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RESEARCH ARTICLE

# Photoelectrochemical degradation of methyl orange on CdS–decorated $Cr_2O_3$/electroreduced graphene oxide nanocomposites

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## HIGHLIGHTS

- Chromium(III) oxide /electroreduced graphene oxide ($Cr_2O_3$/ERGO) nanocomposites were fabricated via electrochemical deposition.
- Prepared $Cr_2O_3$/ERGO was decorated by CdS nanoparticles using the SILAR technique.
- A ternary CdS/$Cr_2O_3$/ERGO hybrid nanostructure was used for high-performance photoelectrochemical degradation of methyl orange.

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## ABSTRACT

Chromium(III) oxide ($Cr_2O_3$) and electroreduced graphene oxide (ERGO) nanostructures were synthesized for the first time using a one-pot electrochemical technique on a tin oxide-coated glass (ITO) electrode surface. The surface of the synthesized $Cr_2O_3$/ERGO nanostructures was decorated with CdS nanoparticles by a simple successive ionic layer adsorption and reaction (SILAR) technique. The characterization of synthesized nanocomposites has been carried out using XRD, FESEM, and EDS techniques. The photodegradation of methyl orange (MO) was investigated in an aqueous suspension containing CdS/$Cr_2O_3$/ERGO catalyst under artificial sunlight irradiation. The results indicated that the modification of $Cr_2O_3$/ERGO with CdS nanoparticles exhibits a high performance for the removal of azo dyes.

## 1. Introduction

Azo dyes, which are highly water-soluble and stable over long periods, are widely used in textile, printing, pharmaceutical, and research laboratories and have been shown to be toxic, carcinogenic, and mutagenic [1–5]. It can enter the human body through the skin and cause lung tissue death, rapid heartbeat, and vomiting. These mostly contain aromatic rings, which are resistant to biodegradation. In addition, due to the presence of the azo group in the dye structure, they can turn into toxic amines [6–8]. Especially for the continuity and development of the textile industry, there is a strong need for the removal of waste dyes by using a non-toxic, highly efficient, and environmentally friendly treatment method [9]. Methyl orange (MO) is the most widely known azo dye [10]. Therefore, MO was chosen as a model dye for photoelectrochemical degradation in this study.

Different metallic oxide-based semiconductor photocatalysts (such as $TiO_2$, ZnO, $CeO_2$, $SnO_2$, $MnO_2$, $ZrO_2$, $Cr_2O_3$ and $WO_3$, etc.) showed improved performance in dye degradation [11–14]. Among them, $Cr_2O_3$ is an important transition metal oxide [15]. The $Cr_2O_3$ remains stable over a wide range of temperature and pressure changes [16]. However, limited by its wide band gap (Eg = 3.45 eV), $Cr_2O_3$ can only absorb UV light, which leads to exhibit weak photocatalytic activity under visible light irradiation. Therefore, it is necessary to develop a photocatalyst material having improved visible light activity to more effectively use visible light [17]. Recently, many researchers have immobilized catalysts on supporting materials such as

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activated carbon, glass, and graphene. Similarly, decorating the composite with semiconductor metal sulfides such as CdS, PbS or ZnS can be greatly beneficial to extend the light absorption into the visible light region [18–20]. For this reason, CdS nanoparticles decorated $Cr_2O_3$/electrochemically reduced graphene oxide (CdS/$Cr_2O_3$/ERGO) electrodes have been considered to be used in photocatalytic applications to collect maximum solar energy.

## 2. Material and method

Firstly, $Cr_2O_3$/ERGO was prepared by electrochemical method. Typically, a mixture of 0.1 M $KNO_3$ aqueous solution containing 2 mg/mL graphene oxide and 10 mM $Cr(NO_3)_3$ was used for $Cr_2O_3$/ERGO synthesis. Before and during the electrochemical deposition, $O_2$ gas was passed through the electrolyte solution. CV measurements were recorded at a scanning rate of 100 mV/s in a potential window of 0 V to -1.5 V at room temperature. The $Cr_2O_3$/ERGO electrochemically deposited on the ITO surface for 5, 10, and 15 minutes under -1.3 V constant potential, were heat treated at 500 °C for 1 hour. Then, the surface of the prepared $Cr_2O_3$/ERGO nanocomposites was decorated with CdS nanoparticles using the SILAR technique. For the CdS solution medium, 0.1 M $Cd(CH_3COO)_2.2H_2O$ and 0.1 M $Na_2S$ solutions were chosen.

Electrochemical tests were conducted in a standard three-electrode system by a BAS 100i. Ag/AgCl electrode was used as the reference electrode, the Pt wire was employed as counter electrode, and the tin oxide-coated glass (ITO) was used as a working electrode. Structural characterization of the synthesized nanostructures was performed by X-ray diffraction spectroscopy (XRD) and Energy dispersive X-ray spectroscopy (EDS). Field-emission scanning electron microscopy (FESEM) was used for morphological characterization. The photoelectrochemical catalysis ability of CdS/$Cr_2O_3$/ERGO nanocomposites was investigated for the degradation of MO dye under artificial sunlight. 0.1 M NaCl solution containing 2 mg/L MO was used in photoelectrochemical experiments. Samples were collected from the MO solution at certain times under continuous stirring and absorbance values were measured in the range of 300-800 nm using the Shimadzu UV3101PC visible spectrophotometer. The photoelectrocatalytic performances of the electrodes were calculated using the % decay rates of MO (Equation 1). In Eq.1, $A_0$ and $A_t$ are the absorbance of MO at 0 min and t min, time respectively.

$$\text{Degradation\%} = [(Ao - At)/Ao]x100 \quad (1)$$

## 3. Result and discussion

XRD spectrum was recorded for the structural characterization of CdS/$Cr_2O_3$/ERGO nanostructures (Figure 1. a). As shown in Figure 1. a, the diffraction peaks could be indexed to $Cr_2O_3$ with at 39.9°, 44°, 58° and 64° degrees. Also, the observed characteristic diffraction peaks at 24.9° and 43.7° are attributed to the (100) and (110) reflections of CdS. Moreover, 2θ= 24.6° (002) peak was obtained for ERGO. No other impurity peak is detected.

The morphological changes that occurred on the ITO surface with the modification were investigated by the FESEM technique. The surface of the ITO electrode, which has a defined surface, is completely covered with nanostructures (Figure 1. b-c). Before the decoration of CdS nanostructures, the surface of $Cr_2O_3$/ERGO electrode was investigated by FESEM image. Compared to Figure 1b and Figure 1c, it was seen that the $Cr_2O_3$/ERGO surface consisted of smaller particles. Nanoparticles with graphene structures are observed more clearly in the FESEM image of CdS/$Cr_2O_3$/ERGO (Figure 1. c, inner picture) recorded for high magnification. Elemental analysis of the prepared nanocomposites was investigated using the EDS spectrum (Figure 1. d). In the EDS spectrum, Cd and S peaks from CdS, Cr and O peaks from $Cr_2O_3$, and C peaks from ERGO were obtained. The results of characterizations showed that CdS/$Cr_2O_3$/ERGO nanocomposites were successfully synthesized.

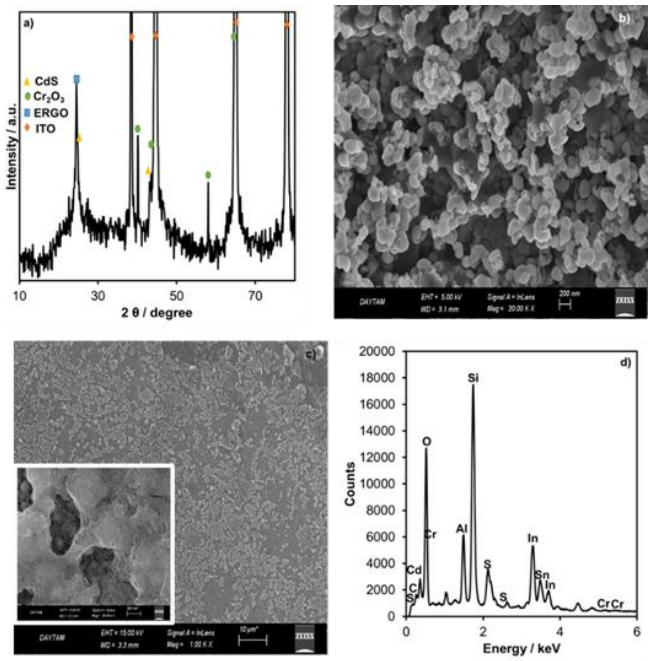


**Figure 1.** XRD spectra of CdS/$Cr_2O_3$/ERGO (a). FESEM image of $Cr_2O_3$/ERGO (b). FESEM images (c), and EDS spectra (d) of CdS/$Cr_2O_3$/ERGO nanocomposites.

For photoelectrochemical degradation of MO, the photoelectrochemical activities of the prepared CdS/$Cr_2O_3$/ERGO nanocomposites were investigated depending on the decrease in the UV spectrum peak intensity of MO. Firstly, the effect of $Cr_2O_3$/ERGO deposition time was investigated. The $Cr_2O_3$/ERGO nanocomposites deposited at various deposition times (1, 5, and 10 minutes) were examined for removal amount of MO at 1 hour. It was determined that the removal rate (73%) was high in the sample prepared for 5 minutes (Figure 2. a). Secondly; the effect of immersion time (Figure 2. b) and the number of cycles (Figure 2. c) of CdS, which are essential parameters for the SILAR technique, were tested. It was immersed in each ion solution for 10, 20, and 30 s at one cycle. The best immersion time was determined as 20 s in MO removal at 1 hour with a removal rate of ~86%. For the effect of the number of cycles, 1, 3, 5, and 10 cycle samples were prepared at 20 s immersion time. The best photoelectrocatalytic result with a removal rate of 92% in 1 hour of MO removal was obtained in the sample prepared in 5 cycles. According to the above results, CdS/$Cr_2O_3$/ERGO nanocomposites, prepared for photoelectrocatalytic removal of MO, exhibited high-performance thanks to the synergistic effect between CdS, $Cr_2O_3$, and ERGO.

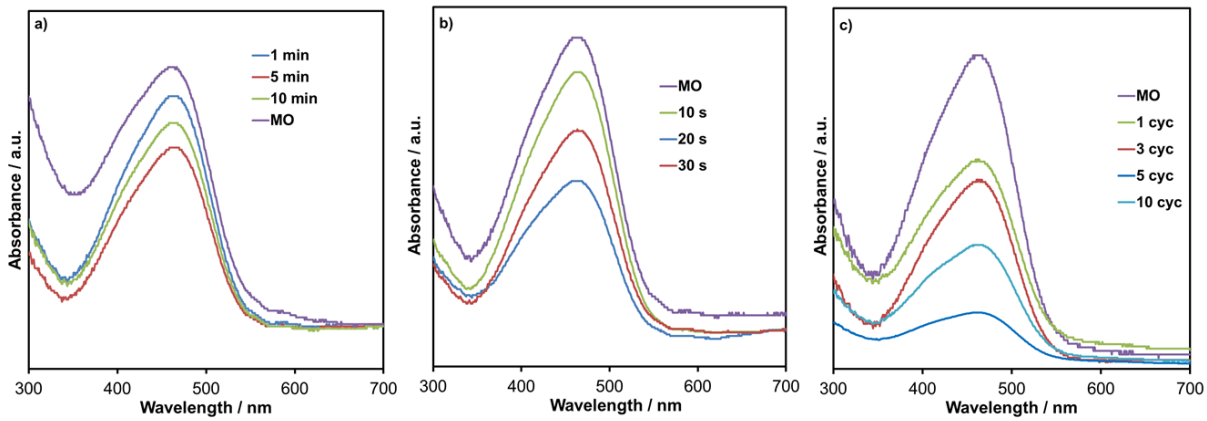


**Figure 2.** The absorption spectrums of MO on various electrodes: $Cr_2O_3$/ERGO (a), CdS/$Cr_2O_3$/ERGO (for the immersion time (b), and the number of cycles (c)).

## 4. Conclusion

$Cr_2O_3$/ERGO electrodes were successfully synthesized using an electrochemical technique. The nanocomposite surface was modified with CdS nanoparticles using the SILAR technique. Compared to the $Cr_2O_3$/ERGO catalyst, the hybrid CdS/$Cr_2O_3$/ERGO catalyst presented an obvious enhancement in the photocatalytic performance for the MO degradation, resulting from their several merits in both morphology and electronic structure. Furthermore, the deposition time of the $Cr_2O_3$/ERGO composite, the immersion time of CdS, and the number of cycles were found to be important factors affecting the photoelectrocatalytic degradation of MO in CdS/$Cr_2O_3$/ERGO electrodes. Experimental results show that CdS/$Cr_2O_3$/ERGO catalysts with nanoporous structures can serve well to remove organic pollutants from wastewater.

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## Conflict of Interest

The author(s) declares no known competing financial interests or personal relationships.

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