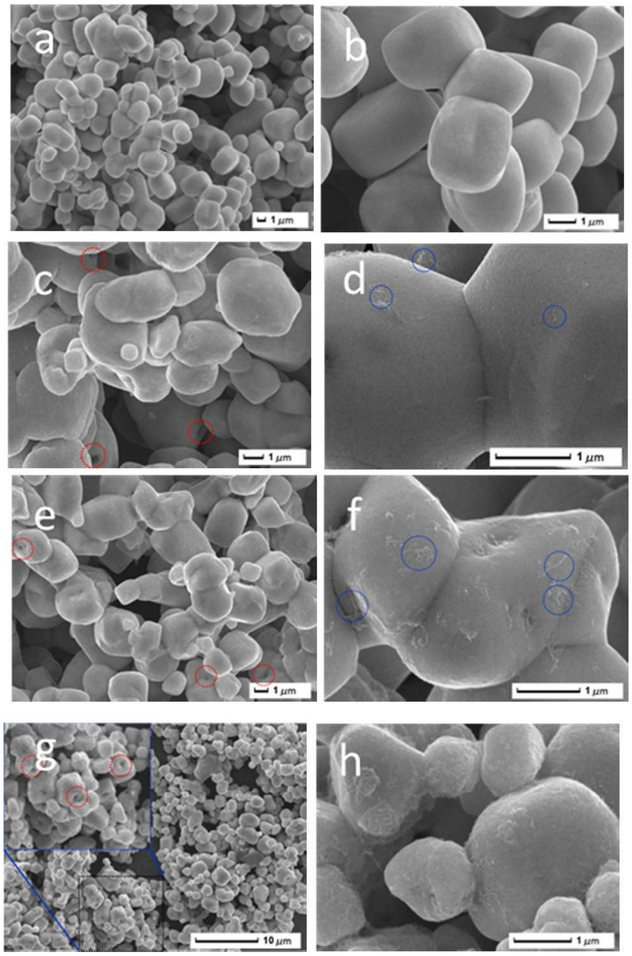


Fig. 1 XRD patterns of (a) Ag/AgCl, (b) 0.1 % CNT/Ag/AgCl, (c) 0.5 % CNT/Ag/AgCl, (d) 1 % CNT/Ag/AgCl and (e) 5% CNT/Ag/AgCl.



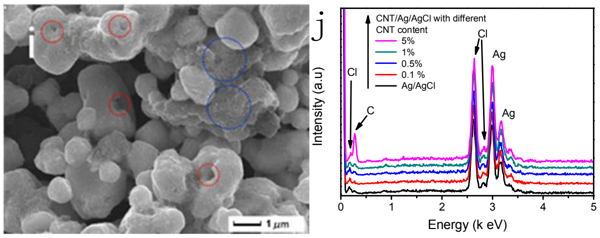


Fig. 2 SEM images of Ag/AgCl (a, b), 0.1 % CNT/Ag/AgCl (c, d), 0.5 % CNT/Ag/AgCl (e, f), 1 % CNT/Ag/AgCl (g, h), 5 % CNT/Ag/AgCl (i) and EDS of the samples (j).

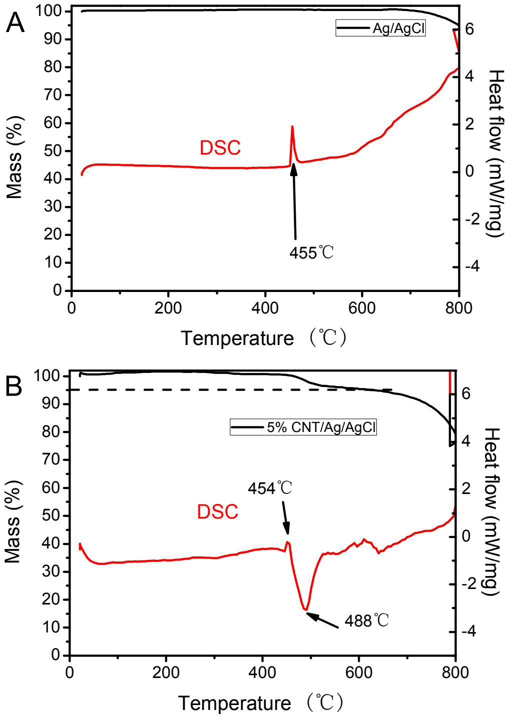


Fig. 3 The TG and DTA of the Ag/AgCl (A) and 5 % CNT/Ag/AgCl (B).

3.2 The possible formation process

The formation process of the CNT/Ag/AgCl was proposed based on the SEM-EDS results and shown in Fig. 4. Firstly, Ag^+ was adsorbed to CNT-COO$^-$ by the electrostatic attraction. Then, Cl^- was added into the reaction solution and combined with the Ag^+ into white precipitate AgCl. The AgCl formed and attached on the surface of CNT. At last, the mixture was transferred into 25 mL Teflon-lined stainless steel autoclaves and went through a solvothermal process. In the solvothermal process, the AgCl may further grow and form the "hole" on the surface because of the CNT in the interior of the particles. It also consistent with the SEM results, 0.1 % CNT/Ag/AgCl has few CNT on the surface, while 0.5 % CNT/Ag/AgCl has so many CNT on the surface. When CNT content increased to 1 %, the "hole" can be observed on many particles. This phenomenon further supports the above opinion that CNT was both in the interior and surface of the particles. Besides, the white precipitate changed into purple colour after the solvothermal reaction (as shown in the Fig. 5), which indicates that the AgCl was reduced into Ag/AgCl in the solvothermal process.

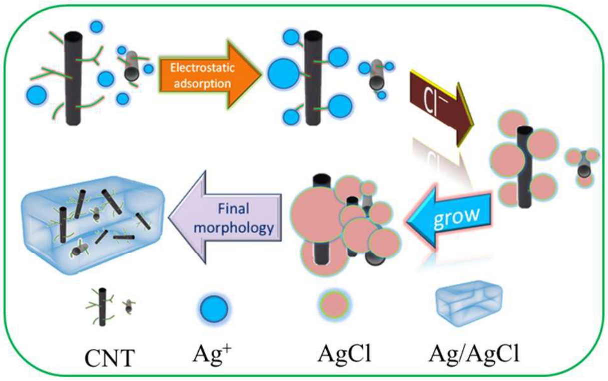


Fig. 4 The proposed formation process of the CNT/Ag/AgCl.

3.3 Optical absorption properties

The UV–vis absorption spectra were used to investigate the optical properties of the photocatalytst. Fig. 5 shows the UV–vis absorption spectra of the photocatalyst, it is clear that Ag/AgCl shows an obvious absorption peak at about 550 nm (pure AgCl has no absorption peak and almost has no absorption in the range of 400-800 nm [12, 41]), which is ascribed to the surface plasmon absorption of Ag [12, 31]. It suggests the formation of Ag on the surface of AgCl. When CNT was introduced, the absorption intensity of the composite increased with the increasing CNT content (which is in good accordance with our previous work (CNT/Ag/AgBr [33])). It can be seen that the plasmon absorption peak become unobvious, when the CNT content higher than 0.5 %. This may not beneficial to the photoactivity of the composite. The insert photos show the colour of the samples, from left to right are Ag/AgCl, 0.1 % CNT/Ag/AgCl, 0.5 % CNT/Ag/AgCl, 1 % CNT/Ag/AgCl and 5 % CNT/Ag/AgCl, respectively. It is clear that the Ag/AgCl exhibits the purple colour (which is another evidence of the formation of Ag on the surface of AgCl [12, 41, 42]) and the colour of the composites become gray and dark with the increasing CNT content (because CNT is a black material).

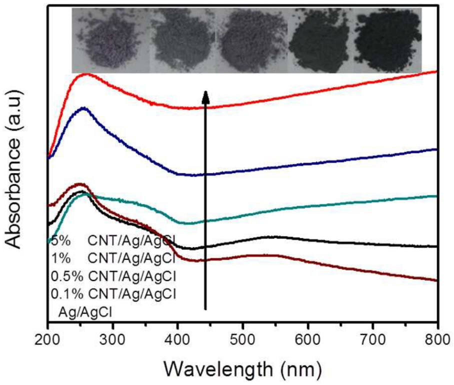


Fig. 5 UV–vis absorption spectra (in the diffuse reflectance spectra mode) of the photocatalyst.

3.4 Elemental compositions

The elemental compositions of the samples were studied by XPS. Fig. 6 A shows the survey spectrum of Ag/AgCl and CNT 0.1 % CNT/Ag/AgCl. No obvious difference between the two samples was observed in the survey spectrum. Fig. 6 B, C and D show the high-resolution XPS spectrum of C 1s, Ag 3d and Cl 2p of the two samples. The C 1s of the two samples are both at about 284.8 eV (which is attributed to the adventitious pollutant from the XPS instrument itself.) and no obvious difference is observed, which may because of the content of CNT is very low in the composite. Ag 3d and Cl 2p of the samples are shown in Fig. 6 C and D. Ag 3d of the Ag/AgCl have two bands at ca. 367.9 and 373.9 eV, which can be ascribed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$. Besides, Cl 2p of the Ag/AgCl have two bands at ca. 198.1 and 199.7 eV, respectively. The positions of Ag and Cl peaks of the pure Ag/AgCl are similar to our previous work [19]. Furthermore, the Ag 3d and Cl 2p of the 0.1 % CNT/Ag/AgCl all shifts to lower binding energy. Similar phenomenon in the GO/AgX@Ag (Cl and Br) system has been observed [43]. The shift of the Ag and Cl peaks indicates the existence of the interaction between the CNT and Ag/AgCl. The interaction between them is beneficial for the transfer of electrons and thus leads to the enhancement of the activity of the composite.

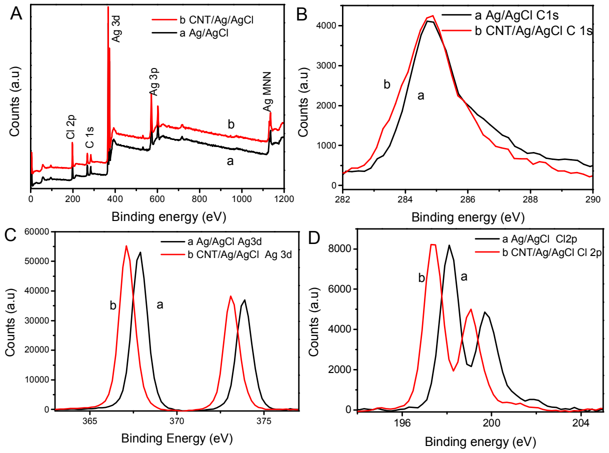
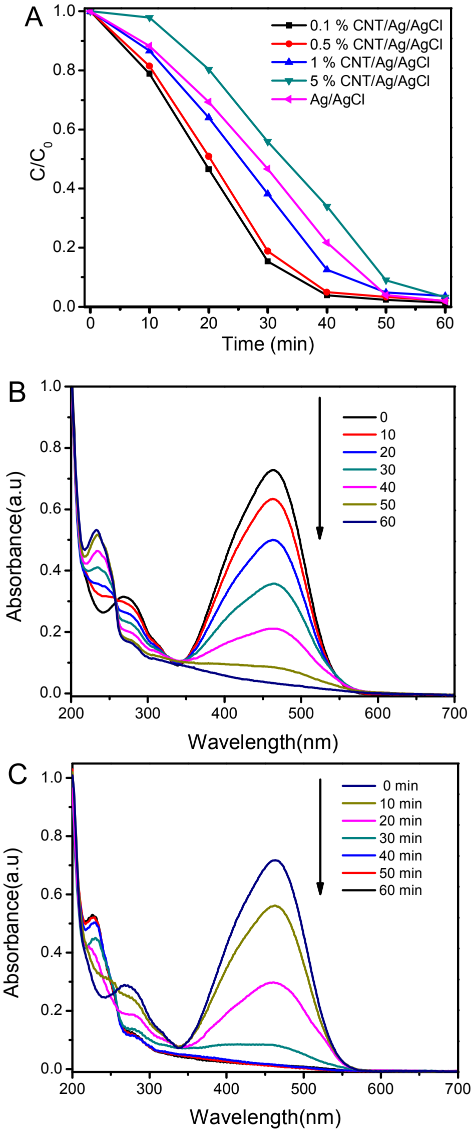


Fig. 6 XPS survey spectrum of Ag/AgCl and 0.1 % CNT/Ag/AgCl (A) and the high-resolution XPS spectra of C 1s (B), Ag 3d (C) and Cl 2p (D).

3.5 Photocatalytic activity

The photocatalytic activity of Ag/AgCl and CNT/Ag/AgCl was evaluated by the degradation of MO (10 mg/L) under visible-light irradiation (λ > 400 nm). As shown in Fig. 7 A, a serial of CNT content photocatalyst were tested by the experiment under the same condition (MO dye cannot be decomposed by pure CNT has been confirmed in our previous work [33]). Ag/AgCl (with CNT content of 0 %) can decompose the MO dye about 53.4 % at 30 min, about 78.3 % at 40 min and about 96.1 % at 50 min. When CNT was combined into Ag/AgCl, the activity of the composite was obviously enhanced. The 0.1 % CNT/Ag/AgCl composite can decompose the MO dye about 84.7 % at 30 min, which is much higher than that of pure Ag/AgCl (53.4 %). It can decompose about 96.1 % MO at 40 min, much higher than that of pure Ag/AgCl (78.3 %). The results show that the 0.1 % CNT/Ag/AgCl can decompose the MO dye more efficient than Ag/AgCl (see Fig. 7 B and C). However, when the CNT amount in the composite further increased to 0.5 %, the 0.5 % CNT/Ag/AgCl can decompose about 81.2% MO at 30 min and about 95.1% at 40 min. The photoactivity of the 0.5 % CNT/Ag/AgCl is a little lower than that of 0.1 % CNT/Ag/AgCl. When the CNT amount in the composite further increased to 1 %, the 1 % CNT/Ag/AgCl can decompose about 61.8 % MO at 30 min and about 87.4 % at 40 min. Its photoactivity is much lower than that of 0.1 % CNT/Ag/AgCl but still higher than that of pure Ag/AgCl. When the addition amount of CNT reaches up to 5%, the 5% CNT/Ag/AgCl can only decompose about 44.1 % MO at 30 min and about 66.0 % at 40 min. Its photoactivity is even lower than that of pure Ag/AgCl. In order to investigate the ability of CNT/Ag/AgCl in degrading the colourless pollutant, the 4-CP was used as the target pollutant. The absorption spectral changes of 4-CP is shown in Fig. 7D, it can be seen that the 4-CP can be quickly decomposed by the 0.1% CNT/AgCl/AgCl under visible light irradiation.

The results showed that a trace amount CNT loading is beneficial to enhance the photocatalytic ability of the Ag/AgCl, while a large CNT amount leads to the decreasing photocatalytic ability. From the SEM-EDS and UV-vis absorption spectra results, it can be inferred that the superfluous CNT covered on the surface of the Ag/AgCl leads to the enhanced absorption intensity of the composite. It is mainly ascribed to the black CNT, which can absorb the light in the region of 400-800 nm [33]. The very low content of CNT is good for transferring the electrons, and thus enhancing the photoactivity of the composite. Especially, the CNT in the interior of the particles can transfer the electrons formed in the internal of particle to its surface. It can reduce the recombination of the electron-hole pairs in Ag/AgCl and solve the problem of the Ag/AgCl. However, high content of CNT in the composite not only transfers the electrons, but also shields the Ag/AgCl from absorbing the light. Therefore, high content CNT in the composite leads the low yields of successfully separated electrons in the composite and leads to the decreasing photoactivity of the composite.



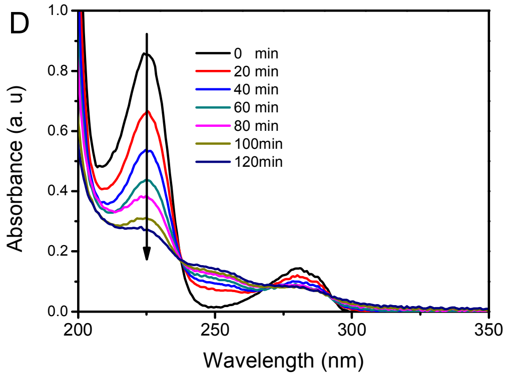


Fig. 7 Photocatalytic degradation of MO solution by different catalysts (A), and of MO by Ag/AgCl (B), and 0.1 % CNT/Ag/AgCl (C); the absorption spectral changes of 4-CP by 0.1% CNT/Ag/AgCl (D).

3.6 Electron-hole recombination, charge transfer resistance performance and the possible reactionmechanism

In order to support the opinion in the above, PL and EIS of the photocatalyst were investigated and the results are shown in Fig. 8 and Fig. 9. The electron-hole separation property of Ag/AgCl and 0.1 % CNT/Ag/AgCl were studied by PL spectra. Fig. 8 shows that the emission peak intensity of 0.1 % CNT/Ag/AgCl is lower than that of pure Ag/AgCl, it suggests that the addition of CNT is beneficial for the separation of the electron-hole pairs. Therefore, the 0.1 % CNT/Ag/AgCl has lower recombination rate of electron-hole pairs compared with Ag/AgCl. It may be one reason of the 0.1 % CNT/Ag/AgCl showed higher photoactivity than that of Ag/AgCl. Besides, the charge transfer resistance of the photocatalyst was also tested by the EIS measurements. As shown in Fig. 9, the arc radius in EIS of 0.1 % CNT/Ag/AgCl is smaller than that of Ag/AgCl. It suggests that the 0.1 % CNT/Ag/AgCl has a lower resistance, which is beneficial for the interfacial charge-transfer process [45]. Both of the PL and EIS results suggest that the introduced CNT is good for the transfer of electrons and thus enhances the electron-hole separation ability and leads to the enhanced photoactivity.

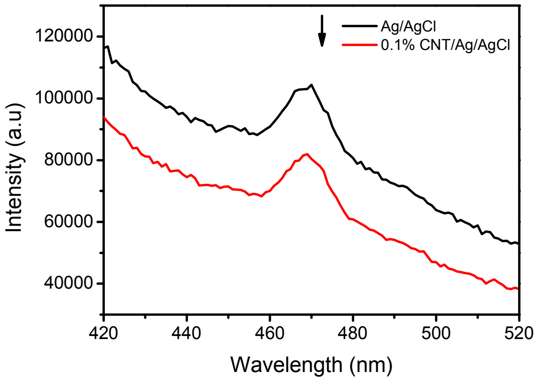


Fig. 8 The PL spectra of the Ag/AgCl and 0.1 % CNT/Ag/AgCl.

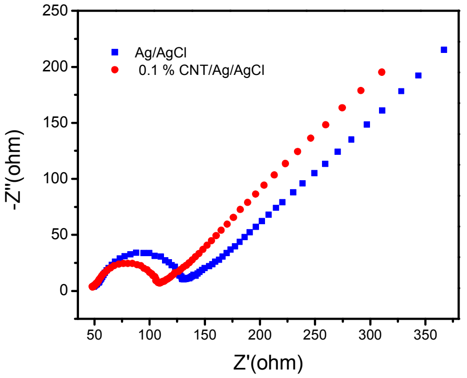


Fig. 9 The electrochemical impedance spectra of Ag/AgCl/ITO and 0.1 % CNT/Ag/AgCl/ITO in 0.1 M KCl solution which contains 5 mM $Fe(CN)_6^{-3}/(Fe(CN)_6^{-4}$.

Based on the above results, analysis and the reported papers [24,45,46], a possible reaction mechanism is supposed and showed in Fig. 10. The excellent photocatalytic activity is because (1) the carbon nanotube (CNT) in the interior of Ag/AgCl can transfer the photogenerated electrons in the interior of the Ag/AgCl to its surface. It is beneficial to improve the electron-hole separation efficiency of Ag/AgCl. (2) the Ag formed on the surface of AgCl can efficiently trap the electrons and utilize the visible light, and the AgCl offers the Cl^0 for degrading the pollutant. In conclusion, the photogenerated electrons in the CNT/Ag/AgCl system can be separated more efficiently than that of pure Ag/AgCl and leads to the enhancing photoactivity.

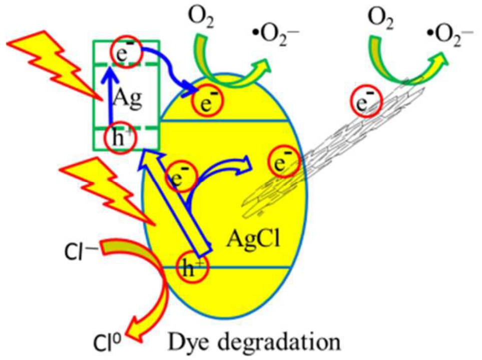


Fig. 10 The possible photocatalytic mechanism of the CNT/Ag/AgCl.

4. Conclusions

In summary, the CNT/Ag/AgCl photocatalyst with trace carbon nanotube (CNT) amount was fabricated by the simple solvothermal method, and the possible formation process was proposed. The carbon nanotube has played an important role in the formation process and affected the morphology of the composite. The carbon nanotube content in the composite determines the photoactivity of the CNT/Ag/AgCl composite. The introduced carbon nanotube can efficiently transfer the separated electrons. Especially, the carbon nanotube in the interior of the Ag/AgCl can transfer the electrons generated in the interior of the Ag/AgCl to its surface, which is very useful to solve the problem of high recombination of electron-hole pair of Ag/AgCl. Therefore, the photoactivity of the CNT/Ag/AgCl composite with low carbon nanotube content (≤ 1 %) was enhanced. However, too much carbon nanotube will cover the surface of the Ag/AgCl and lead the low yields of the separated electron-hole pairs. Thus, the photoactivity of the CNT/Ag/AgCl composite decreased. This work opens up a new insight to prepare other carbon nanotube hybrid composite with carbon nanotube in the interior of the material to enhance their certain property.

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