

# Enhanced photocatalytic activity of ternary multilayered Ag/TiO<sub>2</sub>/CNT composites for methylene blue degradation

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The TiO<sub>2</sub> modified carbon nanotube composites (TiO<sub>2</sub>/CNT) and Ag deposited ternary multilayered composites (Ag/TiO<sub>2</sub>/CNT) were prepared by chemical deposition and sonochemical reaction, respectively. The composites were characterised by transmission electron microscopy, scanning electron microscopy, X-ray diffraction, Fourier-transform infrared spectroscopy, and ultraviolet–visible (UV–vis). The results showed that anatase TiO<sub>2</sub> layers were wrapped on the surfaces of the CNTs. The face-centred-cubic structure of Ag nanoparticles (NPs) was dispersedly formed on the surfaces of the Ag/TiO<sub>2</sub>/CNT composites. The expected formation and good dispersion of Ag was obtained by high-intensity ultrasound irradiation assistance. All the resulted TiO<sub>2</sub>/CNT and Ag/TiO<sub>2</sub>/CNT composites exhibited a higher photocatalytic performance than that of TiO<sub>2</sub> for the degradation of methylene blue. The novel nanocomposite photocatalysts were developed through structural changes and double effects of carbon materials and noble metals as electron acceptors. Inhibited recombination of electron-hole pairs allows effective electron transfer and active redox reaction on the surfaces of the composites. The novel composite combines the CNTs with excellent electronic nature and noble metallic NPs with the special semiconductor-metal junction. It can provide new guidance for the application of carbon nanotube-based photocatalytic materials in photocatalysis field from UV–vis spectrum.

**1. Introduction:** In recent years, increased attention has been given to such global environmental issues such as sustainable water management, environmental toxic pollutants, and climate change [1, 2]. Multi-component photocatalysts, compared to a single material, are being considered for their potential applications to address environmental problems by optimising internal structures of materials, improving the photocatalytic effect, and even extending the optical absorption region [3, 4]. As a single photocatalytic material, TiO<sub>2</sub> has been widely focused on and has been employed as one of the best candidate photocatalytic materials owing to its excellent photocatalytic activity, low cost, non-toxicity, convenient synthesis etc. [1, 5–7]. Based on deep research on electronic states of two crystal structures of TiO<sub>2</sub>, the proposed mechanism of electron transfer has been established, which provides guidance for further modification of TiO<sub>2</sub> [8]. To obtain better photocatalytic efficiency of TiO<sub>2</sub>, various efforts have been made to develop the nanocomposite systems with high photoactivity such as CNT–TiO<sub>2</sub> [9–11], M–TiO<sub>2</sub> (M = Au, Ag, Cu *et al.*) [12], and Ag–CNT–TiO<sub>2</sub> [13] for the extensive application to dye degradation. During synthesis of these binary or ternary systems, CNTs or Ag play an important role in the improvement of photoactivity of the nanocomposites. CNTs are an excellent candidate with large specific surface area, good mechanical properties, tailored surface modification, and electronic properties. Hoffmann *et al.* [14] have proposed a modified mechanism to explain the development of the photocatalytic activity of the CNT–TiO<sub>2</sub> composites. Here, CNTs act as an electron sink as a consequence of electron-storage capacity. Simultaneously, CNTs may exhibit photosensitising properties and act as a sensitiser for the transferring electrons between the TiO<sub>2</sub> and CNTs [15, 16]. Furthermore, in a metal-participated M–TiO<sub>2</sub> composite structures, a junction called Schottky barrier is formed and retards the recombination of electron-hole pairs so as to enhance the photocatalytic efficiency [17]. In the case of ternary composites, many physical and chemical methods have been reported for Ag synthesis and deposition. Conventional physical methods, such as spark discharge and pyrolysis have

been applied for the preparation of Ag nanoparticles (NPs) [18, 19]. The disadvantages include low-yield and high energy consumption. Chemical methods usually utilise water or organic solvents to prepare the Ag NPs. The synthesis process usually employs several components, such as metal precursors, reducing agents, and stabilising/capping agents [20]. Moreover, a relatively wild reducing agent participates in the reaction. Zhang *et al.* [21] have designed the Ag–CNT/TiO<sub>2</sub> composite electrodes and reported that TiO<sub>2</sub> was dispersed in the networks of Ag-adorned CNTs by the solution chemical method. Another kind of ternary Ag/TiO<sub>2</sub>/CNT photoanode, fabricated by grafting Ag NPs onto TiO<sub>2</sub>/CNT nanocomposites, has recently been reported, resulting in superior photoactivity [13]. Koo *et al.* have reported a similar system of Ag–TiO<sub>2</sub>–CNT nanocomposites with high photocatalytic activity under artificial light with different inner structures of Ag-decorated TiO<sub>2</sub> NPs on CNTs by the photochemical reduction method [22].

Based on the design and mechanism described above, in this Letter, we report a new and successive process by chemical deposition and sonochemical methods for the synthesis of ternary Ag/TiO<sub>2</sub>/CNT composites. The sonochemical method was used for the fabrication of Ag NPs, and it was a relatively easier method under physical conditions. The structure, composition, and crystal type were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy and ultraviolet–visible (UV–vis) absorption spectrometer. The photoactivity of the ternary composites of Ag/TiO<sub>2</sub>/CNT by comparison of TiO<sub>2</sub> and TiO<sub>2</sub>/CNT was evaluated through detecting the degradation of methylene blue (MB) dye solution under UV irradiation. The results might be used as the instruction for the extended visible light irradiation.

**2. Experimental:** The TiO<sub>2</sub>/CNT composites were prepared by using a chemical deposition method. Multi-walled carbon nanotubes (hydroxylated CNTs, the content of hydroxyl is 1.63 wt%)

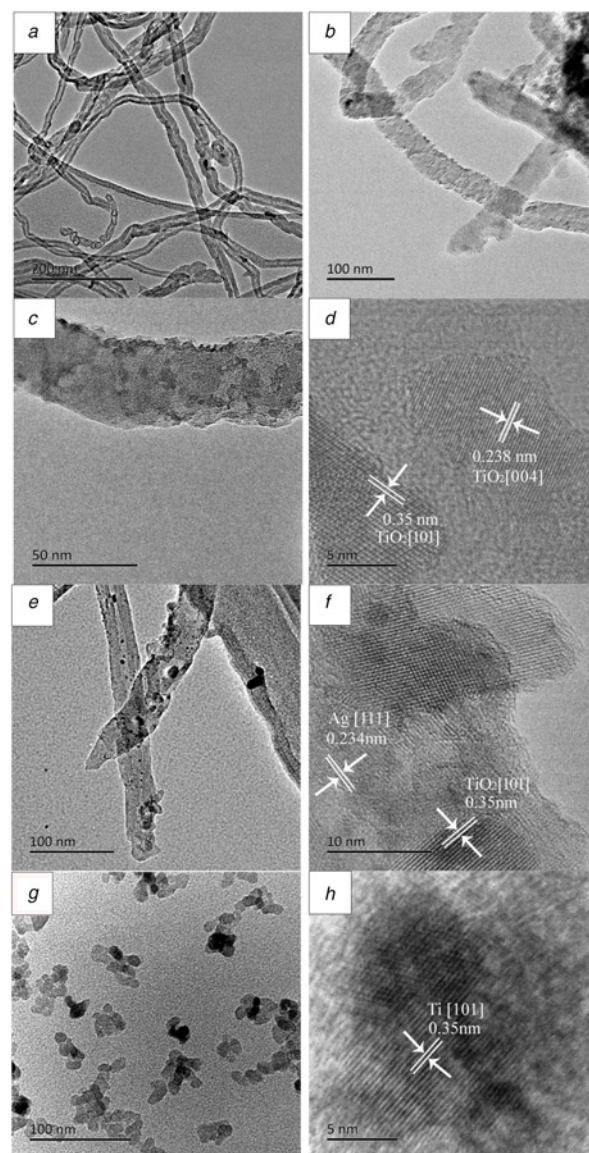
were of 95% purity with an outer diameter of 30–50 nm and length of 10–20  $\mu\text{m}$ . The CNTs of 100 mg were dispersed in 40 ml ethanol and sonicated for 20 min. Further, 0.226 g of tetrabutyl orthotitanate dissolved in 40 ml ethanol and 0.75 g deionised (DI) water were added separately with stirring. The mixtures were refluxed at 85°C for 1.5 h. The as-synthesised  $\text{TiO}_2/\text{CNT}$  composites were collected by centrifugation and rinsed with ethanol and DI water repeatedly for removal of impurities. The samples were then dried at 80°C for 6 h and roasted at 500°C for 3 h. Dark brown  $\text{TiO}_2/\text{CNT}$  composite NPs were obtained and kept for future use.

The  $\text{Ag}/\text{TiO}_2/\text{CNT}$  composites were synthesised by using a sonochemical method. The  $\text{TiO}_2/\text{CNT}$  composites (20 mg) were mixed with 45 ml dimethylformamide and 0.04 g polyvinyl pyrrolidone by sonication for 15 min, followed by adding 5 ml of 0.05 M silver nitrate ( $\text{AgNO}_3$ ). The mixture was exposed to high-intensity ultrasound irradiation (20 kHz, 1000 W) for 30 min at 30°C. The obtained composites were centrifuged and washed by ethanol and DI water. The collected products were dried and vacuumed in an oven at 80°C overnight.

The degradation of MB under UV irradiation was used to evaluate the photocatalytic activity of the  $\text{Ag}/\text{TiO}_2/\text{CNT}$  composites compared to the  $\text{TiO}_2/\text{CNT}$  composites and the  $\text{TiO}_2$  NPs with nitrate as a catalyst [23]. Typically, 10 mg of photocatalyst was mixed with 50 ml of 10 mg/l concentration MB aqueous solution. The solution was stirred with a magnetic bar throughout the experiment. The dark adsorption/desorption time was set for 20 min. A 300 W Xenon arc lamp (CEL-HXF 300) was used as light source and irradiated directly on the MB suspension with the distance from the lamp maintained at 15 cm. The adsorption rate was measured at several minute intervals. The solids were taken out from the reaction solution and separated by centrifugation. The concentration of MB in the supernatant was measured by a UV–vis spectrometer.

The crystal structures of the samples were studied by XRD on a Bruker D8 advanced diffractometer under Cu K $\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ). The size and morphological analysis were performed with the NANO NOVA SEM450 field emission SEM (FESEM) and JEM-2100 TEM using the accelerating voltage at 15 and 200 kV, respectively. Energy dispersive X-ray spectroscopy (EDX, Oxford Instruments) was carried out to get elements information for chosen samples. FT-IR spectra were obtained by using a 6700 spectrometer of American Thermo Nicolet. UV–vis absorption spectra were taken by a UV-2201 spectrophotometer of Japanese SHI-MADZU.

**3. Results and discussion:** TEM images of pure CNTs,  $\text{TiO}_2/\text{CNT}$  composites,  $\text{Ag}/\text{TiO}_2/\text{CNT}$  composites, and pure  $\text{TiO}_2$  are shown in Fig. 1. The pure CNTs are  $\sim 15 \text{ nm}$  in diameter with good dispersion and clear surfaces (Fig. 1a). The aggregation still inevitably occurs in some junctions between CNTs. Moreover, the well-dispersed  $\text{TiO}_2/\text{CNT}$  composites are quite similar to those of pure CNTs despite covering the additional layers of the  $\text{TiO}_2$  (Fig. 1b). The  $\text{TiO}_2$  is relatively uniform and decorates on the surfaces of the CNTs, as can be seen from the enlarged  $\text{TiO}_2/\text{CNT}$  composite (Fig. 1c). For further observation, the detailed combination state of CNTs and  $\text{TiO}_2$  is identified by high-resolution TEM (HRTEM). The crystal plane distances of 0.238 and 0.35 nm labelled in Fig. 1d correspond to the (004) and (101) crystal planes of anatase  $\text{TiO}_2$ , respectively. Based on the  $\text{TiO}_2/\text{CNT}$  composite matrices, Ag NPs are loaded with assistance from the sonochemical process. Sufficient power and reaction temperature are adaptive for the growth and further loading of Ag particles onto the surfaces of  $\text{TiO}_2/\text{CNT}$  composites, resulting in the formation of  $\text{Ag}/\text{TiO}_2/\text{CNT}$  composites (Fig. 1e). The enlarged image in Fig. 1f displays an interplanar spacing of 0.234 nm, which corresponds to the (111) crystal plane of face-centred-cubic (fcc) Ag. It is manifested good crystallisation of loaded Ag. Meanwhile, the uncovered  $\text{TiO}_2$  loading retains a good crystal



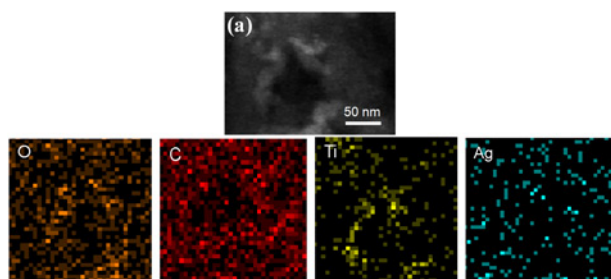
**Fig. 1** TEM and HRTEM micrographs of the samples

- a Pure CNTs
- b, c  $\text{TiO}_2/\text{CNT}$
- d Local enlarged c
- e  $\text{Ag}/\text{TiO}_2/\text{CNT}$  composites
- f Local enlarged e
- g Pure  $\text{TiO}_2$
- h Local enlarged g

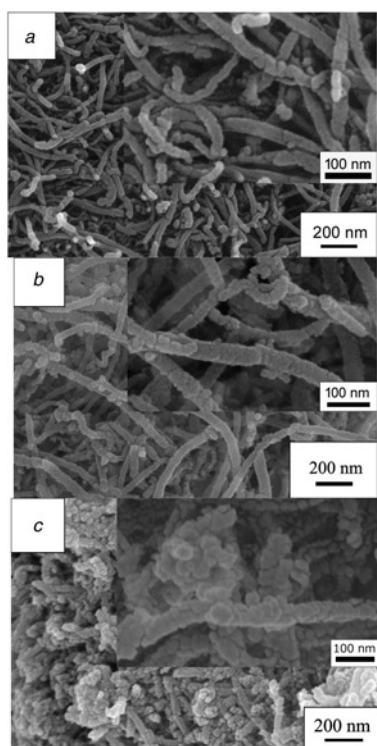
form of anatase by the crystal plane (101). For the comparison of photocatalytic activity, the granular  $\text{TiO}_2$  NPs (Figs. 1g and h) were fabricated by the microemulsion-assisted hydrothermal method reported in previous work [23]. It can be seen that the nano-sized  $\text{TiO}_2$  has a diameter of 10–15 nm.

The energy-dispersive X-ray spectroscopy (EDS) mappings of the  $\text{Ag}/\text{TiO}_2/\text{CNT}$  composite were measured to further obtain the information of the  $\text{TiO}_2$  and Ag NPs on the surface of the composite. As shown in Fig. 2, the elements of O, C, Ti and Ag have been detected. The signal of the Ti and Ag is relatively weak owing to the low content of loading, which can be further verified by element analysis.

For further investigating the structure of samples, Fig. 3 presents the corresponding SEM images. The pure CNTs (Fig. 3a) have smooth surfaces. The  $\text{TiO}_2$ -modified layer can be easily identified in Fig. 3b owing to its distinct morphologies compared to that of the pure CNTs. With the addition of Ag NPs, the surface roughness



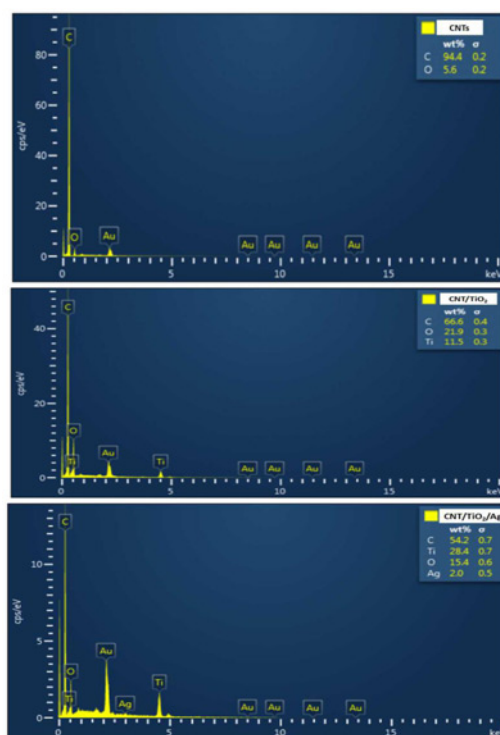
**Fig. 2** EDS mappings of the Ag/TiO<sub>2</sub>/CNT composites. (all the scale bars are the same)



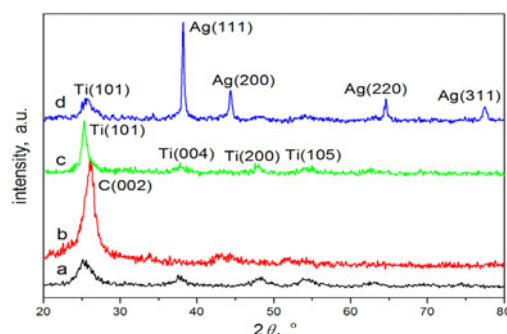
**Fig. 3** SEM micrographs of the samples  
a Pure CNTs  
b TiO<sub>2</sub>/CNT  
c Ag/TiO<sub>2</sub>/CNT composites

is obviously increased. Rare nanoparticle aggregations can be identified in Fig. 3c. The selected EDX spectroscopy images of pure CNTs, TiO<sub>2</sub>/CNT, and Ag/TiO<sub>2</sub>/CNT composites are also shown in Fig. 4, displaying the typical element (C, O, Ti, Ag) of corresponding samples after different fabrication processing.

The XRD patterns of pure TiO<sub>2</sub>, CNTs, TiO<sub>2</sub>/CNT composites and Ag/TiO<sub>2</sub>/CNT composites were collected as shown in Fig. 5. Pure TiO<sub>2</sub> (Fig. 5a) exhibits the diffraction peaks at 25.3°, 37.9°, 48°, and 54.4° that correspond to (101), (004), (200), and (211) crystal planes of anatase, respectively [22]. In Fig. 5b, the diffraction peak at 25.9° can be attributed to the (002) crystal plane of pure CNTs. It is well known that the crystalline and the crystal phases are crucial factors in the photocatalytic activity of TiO<sub>2</sub>, especially in which anatase phase TiO<sub>2</sub> is the most active form [16]. These features are also observed in the XRD spectra for TiO<sub>2</sub>/CNT and Ag/TiO<sub>2</sub>/CNT composites, as expected. The characteristic peaks of anatase are observed from Fig. 5c, indicating the formation of TiO<sub>2</sub>-modified surfaces of CNTs. In this case, the peak of CNTs in the similar position of 25.9° towards anatase TiO<sub>2</sub> is obscured. Furthermore, the major crystal peaks of Ag located at



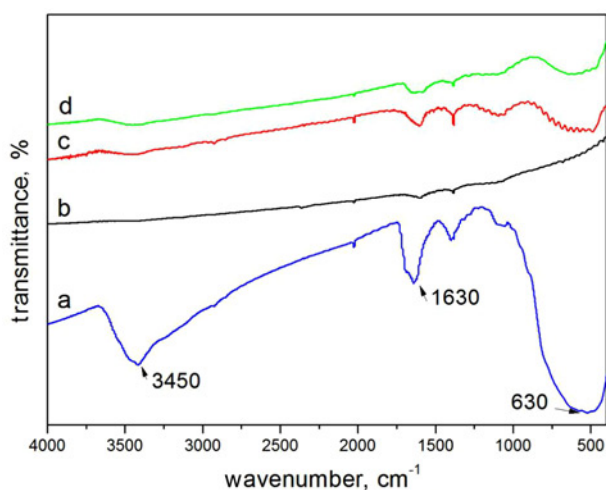
**Fig. 4** EDX elemental spectra of CNTs, TiO<sub>2</sub>/CNT and Ag/TiO<sub>2</sub>/CNT composites



**Fig. 5** XRD patterns of the samples  
a TiO<sub>2</sub>  
b Pure CNTs  
c TiO<sub>2</sub>/CNT  
d Ag/TiO<sub>2</sub>/CNT

38°, 44.5°, 64°, and 77° are attributed to (111), (200), (220), and (311) planes of fcc Ag (Fig. 5d). The observed diffraction peaks indicate the formation of Ag NPs with high crystallinity.

FT-IR analysis was further carried out to verify the compositions in the samples. As shown in Fig. 6a, pure TiO<sub>2</sub> exhibits two peaks at ~3450 and 1630 cm<sup>-1</sup>, which are attributed to the asymmetrical stretching vibration of hydroxyl on the surface of TiO<sub>2</sub> and the stretching vibration of hydroxyl from the adsorbed molecular water, respectively [24, 25]. In addition, the broad peak at 630 cm<sup>-1</sup> corresponds to the Ti–O–Ti bridge bonds. No obvious characteristic peak of hydroxyl from pure hydroxylated CNTs can be observed in Fig. 6b. It could be explained that there are less than 2 wt% of hydroxyl groups on the hydroxylated CNTs. However, a small amount of O element remained that is shown in the EDX spectrum (Fig. 4). Surface functional groups of hydroxyl will be allowed to form chemical bonds or van der Waals bonds with TiO<sub>2</sub>. After being modified with TiO<sub>2</sub>, the characteristic



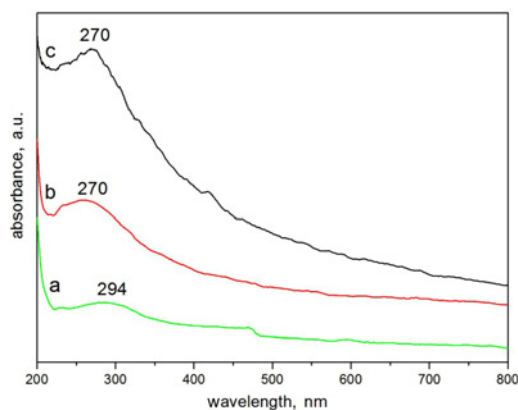
**Fig. 6** FT-IR spectra of the samples

a Pure TiO<sub>2</sub>  
b Pure CNTs  
c TiO<sub>2</sub>/CNT  
d Ag/TiO<sub>2</sub>/CNT

peaks of TiO<sub>2</sub> layers at 3450, 1380, and 630 cm<sup>-1</sup> appear (Fig. 6c), which are all weakened as a result of the CNT matrices. Simultaneously, the introduction of an Ag metal component for the formation of Ag/TiO<sub>2</sub>/CNT composites maintains almost the same feature peaks as TiO<sub>2</sub>/CNT composites in the measured range of the spectrum (Fig. 6d).

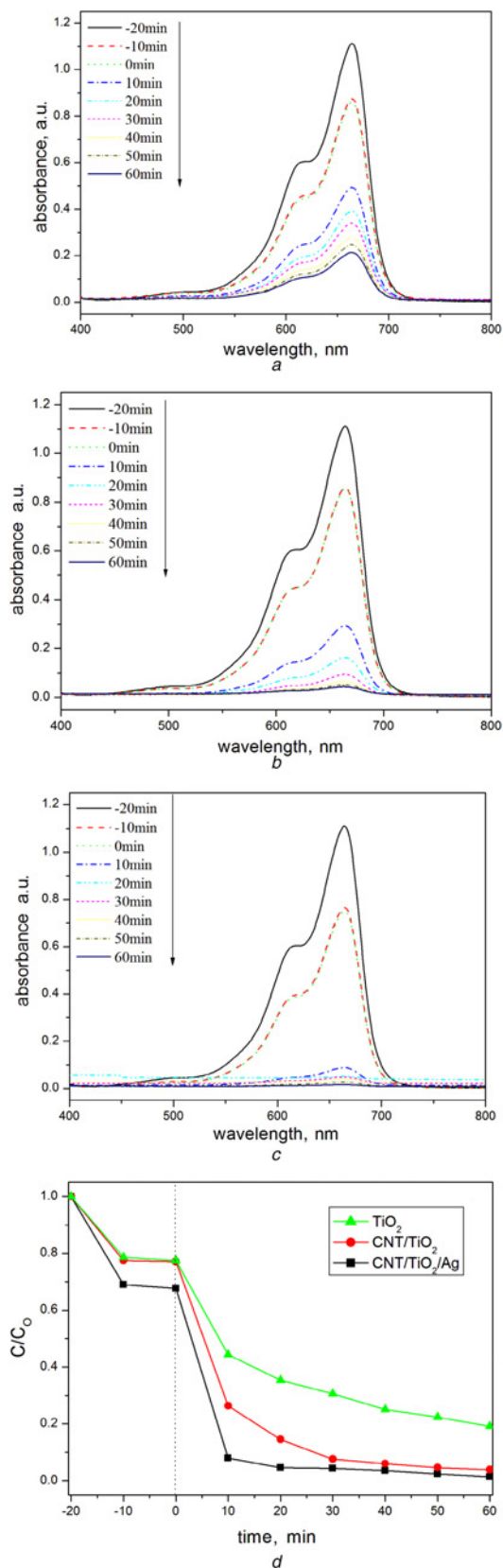
UV-vis spectra of the samples are shown in Fig. 7. It is clear that the pure TiO<sub>2</sub>, TiO<sub>2</sub>/CNT and Ag/TiO<sub>2</sub>/CNT composites exhibit UV absorption at peaks of ~294 and 270 nm. With the incorporation of CNTs and Ag, the absorption peak strength of the TiO<sub>2</sub>/CNT and Ag/TiO<sub>2</sub>/CNT composites is significantly increased with comparison to pure TiO<sub>2</sub>. It can be attributed that CNTs have a strong UV-vis absorption at a wide range [26]. Ag NPs can not only enhance the surface plasmon resonance but also cause increased scattering of the Ag/TiO<sub>2</sub>/CNT composites in UV regime [27, 28]. It is indicated that CNTs and Ag NPs added in sequence could enhance the UV absorption of the TiO<sub>2</sub> and further improve light utilisation efficiency, which might be beneficial to the UV-light induced photocatalytic activity.

Fig. 8 shows the concentration loss of MB dye as a function of reaction time under ultraviolet irradiation with the photocatalysts of TiO<sub>2</sub>, TiO<sub>2</sub>/CNT, and Ag/TiO<sub>2</sub>/CNT composites.



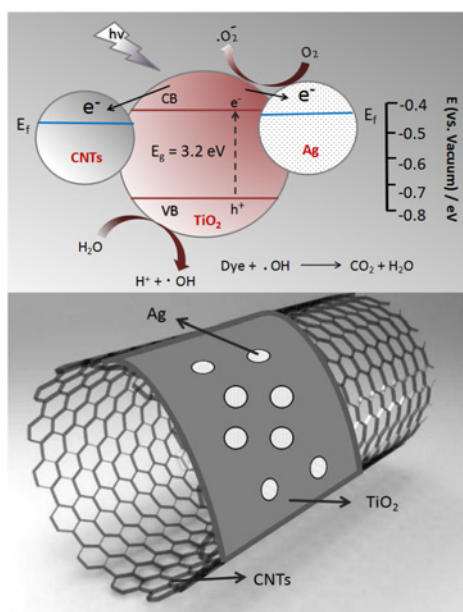
**Fig. 7** UV-vis spectra of the samples

a Pure TiO<sub>2</sub>  
b TiO<sub>2</sub>/CNT  
c Ag/TiO<sub>2</sub>/CNT



**Fig. 8** Photocatalytic activities of different samples: (a-c) The time-dependent absorption spectra of the MB solution in the presence of different photocatalysts

a TiO<sub>2</sub> NPs  
b TiO<sub>2</sub>/CNT composites  
c Ag/TiO<sub>2</sub>/CNT composites under irradiation  
d Comparison of photocatalytic activities of photocatalysts for the photocatalytic decolourisation of MB aqueous solution at ambient temperature



**Fig. 9** Schematic illustration of photocatalytic mechanism of Ag/TiO<sub>2</sub>/CNT composites

The pre-treatment for the initial 20 min in the dark is to reach an adsorption/desorption equilibrium. It is found that the adsorption effect of Ag/TiO<sub>2</sub>/CNT is better than that before Ag adsorption, which may be related to the increased specific surface area after Ag NP addition. The enhanced adsorption is conducive to the improvement of photocatalytic performance. Moreover, the degradation activity of TiO<sub>2</sub> is gradually increased stemming from the successive introduction of CNTs and Ag. The photocatalytic degradation efficiency of TiO<sub>2</sub>/CNT composites reached ~96% in comparison to ~80% of TiO<sub>2</sub>. The degradation efficiency of Ag/TiO<sub>2</sub>/CNT composites was further increased in the initial 20 min and up to a final amount of ~98%. The effect of CNTs and Ag components in the TiO<sub>2</sub> matrix on the enhancement of photocatalysis should be taken into account to explain these results. Usually, the degradation follows the Langmuir–Hinshelwood reaction kinetics, that is, exponential concentration decay as a function of time. The reaction rate strongly depends on the properties of the photocatalysts, including the surface area, electron-transfer ability, and the addition amount. It is proposed that the improvement of the photocatalytic activity of Ag/TiO<sub>2</sub>/CNT composites is promoted by the double effects of CNTs and Ag.

The related mechanism for the photocatalytic reaction of Ag/TiO<sub>2</sub>/CNT composites is shown in Fig. 9. It is important to note that the Ag/TiO<sub>2</sub>/CNT composites consist of decorated titania layers on the surfaces of CNTs and subsequently modified Ag NPs on the titania layers. Therefore, the photocatalytic mechanism of such ternary structures of Ag/TiO<sub>2</sub>/CNT composites can be more reasonably explained. That is, excited photoelectrons that are yielded from the valence band to the conduction band (CB) of TiO<sub>2</sub> are transferred to the electron acceptors of CNTs and Ag, although there is another mechanism, reported by Wang *et al.* [15], that describes the CNTs used as sensitizers. CNTs can not only provide a large surface area to adsorb organic dye, but they can also present good electron acceptance for electron storage, resulting in the enhancement of the charge separation of photon-generated electron-hole pairs. In previous discussions, two contributions were thought to act on the photocatalytic efficiency of the TiO<sub>2</sub>-decorated CNT composition system. One is the chemical bond of Ti–O–C between TiO<sub>2</sub> and CNTs [29], and the other is the electronic configuration of CNTs. However, the characterisation and detailed effects have rarely been reported for

the former. In spite of the probable presence of Ti–O–C bonds in the composites owing to the small amount of hydroxyl of 1.63 wt % in hydroxylated CNTs and the chemical deposition of TiO<sub>2</sub>, the electron structure of the CNTs might still be the dominant factor in photocatalysis that we are focused on.

Furthermore, it has been reported that the bandgap of anatase is about 3.2 eV, with a CB position of about –4.21 eV using a vacuum level as a reference [9]. The work function of noble metal Ag is about 4.24 eV [30]. Also the work function of CNTs is similar to that of graphene (~4.7 eV), depending sensitively on the number of layers [31]. The difference in work functions between TiO<sub>2</sub> and Ag (or CNTs) leads to the formation of a junction called Schottky barrier [12], resulting in the transfer of electrons from TiO<sub>2</sub> to Ag and CNTs. Namely, the electrons photo-initiated from TiO<sub>2</sub> are believed to be captured by Ag deposition and CNTs and scavenged by O<sub>2</sub> species absorbed on the surfaces of the compositions, resulting in the extending of recombination times of electron-hole pairs for photocatalytic reactions [32].

**4. Conclusions:** In summary, we have successfully demonstrated that a kind of novel ternary multilayer-assembled structures of the Ag/TiO<sub>2</sub>/CNT composites is developed to optimise the photocatalytic properties of the composites. The combination of the chemical deposition and sonochemical reaction has been used for the fabrication of the compositions with the modification of TiO<sub>2</sub> onto CNTs and followed Ag dispersion. The morphologies, crystal type and structures of the composites are characterised by TEM, SEM, XRD, IR and UV–vis. Each component in the composites plays a critical role in the enhancement of the photocatalytic activity. The ternary Ag/TiO<sub>2</sub>/CNT composites exhibit a higher photocatalytic activity in comparison to that of TiO<sub>2</sub> and TiO<sub>2</sub>/CNT. A series of positive influence of the increased light absorption, organic dye adsorption, prolonged recombination time of electron-hole pairs, and improved electronic transfer on the composites is attributed to the unique structure of ternary Ag/TiO<sub>2</sub>/CNT composites through surface modification of CNTs with TiO<sub>2</sub> and TiO<sub>2</sub>–Ag junction. This kind of composite consists of carbon materials with various electronic properties and noble metal with optical characteristic is expected to be used as potential photocatalysts to extend light spectrum and enhance the photocatalytic activity for addressing various environmental issues.

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