

## Research Article

# Preparation and Photocatalytic Performance of $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$ Ternary Nanocomposites

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$\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  nanocomposites were synthesized via the decomposition of a mixture of  $\text{Ti}_3\text{C}_2$  (a novel two-dimensional carbide) and cupric nitrate under an argon atmosphere. The morphology and structures of the obtained samples were characterized. X-ray diffraction and energy dispersive spectrometer analysis indicate that the sample is composed of  $\text{Ti}_3\text{C}_2$ , anatase- $\text{TiO}_2$ , and  $\text{CuO}$ . Scanning electron microscopy images show that  $\text{CuO}$  and  $\text{TiO}_2$  nanoparticles were evenly distributed on the surface of  $\text{Ti}_3\text{C}_2$ . The particles size increased with an increase in the cupric nitrate content. Photocatalytic degradation of methyl orange shows that the  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  nanocomposite has good photocatalytic degradation efficiency. A possible photocatalytic mechanism of the  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  nanocomposites was proposed. The data indicated that  $\text{CuO}$  and  $\text{Ti}_3\text{C}_2$  effectively promote the separation of photoelectrons from vacancies.

## 1. Introduction

Industrial wastewater has become one of the major factors in water pollution, and in particular, wastewater from dye industries is difficult to treat. Of the various techniques for cleaning the environment, photocatalytic degradation has been widely researched to treat pollutants that are difficult to degrade.  $\text{TiO}_2$  and  $\text{ZnO}$  are the most widely studied photocatalysts [1, 2]. To improve the photocatalysis efficiency of  $\text{TiO}_2$ , binary nanocomposites, such as  $\text{TiO}_2/\text{metal}$  (Ag [3, 4], Au [5, 6], and Pt [7]),  $\text{TiO}_2/\text{graphene}$  [8–10],  $\text{TiO}_2/\text{ZnO}$  [11],  $\text{TiO}_2/\text{CuO}$  [12],  $\text{TiO}_2/(\text{CdSe}, \text{CdS}, \text{and CdSeS})$  [13, 14], and  $\text{TiO}_2/\text{SnO}_2$  [15, 16], have been extensively studied, and the results show that the binary nanocomposites perform better than the single components. Less research has been done on ternary nanocomposites [17] than on binary nanocomposites.  $\text{Ti}_3\text{C}_2$  is a member of a family of novel two-dimensional carbides or carbonitrides called MXenes, which are synthesized by etching an A-group element from the corresponding MAX phase using hydrofluoric acid [18]. Because of its special laminated structure,  $\text{Ti}_3\text{C}_2$  has been widely researched in many fields [19–23]. However, the resistance to oxidation

of  $\text{Ti}_3\text{C}_2$  is not good. Under hydrothermal conditions or in an oxygen atmosphere, the surface of  $\text{Ti}_3\text{C}_2$  easily oxidizes to form  $\text{TiO}_2$  at temperatures above  $100^\circ\text{C}$  [18, 24, 25]. Hence,  $\text{Ti}_3\text{C}_2$  can be used as a precursor for  $\text{TiO}_2$  and as a carrier for other oxides.

In this study,  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  ternary nanocomposites were successfully fabricated using cupric nitrate decomposition with  $\text{Ti}_3\text{C}_2$  under an argon atmosphere. The photocatalytic performance of  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  was studied using MO as a simulated pollutant. The results show that the  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  ternary composite has good catalytic activity for MO photodegradation.

## 2. Experimental

In these experiments, 0 g, 0.005 g, 0.01 g, 0.02 g, and 0.04 g of cupric nitrate were each dissolved in 1 mL of deionized water, and then 1 g of  $\text{Ti}_3\text{C}_2$  powder (prepared according to the literature [18]) was added. The mixture was kept at room temperature for 24 h and then dried at  $70^\circ\text{C}$  in a vacuum. The  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  nanocomposites were synthesized by annealing the mixture under an argon atmosphere at  $500^\circ\text{C}$

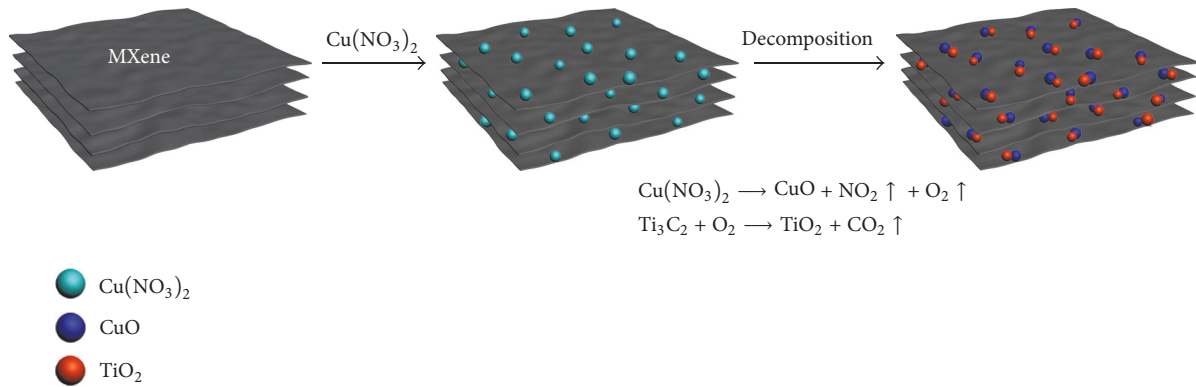


FIGURE 1: Procedure for synthesizing the  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  nanocomposite.

for 30 min. The heating rate was set at  $10^\circ\text{C}/\text{min}$ . The obtained samples were denoted as sample a, sample b, sample c, sample d, and sample e according to cupric nitrate masses, respectively.

The detailed procedure is represented schematically in Figure 1. In this process, the chemical reaction for the formation of  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  may be expressed as follows:



The crystal structure of the obtained samples was characterized using powder X-ray diffraction (XRD, Philips X'Pert-MPD system,  $\text{Cu K}\alpha$  radiation). The morphology and microstructures of the samples were examined using a Quanta 250 field emission gun scanning electron microscope (FEI Quanta 250 FEG-SEM) equipped with a Bruker Nano GmbH with an X-Max  $30\text{ mm}^2$  detector energy dispersive X-ray spectrometer (Bruker Quantax 200 XFlash 6 | 30 EDS).

The photocatalytic activity of the samples was evaluated for the photodegradation of MO (20 mg/L) under UV illumination. First, the obtained powder catalyst (100 mg) was dispersed in a solution of MO (100 mL) and was magnetically stirred in the dark for 30 min to establish the adsorption equilibrium. The whole photocatalytic reaction was carried out at  $10^\circ\text{C}$ . The solution was then irradiated with a 175 W mercury lamp light (GGZ175, Shanghai Jiguang Special Lighting Electrical Appliance Factory, China). 5.0 mL of solution was transferred every 10 min, centrifuged to remove the catalyst, and then analyzed using a UV-vis spectrophotometer (TU-1900, Beijing Purkinje General Instrument Co. Ltd., China).

### 3. Results and Discussion

XRD results of the samples are shown in Figure 2. The peaks detected at  $2\theta = 9.02^\circ$ ,  $18.2^\circ$ , and  $27.5^\circ$  were assigned as the diffraction peaks of  $\text{Ti}_3\text{C}_2$  [20]. The peaks at  $25.34^\circ$ ,  $37.90^\circ$ ,  $48.17^\circ$ ,  $54.02^\circ$ , and  $55.16^\circ$  were indexed to the (101), (004), (200), (105), and (211) planes, respectively, of anatase- $\text{TiO}_2$  (JCPDF Number 21-1272). This means  $\text{Ti}_3\text{C}_2$  was partially oxidized to  $\text{TiO}_2$  after treatment at  $500^\circ\text{C}$  for 30 min. The

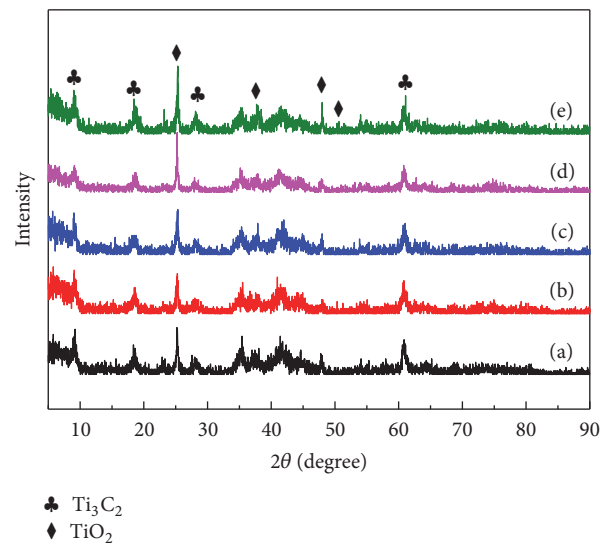


FIGURE 2: XRD patterns of the as-prepared samples.

oxygen came from the adsorbed water and the thermal-decomposition of cupric nitrate. Because of the low content and the small crystalline size of  $\text{CuO}$  in the nanocomposites, the XRD signal was weak and may have been covered by the robust signal of  $\text{TiO}_2$  and  $\text{Ti}_3\text{C}_2$ . Thus, the diffraction peaks of  $\text{CuO}$  were not observed.

SEM images of samples a–e are shown in Figures 3(a)–3(e). Figure 3(a) is the SEM image of the sample which was obtained by  $\text{Ti}_3\text{C}_2$  that was kept at  $500^\circ\text{C}$  for 30 min under an argon atmosphere. It can be observed that the sample had a smooth surface with small nanoparticles, which may be  $\text{TiO}_2$ . Figures 3(b)–3(e) show the SEM image of the  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  ternary nanocomposites. From these figures, it can be seen that a large number of  $\text{CuO}$  and  $\text{TiO}_2$  nanoparticles were densely connected to one another on the surface of the  $\text{Ti}_3\text{C}_2$  nanosheets. With an increase in the cupric nitrate content, the density of the particulates on  $\text{Ti}_3\text{C}_2$  increased. The increase of the size of the nanoparticles (see Figures 3(d) and 3(e)) indicates an agglomeration of nanoparticles. It can be also observed that the thickness of

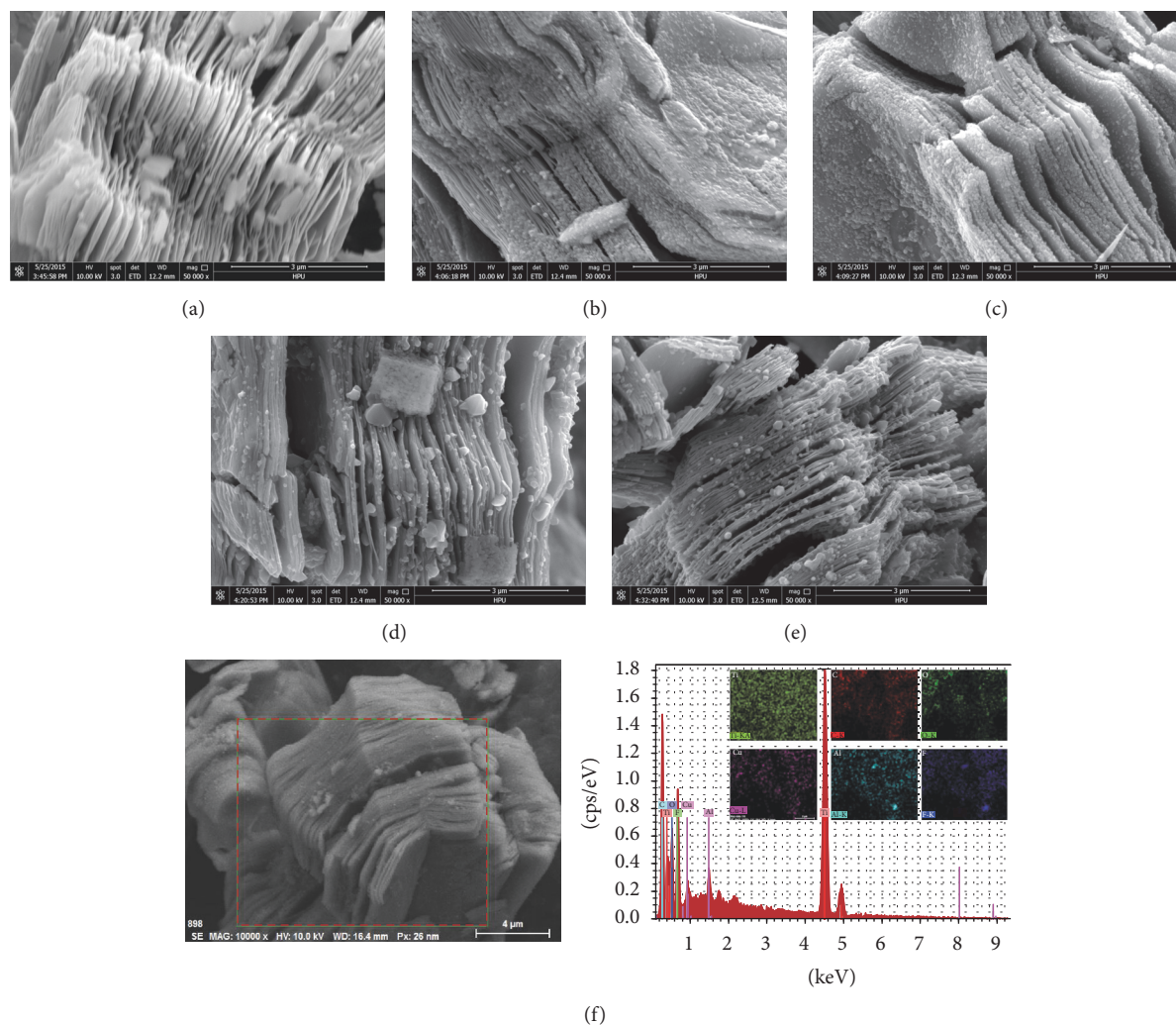


FIGURE 3: SEM images of the samples: (a)  $\text{Ti}_3\text{C}_2$ , (b–e)  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  (samples a–d), and (f) EDS spectra and mapping of the marked domain in (f).

the layer increased. In order to observe the distribution of different elements, sample c was further identified using EDS mapping analysis of Ti, C, O, Cu, Al, and F in SEM from the selected areas in Figure 3(f). The results show that  $\text{CuO}$  was distributed evenly on the surface of  $\text{Ti}_3\text{C}_2$ .

The photocatalytic activities of the samples were measured, and the results are shown in Figure 4. It can be seen that the  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  nanocomposites have good photocatalytic activity. The MO quickly degraded to about 99% in 80 minutes with sample c as the catalyst. The photocatalytic activity of the nanocomposites was enhanced with an increase in the cupric nitrate content and was best when 0.01 g of cupric nitrate was added. After that, with an increase in the mass of cupric nitrate, agglomeration occurred and led to a decrease in the photocatalytic performance.

A possible photocatalytic mechanism of the  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  nanocomposites is shown in Figure 5. The band gap between the  $\text{TiO}_2$  valance band (VB) and the conduction band (CB) is 3.2 eV. Under UV radiation, an electron and

hole are generated on the surface of  $\text{TiO}_2$  and  $\text{CuO}$ . Because the CB of  $\text{CuO}$  is situated below that of  $\text{TiO}_2$ , the electrons in the CB of  $\text{TiO}_2$  are easily transferred to the CB of  $\text{CuO}$ . On the other hand, the photoelectrons of  $\text{TiO}_2$  and  $\text{CuO}$  are transferred promptly by  $\text{Ti}_3\text{C}_2$  because of its good electron conductivity which lowers the electron-hole recombination rate. Analysis indicates that  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  exhibited a more effective electron-hole separation under UV radiation. Thus, the surface redox process by photogenerated electrons and holes occurs more easily, and, correspondingly, the photocatalytic activity of the samples significantly improved.

#### 4. Conclusion

$\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$  ternary nanocomposites were fabricated via cupric nitrate decomposition on the surface of  $\text{Ti}_3\text{C}_2$ . Analysis indicates that the samples were composed of  $\text{Ti}_3\text{C}_2$  nanosheets,  $\text{TiO}_2$ , and  $\text{CuO}$  nanoparticles. The photocatalytic degradation experiments showed that the  $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{CuO}$

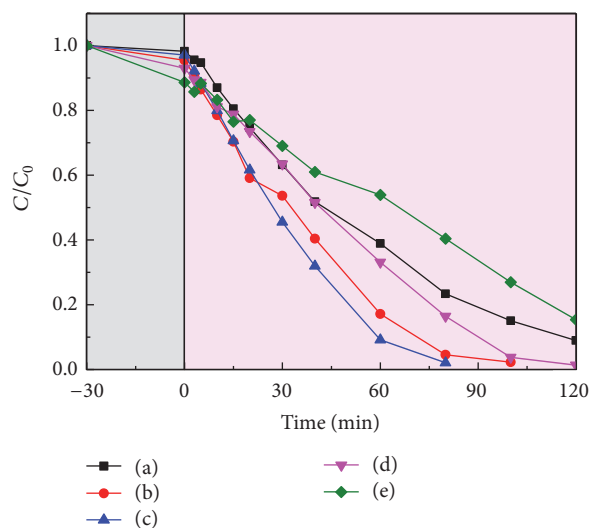


FIGURE 4: Curves of  $C/C_0$  versus time for the photodegradation of MO with samples a–e.

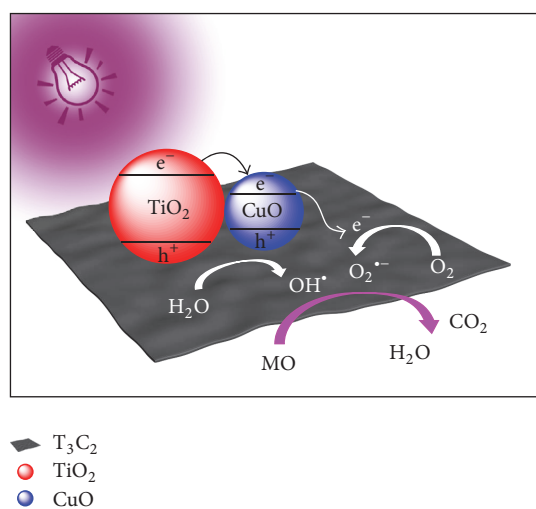


FIGURE 5: Schematic illustration of a possible photocatalytic mechanism of the  $Ti_3C_2/TiO_2/CuO$  nanocomposites.

nanocomposite has a better efficiency of electron-hole separation than  $TiO_2$ , and this significantly improved the photocatalytic activity of the nanocomposites.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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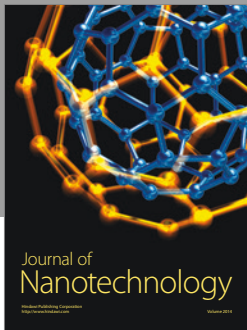
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