



## Regular Article

Hierarchical layered Ni<sub>3</sub>S<sub>2</sub>-graphene hybrid composites for efficient photocatalytic reduction of Cr(VI)

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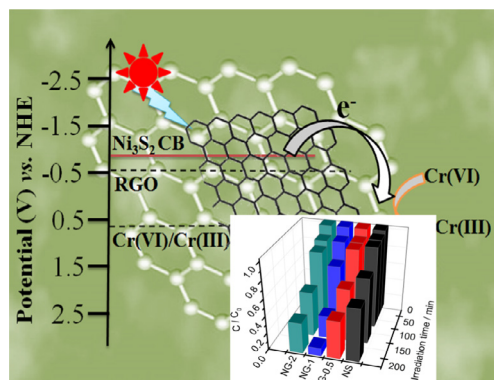
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Exploring visible light responsive media remains a challenge for solar energy photocatalysis applications. We report the Ni<sub>3</sub>S<sub>2</sub>-reduced graphene oxide (NG) hybrid composites with sheet-on-sheet structures synthesized by a facile microwave-assisted method. Their morphology, structure and photocatalytic activity in the reduction of Cr(VI) were characterized by scanning electron microscopy, X-ray diffraction, UV-Vis absorption spectroscopy, and electrochemical impedance spectra, respectively. The results show that NG hybrid composites show excellent visible light photocatalytic activity in the reduction of Cr(VI) compared to pure Ni<sub>3</sub>S<sub>2</sub>. The Cr(VI) reduction rate of higher than 90% has been achieved with 1 wt.% reduced graphene oxide under visible light irradiation at 180 min. Improvement is attributed to its efficient charge separation and more active sites due to the integrative effect and good interfacial contact between Ni<sub>3</sub>S<sub>2</sub> and reduced graphene oxide.

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## 1. Introduction

Semiconductor photocatalysis as a green technology has attracted tremendous attention due to its promising potential application for solving serious environmental and energy problems [1–3]. Considerable efforts have been devoted to develop the semiconductor photocatalysts such as metal oxides, sulphides, oxynitrides, perovskite for organic pollutants degradation [4–7], heavy metal ion and CO<sub>2</sub> reduction [8–11], selective organic synthesis [12], and water splitting to produce hydrogen [13]. Heavy metal ions such as Cr(VI) are highly toxic in the environment, which is discharged from electroplating, leather tanning, metal finishing, textile manufacturing, steel fabricating, paint and pigments, and fertilizing [14,15]. Photocatalytic reduction of Cr(VI) to Cr(III) is considered as an efficient way to remove Cr(VI), because Cr(III) is less toxic and can be readily precipitated in aqueous solution in the form of Cr(OH)<sub>3</sub>. However, the photocatalytic activity is limited on account of the quick recombination rate of charge carriers and relatively low solar energy conversion efficiency. Therefore, it is very urgent to develop visible light responsive photocatalysts with considerable efficiency and good stability that can satisfy industrial requirements [16–20].

Transition metal dichalcogenides (TMDs) have crafted enormous interest because of their high specific surface area, outstanding electron conductivity, and promising applications in solar cell, energy storage, sensors, and photocatalysis [21,22]. Among various TMDs, MoS<sub>2</sub> and MoSe<sub>2</sub> have been strongly demonstrated to show good visible light photocatalytic activity [23,24]. MoSe<sub>2</sub> synthesized via a solvothermal method exhibits excellent photocatalytic activity for the reduction of Cr(VI) under ultraviolet (UV) and visible light even near infrared light irradiation [25]. Furthermore, it is also demonstrated that TiO<sub>2</sub> as co-catalyst can enhance the visible light photocatalytic activity of pure MoSe<sub>2</sub> in the reduction of Cr(VI). The stepwise energy structure in the TiO<sub>2</sub>-MoSe<sub>2</sub> composites is beneficial to the separate of photo-induced charge carriers in the photocatalytic process, which could efficiently suppress their recombination and improve the photocatalytic activity of pure MoSe<sub>2</sub> [26].

Besides MoS<sub>2</sub> and MoSe<sub>2</sub>, nickel sulphide such as Ni<sub>3</sub>S<sub>2</sub> (NS) has a suitable bandgap of 2.5 eV that can respond the visible light, making it a promising candidate as a visible light photocatalyst [27]. It is well known that the rapid recombination of photo-induced charge carriers will hamper the photocatalytic reaction process. Recently, constructing sheet-on-sheet hybrid materials between semiconductors and carbon materials has been regarded as an efficient strategy to overcome above problems [28,29]. Graphene (normally called as reduced graphene oxide (RGO)) as a typical two dimension material has high special surface area, unique optical and electron properties, and good chemical stability, thus has regarded as an ideal matrix to support the semiconductors [30]. Intensive efforts have been made to focus the RGO-based composites with excellent photocatalytic activity [31,32]. RGO with high specific surface areas could provide much active site in the photocatalytic reaction process [33]. In particular, the incorporation of RGO can prolong the lifetime of photo-induced charge carriers and suppress the recombination due to its unique network structure and good electron conductivity [34,35]. Therefore, combining NS nanosheets and RGO to form sheet-on-sheet hybrid composites should exhibit enhanced photocatalytic activity in the reduction of Cr(VI), which has remained unavailable so far.

Here, we reported a simple microwave-assisted method to synthesize of NS nanosheets-RGO (NG) hybrid composites and investigated their photocatalytic activity toward reduction of Cr(VI) under UV and visible light irradiation. To the best knowledge, it is the first time to investigate the NG hybrid composites for photo-

catalytic reduction of Cr(VI). The detailed experimental procedure is described in electronic [supplementary information](#). The as-synthesized NG hybrid composites with 0.5, 1, and 2 wt.% RGO were named as NG-0.5, NG-1, and NG-2, respectively. The NG hybrid composites show remarkably improved photocatalytic activity toward reduction of Cr(VI) under UV and visible light irradiation as compared to pure NS. A series of characterization and controlled experiments using electron scavengers have been carried out to investigate the possible mechanism of enhanced photocatalytic activity.

## 2. Results and discussion

### 2.1. Characterizations

Fig. 1 shows the field-emission scanning electron microscopy (FESEM) images of pure NS and NG-1. It can be observed that pure NS displays a two-sheet structure, which is constructed by tiny inter-connecting densely packed layers (Fig. 1(a)). When the RGO is introduced into NS, the ultrathin curled RGO nanosheets uniformly grew on the surface of NS sheets to form a sheet-on-sheet structure (Fig. 1(b)). In addition, the morphologies of NG hybrid composites are similar to that of pure NS. The sheet-on-sheet structure in NG hybrid composites is beneficial to the separation of photo-induced charge carriers, and ultimately contributes to the photocatalytic activity. The composition of NG-1 was identified by energy dispersive X-ray spectroscopy (EDS) linked to FESEM. Fig. 2 shows the element distribution mapping images of NG-1. The Ni, S and C element distribution clearly demonstrates the existence of NS and RGO in the hybrid composites. No other elements such as Cl are observed, indicating the high purity of the products.

The structures of pure NS and NG hybrid composites were characterized by X-ray diffraction (XRD), as shown in Fig. 3. The RGO exhibits the (002) diffraction peak at 26° and (100) peak at 44.5° [36]. The XRD diffraction peaks of pure NS are assigned to the rhombohedral phase NS with phase group R32(155) (JCPDS: 44-1418) [37]. For the NG hybrid composites (NG-1), the main diffraction peaks are similar to those of pure NS, indicating that the presence of RGO does not result in the development of new crystal orientations or changes in preferential orientations of NS. No characteristic diffraction peaks of carbon species are observed, which is due to the low amount and relatively low diffraction intensity of RGO in the hybrid composites.

The specific surface areas and pore structures of NS and NG hybrid composites were studied using the nitrogen adsorption-desorption isotherms, as shown in Fig. 4. All NS and NG hybrid composites display type IV isotherms with H<sub>2</sub> and H<sub>3</sub> hysteresis loops, demonstrating the presence of mesopores. The Brunauer-Emmett-Teller (BET) specific surface areas, pore volumes and mean pore diameters of NS and NG hybrid composites are listed in Table 1. It can be observed that the hybridization of RGO increases the specific surface areas of NG hybrid composites owing to high surface areas of RGO. The larger specific surface areas could provide more active sites, which is beneficial to the adsorption of Cr(VI) in the photocatalytic process. However, when the RGO content is further increased (NG-2), the specific surface area decreases, which may be due to the blocking of pores by the stacked RGO in the composites [37,38]. Moreover, the pore volume and mean pore diameter of NG-1 are larger than those of other samples, which plays an important role in the fast transport of Cr(VI) and allow more Cr(VI) to enter into the photocatalyst, and thus leading to the enhancement of photocatalytic activity [39].

Fig. 5(a) shows the UV-Vis diffuse absorption spectra of pure NS, NG-0.5, NG-1 and NG-2. It can be observed that pure NS and

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