Photocatalytic TiO\textsubscript{2}/rGO/CuO Composite for Wastewater Treatment of Cr(VI) Under Visible Light

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Abstract The harm of chromium pollution to the environment has caused a widespread concern; hexavalent chromium is a toxic, cancerogenic, and genetically mutagenic contaminant to the human body; by contrast, trivalent chromium is almost non-toxic to the human body; therefore, it is a feasible method to reduce hexavalent chromium to trivalent chromium. Photocatalysis is a new environmentally friendly and harmless technology, which can transform pollutants into non-toxic or less toxic products. In this study, we synthesized TiO\textsubscript{2}/rGO/CuO ternary nanocomposites to treat hexavalent chromium pollution under visible light. Under optimal conditions, the photoreduction efficiency of 100 ppm hexavalent chromium solution could reach 100\% in 80 min. The photoreduction rate of hexavalent chromium is 29.4 times than that of pure TiO\textsubscript{2}. The photocatalytic property of CuO in TG2C8 nanocomposites is attributed to accelerate the separation of electrons and holes and the efficient electron transfer through the rGO framework. We believe that TiO\textsubscript{2}/rGO/CuO composites have great potential in wastewater treatment.

Keywords Wastewater treatment · TiO\textsubscript{2} nanorods · CuO nanoparticles · Photocatalysis · Visible light irradiation

1 Introduction

The rapid growth of the battery industry, ceramics, mining, and global plastic production causes pollution of all kinds of heavy metals (Cr, Sb, Au, Ag, Hg, Pb, etc.) which threatens the environment and human health (Zhan et al. 2018; Wang et al., 2018a; Li et al. 2018). Chromium pollution, due to mining, electroplating, pigment production, wood preservation, tanning, and metallurgy, has become a key issue in aquatic ecosystems (Jiang et al. 2019; Guan, et al. 2019; Rahmat et al. 2020). Chromium exists mainly in water in two valence states: hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). By contrast, Cr(VI) is a toxic, cancerogenic, and mutagenic contaminant to creatures (Lyu et al. 2019; Yuan et al. 2019a; Wang et al. 2019). The US Environmental Protection Agency stipulates that the maximum concentration of Cr(VI) in surface water is 0.1 ppm and drinking water is 0.05 ppm (Lyu et al. 2019; Qiu et al. 2015). Compared with Cr(VI), Cr(III) is almost non-toxic and is a vital micronutrient for the human body. Cr(III) is easily chelated by natural clay or converted to Cr(OH)\textsubscript{3} and precipitated from water ($K_{\text{sp}}$(Cr(OH)\textsubscript{3}) = 6.3 × 10\textsuperscript{-31}) (Barrera-Diaz et al. 2012; Zhang et al. 2014; Zhang et al. 2018; Wang et al. 2018b). Therefore, it is a
feasible method to reduce Cr(VI) to Cr(III). Liang et al. synthesized Ag/ZnO@CF with a 3D hierarchical porous structure, which exhibited significant photocatalysis activity because of the enhanced mass transfer and cocatalyst-facilitated charge separation, and the Ag/ZnO@CF could remove 54.54% of Cr(VI) (20 mg mL$^{-1}$) from wastewater after 3 h (Liang et al. 2020). Wang et al. synthesized CoS$_2$/g-C$_3$N$_4$-rGO nanocomposites by a one-pot solvothermal method, and 99.8% of Cr(VI) (20 mg mL$^{-1}$) can be reduced within 120 min (Wang et al. 2020). Photocatalytic technology is a new environmentally friendly technology to convert pollutants in wastewater into harmless products (Froschl et al. 2012; Wang et al. 2009; Setvín et al. 2013). Semiconductor materials recently emerge as efficient heterogeneous photocatalysts. As a chemically stable, non-toxic, and non-polluting semiconductor material (Chen et al. 2017; Lv et al. 2019; Fan et al. 2019; Kumar et al. 2019), TiO$_2$ exhibits excellent performance in photocatalysis (Barkhade and Banerjee 2019; Zielinska-Jurek et al. 2017; Yang et al. 2019; Noreen et al. 2019). However, due to its high electron-hole pair recombination rate and the low utilization of visible light, its application in real life is greatly limited (Liu et al. 2020; Kar et al. 2019; Méndez-Medrano et al. 2016). The problem can be solved by extending the range of optical response, for example, coupling with narrow bandgap semiconductors (Mei et al. 2019; Tahir et al. 2019). CuO is a low-bandgap p-type semiconductor material that is cheap and non-toxic. It also has good optical, electrical, and catalytic properties with a narrow energy gap of 1.2–1.7 eV (de Brito et al. 2018; Méndez-Medrano et al., 2016; Mosleh et al. 2018; Chauhan et al. 2019). Graphene is the most emerging material in the current decade. In recent years, graphene has been applied to photocatalytic materials, due to its large surface area, high electron mobility, strong adsorption capacity, and easy chemical modification (Kamat, 2011; Yuan et al. 2019b; Guo et al. 2019).

In this study, we used the advantages of CuO, combining with GO, and synthesized TiO$_2$/rGO/CuO nanocomposites by a hydrothermal method. CuO can make electron-hole pairs separate faster, and the rGO framework can make electron transfer faster. We evaluated the photocatalytic property of the catalyst by testing the reduction performance of Cr(VI), and the results show that the TiO$_2$/rGO/CuO nanocomposites showed excellent property under visible light.

2 Experimental Methods

2.1 Materials

Graphite powders (325 mesh) and titanium dioxide (TiO$_2$, 99.0%) were purchased from Aladdin Corp (Shanghai, China). Sulfuric acid (H$_2$SO$_4$) and phosphoric acid (H$_3$PO$_4$) were purchased from Fengchuan Chemical Reagent Co., Ltd. (Tianjin, China). KOH, NaOH, HCl (37%), ethanol, CuSO$_4$·5H$_2$O, NH$_3$·H$_2$O, K$_2$Cr$_2$O$_7$, NaNO$_3$, acetone, H$_2$O$_2$ (30%), and KMnO$_4$ were purchased from Zhiyuan Chemical Co., Ltd. (Tianjin, China). They were used as received. Deionized water was used in all experiments.

2.2 Preparation of GO and TiO$_2$ NRs

TiO$_2$ nanorods (NRs) were synthesized by a hydrothermal method. TiO$_2$ (3 g) was dispersed in a KOH solution (10 mol L$^{-1}$) and stirred. Then, the mixture was transferred to a 100 mL autoclave, which was heated up to 180 °C for 24 h, then washed the product with water and ethanol to remove impurities, then dried the composite, and annealed in a muffle furnace at 500 °C for 4 h, and white TiO$_2$ powder was obtained. Graphene oxide (GO) was prepared by the same method as that in the reference (Cao et al. 2018). The calculated concentration of GO is 5 mg mL$^{-1}$.

2.3 Preparation of TiO$_2$/rGO/CuO

TiO$_2$/rGO/CuO (TGC) nanocomposites were prepared by a hydrothermal method. GO aqueous solution (0.2 mL, 5.0 mg mL$^{-1}$) was well dispersed into deionized water (10 mL) by ultrasonic treatment for 30 min. CuSO$_4$·5H$_2$O (0.08 g) and TiO$_2$ NRs (0.2 g) were added to the dispersion, and then continued stirring for 240 min, forming a stable gray suspension. Subsequently, NH$_3$·H$_2$O (0.3 mL) and NaOH (4.0 mL, 0.1 g mL$^{-1}$) solutions were added to the above suspension. Afterward, the above mixture was placed in a 25-mL autoclave, which was heated up to 140 °C for 4 h, and then
washed the composite with deionized water and ethanol to pH = 7, then dried the composites and annealed up to 400 °C for 2 h in an Ar atmosphere.

In comparison, a series of products with additive amount of CuSO₄·5H₂O and GO were prepared in the same way. The composite is denoted as TGₓCᵧ, where x and y represent the amount of GO aqueous solution in volume and CuSO₄·5H₂O in weight, respectively and compared their photocatalytic property. The reagent composition of the samples is shown in Table 1.

2.4 Characterization of TiO₂/rGO/CuO Nanocomposites

The crystal structure was recorded by an X-ray diffractometer (XRD, Rigaku Ultima IV, Japan) with Cu Kα source radiation (λ = 0.1542 nm). The bonding information of the composites was confirmed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, American Thermo Fisher Scientific) equipped with Al Kα radiation (1486.6 eV). The chemical compositions of the composites were examined by Fourier transform infrared (FTIR, Prestige-21, Shimadzu, Japan) spectroscopy. Measurements of Raman spectra were performed on an XperRam Compac Raman spectrometer with excitation laser beam wavelength of 532 nm. The morphology of composites was captured by scanning electron microscopy (SEM, S-4800 Hitachi, Japan) and high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 F20, America) with an HAADF detector. The absorbance was tested by a UV-Vis spectrometer (UV-2550, Shimadzu). The UV-Vis diffuse reflectance spectra (UV-vis DRS) of the nanocomposites in the range of 250–800 nm were measured by using a U-3010 spectrophotometer with BaSO₄ as a reference.

### Table 1 Reagent composition of the samples

| Sample | GO (mL) | CuSO₄·5H₂O (g) | TiO₂ (g) |
|--------|---------|----------------|----------|
| TG1C8  | 0.1     | 0.08           | 0.2      |
| TG2C8  | 0.2     | 0.08           | 0.2      |
| TG3C8  | 0.3     | 0.08           | 0.2      |
| TG4C8  | 0.4     | 0.08           | 0.2      |
| TG2C0  | 0.2     | 0          | 0.2      |
| TG2C4  | 0.2     | 0.04           | 0.2      |
| TG2C16 | 0.2     | 0.16           | 0.2      |

2.5 Photocatalytic Reduction of Cr(VI)

The method of reducing Cr(VI) is the same as that of Mei et al. (2019).

3 Results and Discussion

3.1 XRD

XRD results (Fig. 1) for the TGC samples confirm the presence of CuO crystallites (JCPDS 41–0254) (Zhang et al. 2008) and TiO₂ in anatase phase (JCPDS 21–1272) (Wang et al. 2011). Two peaks at 2θ = 35.8° and 38.4° in the XRD pattern correspond to CuO, which are the (002) and (101) planes, respectively. The strength of these characteristic peaks was significantly enhanced with the increase of added CuSO₄·5H₂O. However, the characteristic peak of GO was not found on XRD, because the amount of GO is too small and the insertion
of TiO₂ and CuO destroyed the conventional accumulation of rGO.

3.2 FTIR and Raman

The FTIR spectrum (Fig. 2a) of TG2C8 exhibits characteristic vibrations at 3430 cm⁻¹ (OH stretch) and 1580 cm⁻¹ (OH in-plane bend) for TiO₂ (Chen et al. 2010), the skeleton vibration of GO is at 2320 cm⁻¹; the stretching vibration of CuO bond is at 470 cm⁻¹ (Gusain et al. 2016). The Raman spectrum of TG2C8 (Fig. 2b) shows a characteristic peak of CuO at 276 cm⁻¹, at the same time. TiO₂ peaks can be found at 360, 445, and 660 cm⁻¹. In the Raman spectra, the characteristic peaks at 1351 cm⁻¹ and 1589 cm⁻¹ are corresponding to the D and G peaks of graphene, respectively. These two peaks feature sp³ defects and amorphous structure of carbon atoms of graphene (D peak) and sp²-bonded carbon atoms in the plane (G peak) (Perera et al. 2012; Zhang et al. 2010).

3.3 XPS

The surface bonding state of the composite material is evaluated by XPS analysis (Nguyen et al. 2019). The survey spectrum (Fig. 3a) of TG2C8 shows the photoelectron peaks of titanium, oxygen, carbon, and copper. In the Ti 2p spectra of TG2C8 (Fig. 3b), the Ti 2p₁/₂(464.1 eV) and Ti 2p₃/₂(458.5 eV) (ΔBE = 5.6 eV) belong to Ti(IV) (Mei et al. 2019). In the Cu 2p spectra of TG2C8 (Fig. 3c), the Cu 2p₁/₂ (954.2 eV) and Cu 2p₃/₂ (934.2 eV) (ΔBE = 20.0 eV) belong to Cu(II) (Shi et al. 2019). The C 1s spectrum (Fig. 3d) of TG2C8 displays two components at 284.8 eV and 288.3 eV. C–H and C–C carbons of rGO skeleton at 284.8 eV, and the peak at about 288.3 eV belong to C=O of rGO (Tung et al. 2012).

3.4 SEM and TEM

In the SEM (Fig. 4a) and HRTEM (Fig. 4b) images of TG2C8, we observed the TiO₂ nanorods in complex with CuO nanoparticles. The observation on a smaller scale as in Fig. 4c and d shows the interplanar fringes of TiO₂ and CuO. We can clearly identify the lattice of both anatase TiO₂ and CuO. In Fig. 4c, the obvious lattice spacings of about 0.35 nm prove the existence of {101} face of anatase TiO₂ (Shi et al. 2019). In Fig. 4d, a spacing of about 0.23 nm was identified, belonging to the {111} face of CuO (Kumar and Chowdhury 2017), and we also observed the lattice spacings of 0.35 and 0.47 nm with an included angle of 70°, showing the {101} face of TiO₂ (Kumar and Chowdhury 2017). Since the amount of rGO is relatively small, the trace of rGO was not obvious under the electron microscope; however, the Raman spectrum and XPS provided strong proof on the presence of rGO.

3.5 UV-Vis DRS

UV-DRS analysis can predict the bandgap of the composite by measuring the light absorbance of the catalyst under visible light (Nguyen et al. 2019). The UV-Vis absorption spectrum is shown in Fig. 5a. TiO₂ has strong absorption below 400 nm, which is due to the absorption of ultraviolet light by TiO₂ (de Brito et al. 2018). In contrast, CuO and TGC show extensive adsorption in the visible light region.

![Fig. 2](https://example.com/fig2)

Fig. 2  a FTIR spectra and b Raman spectra of TG2C8
The bandgap energy of the CuO, TiO$_2$, and TGC nanocomposites is shown in Fig. 5b. The bandgap energy is calculated by the Tauc equation (Viezbicke et al. 2015; Mansingh et al. 2017):

$$\alpha h\nu = A (h\nu - E_g)^n$$

where $E_g$ is the energy of bandgap, $A$ is a proportionality constant, $h\nu$ is the approximate bandgap, $\alpha$ is the absorption coefficient, and $n$ equals to 0.5 and 2, corresponding to the direct and indirect transitions, respectively. Both TiO$_2$ (Zhang et al. 2016) and CuO (Lim et al. 2012) have an indirect bandgap. The calculated bandgap of CuO is about 1.70 eV, the calculated bandgap for TiO$_2$ (3.2 eV) corresponds to anatase TiO$_2$, and the calculated bandgap for TGC is 2.45 eV. From the above results, TGC nanocomposites broaden the absorption range of TiO$_2$.

3.6 Photocatalytic Reduction of Cr(VI)

Cr(VI), a model contaminant, was used for evaluating the photocatalytic property of TGC composites. First, in the dark, we stir the suspension for 40 min until the adsorption-desorption equilibrium is reached. The results in Fig. 6a shows that adsorption-desorption equilibrium can be reached in 20 min. We found that TG2C8 has the highest photocatalytic effect on photoreduction of Cr(VI) and the photoreduction conversion can reach 100% within 80 min, whereas only 63.23% and 9.17% of the added Cr(VI) were photoreduced by using neat TiO$_2$ and P25 as the catalysts in Fig. 6b, respectively. In order to eliminate the influence of Cr(VI), the photocatalytic test of Cr(VI) was carried out under the condition without nanocomposites, as shown in Fig. 6b. The absorbance of pure Cr(VI) is almost unchanged under the same visible light irradiation, so the influence of Cr(VI) can be excluded. The degradation rate constant ($k$) was calculated by using the simplified Langmuir-
Fig. 4  a The SEM image and b–d the HRTEM images of TG2C8

Fig. 5  a UV-Vis DRS and b $h\nu$ versus $(\alpha h\nu)^{0.5}$ graph of $\text{TiO}_2$, CuO, and TG2C8
Hinshelwood model (Wang et al. 2006; Jaafarzadeh et al. 2017):

\[ \ln \frac{C}{C_0} = -k.t \]

where \( k \) is the rate constant (min\(^{-1}\)), \( C_0 \) is the initial concentration of the Cr(VI), and \( t \) is the photodegradation time (min). The calculated rate constant of TG2C8 is 0.0617 min\(^{-1}\), and the calculated rate constants of P25 and TiO\(_2\) were 0.0125 and 0.0021 min\(^{-1}\), respectively. It can be concluded that nanocomposites show excellent photocatalytic property under visible light.

### 3.7 Plausible Mechanism

We propose a feasible mechanism for the photoreduction of Cr(VI) under visible light, as shown in Fig. 7.

Under visible light irradiation, electrons(e\(^-\)) are excited to jump to the valence band (VB), leaving holes (h\(^+\)) in the conduction band (CB), which results in the formation of electron-hole pairs in TiO\(_2\). While rGO is used as an electron transfer medium and electron carrier, and the Fermi level of TiO\(_2\) is higher than that of CuO, the photo-excited of TiO\(_2\) will move to the CB of CuO through rGO layer, and the electron-hole pair recombination is inhibited. While e\(^-\) converts O\(_2\) to superoxide radicals (\( \cdot \)O\(_2^-\)), Cr(VI) can be reduced by e\(^-\) and \( \cdot \)O\(_2^-\) and e\(^-\). At the same time, the presence of h\(^+\) in the VB of TiO\(_2\) and CuO reacts with H\(_2\)O in the reaction medium to form hydroxyl radicals (\( \cdot \)OH), and citric acid acts as a hole sacrificial agent, which consumes some holes and \( \cdot \)OH, thereby further accelerating the separation of e\(^-\)-h\(^+\) pairs to improve photocatalytic property.

### 4 Conclusion

CuO nanoparticles and TiO\(_2\) nanorods were grafted onto the rGO framework and then used for photoreduction of Cr(VI), and the introduction of CuO and rGO heightened the absorption of visible light. Under visible light irradiation, TG2C8 can completely reduce the Cr(VI) (100 ppm) solution in 80 min, and the photoreduction conversion rates of Cr(VI) on TG2C8 are 4.9 and 29.4 times those of P25 and pure TiO\(_2\), respectively. CuO not only accelerates the separation of e\(^-\) and h\(^+\) but also reduces the bandgap of TiO\(_2\). In summary, the improvement in photocatalytic property of TG2C8 composites is attributed to the acceleration of e\(^-\)-h\(^+\) pair separation by CuO and the acceleration of effective e\(^-\) transfer by rGO.
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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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