

# C@Ag/TiO<sub>2</sub>: A Highly Efficient and Stable Photocatalyst Active under Visible Light

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## ABSTRACT

In this paper, preparation and characterization of C@Ag/TiO<sub>2</sub> nanospheres compound photocatalysts was reported. C@Ag nanosphere was firstly synthesized via hydrothermal reaction, and followed by a sol-gel process to obtain the functionalized C@Ag/TiO<sub>2</sub> nanosphere which has highly efficient visible light catalytic ability towards methyl orange (MO). The morphology of the obtained compound was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) technologies. From which we can see that the as-prepared samples show a spherical structure with a diameter of approximately 200 nm, and the silver particle in core was about 10 nm. The catalytic ability of the synthesized photocatalysts under visible light irradiation shows that C@Ag/TiO<sub>2</sub> possesses higher photocatalytic activity towards MO degradation than that of N-P25 (TiO<sub>2</sub>). Furthermore, the C@Ag/TiO<sub>2</sub> photocatalysts exhibited excellent reusability with almost no change after five runs. Finally, the possible photocatalytic mechanism of catalyst under visible light was discussion and proposed.

**Keywords:** Nanoparticles; Sol-Gel Preparation; Visible Light Photocatalyst; Surface Plasma Resonance

## 1. Introduction

The photocatalysis technique has a promising application prospect in pollutant decomposition and hydrogen evolution via the generation of •OH radicals and other oxidative species [1-3]. The semiconductor TiO<sub>2</sub> is considered as one of the best photocatalysts. However, the light response range and the photo-efficiency of TiO<sub>2</sub> are limited because of its wide band gap (3.2 eV) [4,5]. Therefore, the creation of simple, efficient, and sustainable photocatalysts that work well with visible light is a major challenge in this research field [6-8]. Until now, several methods have been reported to improve the photo-catalyzed efficiency of TiO<sub>2</sub>. Among them, surface modification via the addition of metals which can enhance the photocatalytic activities is widely studied, and many metals, such as Pd, Pt, Rh, Ru, Ag, have been investigated to extent the absorption wavelength of noble-metal/TiO<sub>2</sub> compounds into the visible region [9-14]. The reason is that deposition of metals on the surface of TiO<sub>2</sub> would produce traps to capture the photo-induced electrons or holes, leading to the reduction of electron-hole recombination and thus improving the photocatalytic efficiency [15]. Because of non-toxic, relatively inexpensive and obvious modification effect, loading Ag to improve the TiO<sub>2</sub> catalytic activity has been raised ex-

tensive attention. However, a problem is that Ag nanoparticles, which are chemically very reactive, would be easily oxidized when directly contact with TiO<sub>2</sub>. Romanjuk *et al.* confirmed that Ag could have been oxidized at the Ag-TiO<sub>2</sub> interface to form eventually a 10 nm thick layer of silver oxide (AgO) at room temperature by employing time-of-flight secondary ion mass spectroscopy [16]. To prevent this oxidation, a passive material, such as SiO<sub>2</sub>, must be coated on the surface of Ag nanoparticles so as to separate them from TiO<sub>2</sub>. Zhang *et al.* reported core/shell nanofibers of TiO<sub>2</sub>@carbon embedded by Ag nanoparticles with well-dispersed distribution of small Ag NPs in the carbon layer [17]. However, as the near-field amplitude decays in a rough estimation exponentially with the distance from the nanoparticles surface, the protection layer has to be kept sufficiently thin [18].

In this paper, we prepared C@Ag nanospheres by a simple hydrothermal method, and then using the sol-gel, C@Ag/TiO<sub>2</sub> composite visible light catalyst was synthesized. MO was used simulation pollutant, and the degradation experiments of the photocatalysts were carried out under visible light. The results showed the photocatalytic activity of the C@Ag/TiO<sub>2</sub> composite is 3 times higher than that of N-P25. Moreover, stability test showed that the composite photocatalyst is almost inactivating even after five cycles and the good stability is due to the protective effect of the coated carbon layers.

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## 2. Experimental Section

### 2.1. Preparation of the Catalysts

A solution of  $\text{AgNO}_3$  (1 mL, 0.02 M) was added to a glucose solution (40 mL, 0.5 M) with stirring to form clear solutions, which was placed in a 50 mL Teflon-sealed autoclave and maintained at  $180^\circ\text{C}$  for 12 h [19]. The precipitate was collected and washed with distilled water and absolute alcohol three times, respectively, and oven-dried at  $80^\circ\text{C}$  for 24 h.

$\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  (3 mL, Aldrich, 97%) and isopropyl alcohol (40 mL) mixed solution added dropwise to a solution of  $\text{HNO}_3$  (50 mL, pH = 1.0) containing an amount of C@Ag, after aged for 10 h at room temperature, and then dried at  $110^\circ\text{C}$  for 20 h. The resultant gel was calcined at  $500^\circ\text{C}$  for 2 h under a nitrogen atmosphere, which was denoted as CAT-X (X denotes percentage content of C@Ag).

### 2.2. Characterization of the Catalysts

The surface morphology was examined by a scanning electron microscopy (LEO1530VP, LEO), and a transmission electron microscopy (JEOL, JEM2010). UV-Vis diffuse reflection absorption spectra (UV-Vis/DRS) of the samples were recorded by an UV-Vis spectrometer (U3010, Hitachi) equipped with an integrating sphere accessory in the diffuse reflectance mode (R) and  $\text{BaSO}_4$  as a reference material. The chemical nature of C, Ag, Ti, O have been studied by X-ray photoelectron spectroscopy (XPS) in Krato Axis Ultra DLD spectrometer with Al K $\alpha$  X-ray ( $h\nu = 1486.6$  eV) at 15 kV and 150 W. The binding energy was referenced to C 1s line at 284.6 eV for calibration.

### 2.3. Photocatalyst Reaction

The photocatalytic reaction was conducted in the XPA-II photochemical reactor (Nanjing Xujiang Machine-electronic Plant). A 500 W Xe lamp was used as the simulated solar light source, and a house-made filter was mounted on the lamp to eliminate infrared irradiation. MO (20 mg/L) was used as contamination [12]. 20 mg photocatalyst powder was dispersed in 200 mL reaction solutions by ultrasonating for 15 min, then the suspension was magnetically stirred in dark for 1 h. Air was blown into the reaction medium at a flow rate of 200 mL/min during the photocatalytic reaction. One 8 mL of the suspension was sampled and filtered. The concentration of the remaining MO was measured by a Hitachi UV-3010 spectrophotometer. The degradation ratio was calculated by  $X = (A_0 - A)/A_0 \times 100\%$ .

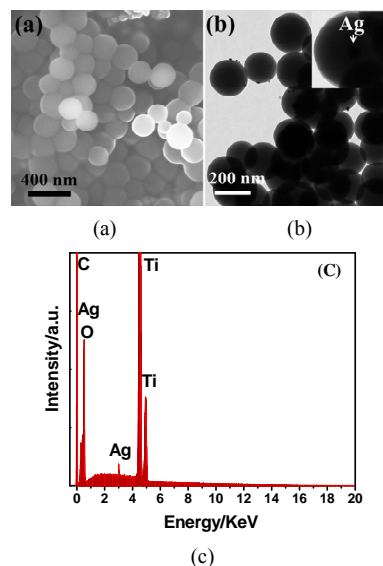
## 3. Results and Discussion

### 3.1. Morphology and Structures of the Samples

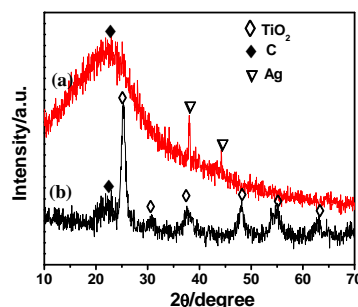
The morphology of the C@Ag/TiO<sub>2</sub> sample is examined

by SEM and TEM, and the images are shown in **Figure 1**. From SEM image, it is clear that C@Ag/TiO<sub>2</sub> is composed of many monodispersed spherical particles with a diameter of about 200 nm (shown in **Figure 1(a)**). The spheres are relatively uniform with very smooth surface. **Figure 1(b)** is a TEM image of C@Ag/TiO<sub>2</sub> sample and the samples shows spherical particles morphology. The diameters are approximately 200 nm, which is in agreement with the result of SEM. It is interesting that the middle of Ag nucleus can clearly be seen after magnified (shown in **Figure 1(b)** inset). A diameter is approximately 10 nm. The energy dispersive spectroscopic (EDS) analysis (**Figure 1(c)**) of the C@Ag/TiO<sub>2</sub> sample reveals the existence of C, Ag, O, and Ti elements. The element content of C, Ag, O, and Ti in the compounds investigated with the results of EDX is 5.35, 0.20, 31.55, 62.90 at%, respectively. It reveals that the samples were consists of C, Ag and TiO<sub>2</sub>.

**Figure 2** displays the XRD patterns of the prepared C@Ag and C@Ag/TiO<sub>2</sub> samples. **Figure 2(a)** exhibits the characteristic diffraction peaks of Ag (JCPDS file No.



**Figure 1.** SEM (a), TEM (b) and EDS (c) image of C@Ag/TiO<sub>2</sub>.

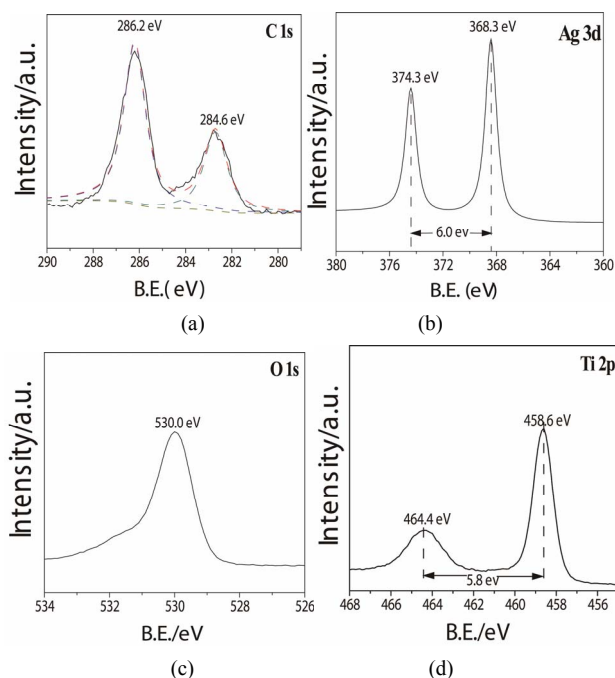


**Figure 2.** XRD patterns of C@Ag and C@Ag/TiO<sub>2</sub> composite photocatalysts.

65-2871) [20] and C, respectively. **Figure 2(b)** shows the characteristic diffraction peaks of anatase TiO<sub>2</sub> (JCPDS file No. 84-1286) [8] expect for Ag and graphitic carbon [17]. The XRD results suggest the obtained samples had three phases of Ag, C and TiO<sub>2</sub>.

The chemical states of C, O, Ti, and Ag in the prepared samples were investigated by XPS. **Figure 3** shows the high-resolution C 1s, O 1s, Ti 2p and Ag 3d XPS spectra of C@Ag/TiO<sub>2</sub> samples, respectively. The C 1s spectrum is deconvoluted into two peaks 284.6 and 286.2 eV. The C 1s peak at 284.6 eV is assigned to the sp<sup>2</sup> C-C bond [21], and the C 1s peak at 286.2 eV is assigned to the sp<sup>2</sup> C = C bond [22]. The XPS spectrum of Ag 3d in **Figure 3(b)** shows that the 3d<sub>5/2</sub> and 3d<sub>3/2</sub> signals are located at 368.4 eV and 374.4 eV, respectively, and the splitting of the 3d doublet is 6.0 eV. This indicates that the deposited Ag mainly exists in the Ag<sup>0</sup> state on the TiO<sub>2</sub> nanotube surface [23]. The O 1s core level peaks at 530.0 eV come from Ti-O-Ti linkages in TiO<sub>2</sub> (**Figure 3(c)**), which is consistent with that of the reports [24]. The pair of peaks of Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> appeared at 458.7 and 464.4 eV, respectively, and the splitting of the 3d doublet is 5.8 eV, which can be assigned to Ti<sup>4+</sup> 2p peaks of TiO<sub>2</sub> (**Figure 3(d)**) [22]. These results further confirm that the obtained sample is composed of C@Ag/TiO<sub>2</sub>.

The UV-vis diffuse reflectance spectra of N-P25 and C@Ag/TiO<sub>2</sub> is shown in **Figure 4**. It can be clearly seen that C@Ag/TiO<sub>2</sub> has a strong visible light absorption ranged from 400 nm to 800 nm, which is stronger than that of N-P25. Furthermore, absorption edge is red



**Figure 3.** XPS of the obtained sample C@Ag/TiO<sub>2</sub>: (a) C 1s; (b) Ag 3d; (c) O 1s; (d) Ti 2p.

shift. These imply that C@Ag/TiO<sub>2</sub> have higher visible light photocatalytic activity than N-P25.

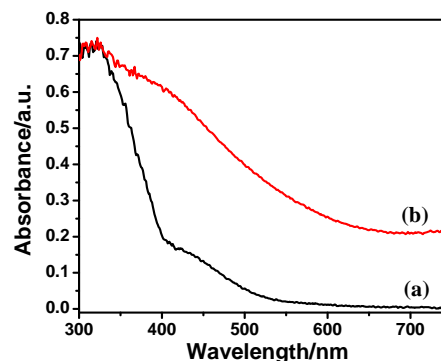
### 3.2. Photocatalytic Activities of Samples

**Figure 5** shows the photocatalytic activity of the as-prepared samples in decomposing organic pollutant MO under visible light irradiation. The photocatalytic activities of C@Ag/TiO<sub>2</sub> are all better than that of N-P25. The degradation ratios of MO go up and then get down with the content of C@Ag increasing, which indicates that the content of C@Ag can effectively influence the photocatalytic activity of the obtained catalysts. Furthermore, compared with other catalysts, CAT-2 exhibits the optimal photocatalytic activity under visible light irradiation, which is 3 times than that of N-P25.

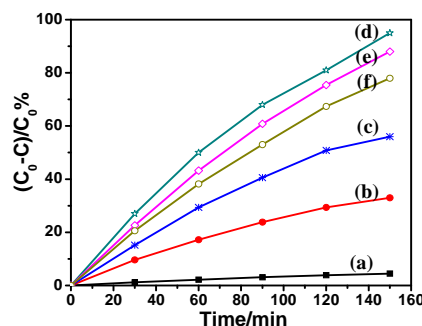
The reusability of CAT-2 towards MO photocatalytic decomposition under visible light irradiation is shown in **Figure 6**. No obvious loss of activity was observed after five cycles, which suggests that the prepared C@Ag/TiO<sub>2</sub> has excellent stability and can be used as a recyclable photocatalyst.

### 3.3. Discussion on the Reaction Mechanism

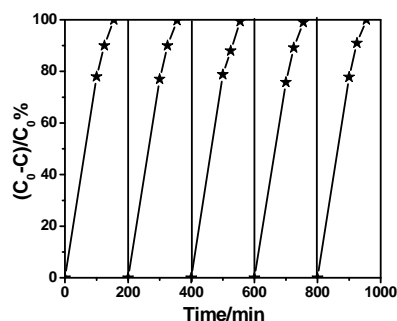
In order to analyze the mechanism of the above performance, we depicted the basic structure of the C@Ag



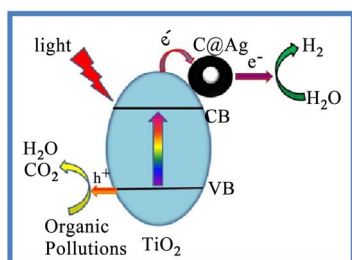
**Figure 4.** UV-vis absorption spectra of as-obtained samples: (a) N-P25; (b) C@Ag/TiO<sub>2</sub>.



**Figure 5.** Photocatalytic activities of as-obtained samples under visible light irradiation: (a) No catalyst; (b) N-P25; (c) CAT-1; (d) CAT-2; (e) CAT-3; (f) CAT-5.



**Figure 6. Reusability of CAT-2 for MO photocatalytic decomposition under visible light irradiation.**



**Figure 7. Mechanism schematic of C@Ag/TiO<sub>2</sub> compound photocatalyst under visible light irradiation.**

modified TiO<sub>2</sub> and the main charge-transfer processes between TiO<sub>2</sub> and C@Ag after being activated under visible light irradiation was proposed (Figure 7). The achieved high efficiency may be attributed to three major improvements. Firstly, the more content of C@Ag in the compound, can not only improve the absorption of visible light, the rapid transfer of photogenerated electron, but also effectively reduce the recombination rates of electron and holes which can afford more photogenerated electron-hole. Secondly, the silver nanoparticles are not likely to be oxidized under the protection of the carbon layer, which is good for the stability of the obtained C@Ag/TiO<sub>2</sub> photocatalysts under visible light irradiation. Thirdly, localized surface plasmon resonance effect was significantly enhanced photocatalytic effect.

#### 4. Conclusion

A new the C@Ag/TiO<sub>2</sub> composite photocatalyst is prepared by a simple hydrothermal method and sol-gel, photocatalytic activity was significantly enhanced under visible light irradiation. The as-prepared photocatalyst exhibits good stability. Good conductive properties of C@Ag nanoparticles and localized surface plasmon resonance effect are to promote the main reason for the enhanced photocatalytic activity.

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