



## Full Length Article

# Ultrafine cobalt nanoparticles supported on reduced graphene oxide: Efficient catalyst for fast reduction of hexavalent chromium at room temperature



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## ABSTRACT

A novel composite ultrafine cobalt nanoparticles-reduced graphene oxide (Co-RGO) was firstly synthesized through a modified one-step solvothermal method with  $\text{Co}(\text{OH})_2$  as the precursor. The prepared low-cost Co-RGO composite exhibited excellent catalytic activity for the reduction of highly toxic Cr(VI) to nontoxic Cr(III) at room temperature when formic acid (HCOOH) was employed as the reductant, and its catalytic performance was even comparable with that of noble metal-based catalysts in the same reduction reaction. Moreover, Co-RGO composite could be readily recovered under an external magnetic field and efficiently participated in recycled reaction for Cr(VI) reduction.

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## 1. Introduction

The widespread use of chromium and its compounds in modern industry has caused extremely serious environmental pollution [1]. Hexavalent chromium (Cr(VI)) is a highly toxic pollutant with mutagenicity and carcinogenicity, which exists stably in the natural environment and is regarded as the third most common pollutant at hazardous waste sites [2]. Contrarily, trivalent chromium (Cr(III)) is relatively inert, nontoxic and accepted as an essential human nutrient [2,3]. Thus, researchers have been committed to search for a practical and economical technology for the conversion of Cr(VI) to Cr(III). Recent studies showed that the conversion of Cr(VI) to Cr(III) could be achieved by various reductants, such as HCOOH,  $\text{H}_2\text{S}$ , Fe(0), Fe(II)-bearing minerals and so on [4]. Among these reductants, HCOOH presented great potential for Cr(VI) reduction due to its superiorities in environmental protection, adequate sources and mild reaction conditions [4,5]. In the previous studies, noble metal-based catalysts were fabricated and played an important role in Cr(VI) reduction. For example, colloidal PdNPs [5], PtNPs@Pro-ESM [6] and Pd- $\gamma$ - $\text{Al}_2\text{O}_3$  [7] were proved to be efficient catalysts for

Cr(VI) reduction. However, these catalysts suffered from expensive price and high reaction temperature, which hindered their practical applications. Hence, developing advanced catalysts with low cost, high activity and good recyclability by a simple fabrication process for fast reduction of Cr(VI) at room temperature remains a challenge.

In recent years, Co nanoparticles have drawn great concerns in the field of catalysis owing to their high catalytic activity, low price, nontoxicity as well as magnetic recyclability [8,9]. However, it is frustrating to find that pure Co nanoparticles with large size are prone to agglomerate together and unfavorable for catalytic reduction of Cr(VI). Therefore, preparing small, well-dispersed and non-agglomerated Co nanoparticles is very necessary. Our previous studies have clearly demonstrated that when metal nanoparticles such as Pt [10] and Cu [11] were decorated on RGO sheets, the unique synergistic effect between metal nanoparticles and RGO will endow the composite high catalytic activity and effective reusability. In addition, the aggregation and oxidation problems of metal nanoparticles could be solved because of the large specific surface area, high electron transport property and excellent adsorptivity of graphene. Herein, for the first time, ultrafine cobalt nanoparticles supported on reduced graphene oxide was successfully prepared via a modified one-step solvothermal method by using  $\text{Co}(\text{OH})_2$  as the precursor, which achieved the growth of Co nanoparticles and the reduction of graphene oxide (GO) simultaneously. The

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formed ultrafine Co nanoparticles were densely and compactly loaded on RGO sheets, which could provide quantities of active sites and be propitious to the improvement of the catalytic properties. The results manifested the as-prepared Co-RGO composite was an efficient catalyst for fast reduction of highly toxic Cr(VI) at room temperature. Moreover, the composite could be readily recovered under an external magnetic field. After eight cycles, it still exhibited considerably high catalytic activity for Cr(VI) reduction.

## 2. Experimental

### 2.1. Materials

Cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ), and other materials purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were of analytical grade except industrial pure ethanol.

### 2.2. Synthetic procedures

Graphite oxide (GO) was successfully prepared according to the modified Hummers method [12,13] by using the natural graphite powder as the raw materials. Co-RGO composites with different graphene contents were synthesized through a modified one-step solvothermal method and denoted as Co-RGO $_x$  ( $x=5, 10, 15, 20, 25$  wt%, respectively). A typical experimental procedure for the synthesis of Co-RGO $_{10}$  composite with 10 wt% graphene was as follows: 0.306 g of the as-prepared colloidal GO (with GO content of 2.14 wt%) was uniformly dispersed in 40 mL of ethanol with sonication. 0.291 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol) was dissolved in 30 mL of deionized water, which was adjusted to pH 11 by NaOH solution (6 M) for generating  $\text{Co}(\text{OH})_2$  precipitation. After that,  $\text{Co}(\text{OH})_2$  was separated from the mixture by vacuum filtration, washed with distilled water and ethanol respectively, and then dispersed in 30 mL of ethanol under sonication for 30 min again. The  $\text{Co}(\text{OH})_2$  dispersion was added tardily into GO dispersion with continuous stirring for 1 h. Then, 6 M NaOH solution was added dropwisely in the above mixture until the pH of the mixture was 11. After vigorously stirring for 30 min, 3 mL of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  was mixed into the above the emulsion and stirred for another 30 min. The resulting stable homogeneous mixture was settled into a 100 mL Teflon-lined stainless autoclave and heated to maintain 180 °C for 12 h under autogenous pressure (Fig. 1). The obtained sample was cooled to room temperature, and purified by filtration, washing and vacuum dried at 60 °C for 10 h. Pure Co nanoparticles and RGO were also respectively prepared by the same method in the absence of GO or  $\text{Co}(\text{OH})_2$  for comparison.

### 2.3. Characterization

The phase structures of the as-prepared catalysts were analyzed by powder X-ray diffraction (XRD) employing a Bruker D8 Advanced diffractometer (Cu K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) with the scanning angle ranging from 5° to 80°. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 370 FTIR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets in the region of 500–4000  $\text{cm}^{-1}$ . Raman spectra were acquired using a Renishaw inVia Reflex Raman microprobe. The Brunauer–Emmett–Teller (BET) surface areas of the catalysts were measured using an ASAP2010C surface aperture adsorption instrument (Micromeritics Instrument Corporation, USA) by  $\text{N}_2$  physisorption at 77 K. The content of Co of the catalyst was determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, ICPS-7510, Shimadzu, Japan). Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 microscope (JEOL, Japan) at an

accelerating voltage of 200 kV. The reduction of Cr(VI) ions was performed by measuring the absorbance values at various time intervals using a Shimadzu UV-2700 UV-vis spectrophotometer at room temperature (25 °C).

### 2.4. Catalytic activity measurement

The reduction process of Cr(VI) to Cr(III) over Co-RGO composite was monitored by observing the absorbance changes of the reaction mixture between 300 and 500 nm with the main absorption peak at 350 nm. Typically, 40 mL of  $\text{K}_2\text{Cr}_2\text{O}_7$  aqueous solution (100 mg/L) and 1 mL of HCOOH (23 g/L) were added to a 100 mL beaker and uniformly stirred at room temperature. The pH of the reaction mixture was 2, which could be adjusted by the addition of NaOH solution to be 4 and 6, respectively. Besides, almost no changes of pH were measured during each reaction process. The absorption spectrum of the reaction solution was recorded and considered as 0 min data. Hereafter, 4 mg of Co-RGO composite powder was added to the reaction solution. The absorption spectra of the reduction process were first recorded at 1 min and then recorded at 2 min intervals. After the first reaction cycle, the Co-RGO composite was recovered by a permanent magnet, washed with distilled water and ethanol respectively, and vacuum dried before reused.

## 3. Results and discussion

### 3.1. Characterization of Co-RGO composites

The typical XRD diffraction patterns of pure Co, Co-RGO $_{10}$ , GO and RGO were presented in Fig. 2A. In the XRD pattern of Co-RGO $_{10}$  composite, almost all the diffraction peaks of the characteristic were well consistent with standard hcp-type Co nanoparticles (JCPDS No. 05-0727), which indicated  $\text{Co}(\text{OH})_2$  was converted into metallic Co after the modified solvothermal reaction. The diffraction peaks at  $2\theta = 41.63^\circ, 44.24^\circ, 47.37^\circ$  and  $75.80^\circ$  could be indexed to the (100), (002), (101) and (110) crystal planes of Co, respectively [14–16]. Compared with pure Co nanoparticles, sharper crystalline peak corresponded to (002) crystal plane was obvious observed in the pattern of Co-RGO $_{10}$  composite, which indicated the introduction of graphene enhanced the crystallinity and orientation of Co nanoparticles [17]. However, neither the typical diffraction peak of GO (001) nor RGO (002) was discovered in the XRD pattern of Co-RGO $_{10}$  composite. This may be attributed to the fact that during the modified solvothermal reaction, GO was reduced to RGO and then exfoliated by the decorated Co nanoparticles, which destroyed the regular layer stacking of RGO [18,19].

Fig. 2B depicts the FTIR spectra of Co-RGO $_{10}$  composite, RGO and GO. By comparison with the FTIR spectrum of GO, it could be obviously noted that the absorption intensities of characteristic peaks of oxygen-containing groups in the Co-RGO $_{10}$  composite decreased considerably, which suggested GO in the Co-RGO $_{10}$  composite was mostly reduced to RGO [20]. Besides, the positions of characteristic peaks in the Co-RGO $_{10}$  composite were consistent with those of RGO and no new characteristic peaks were observed, further indicating the composite was synthesized by the hybridization of metallic Co and RGO. Ordinarily, the reduction of GO caused fragmentation generated along the reactive sites and produced new graphitic domains, leading to smaller size but more numerous of RGO sheets compared with GO before reduction [21]. Thus, it was reasonable to deem that much more active sites might contact with reactants for facilitating the occurrence of the reaction after the reduction of GO.

The representative Raman spectra of Co-RGO $_{10}$  composite, RGO and GO were displayed in Fig. 2C. As shown in the Raman spectrum of Co-RGO $_{10}$  composite, the two characteristic peaks at  $1347 \text{ cm}^{-1}$

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