Postprint: Preparation of Graphene Oxide (GO) and Composites and Their Mercury Adsorption Characteristics

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Abstract

Using graphite powder (G) as raw material, four adsorbent materials were prepared via chemical methods: graphene oxide (GO), nano-Fe3O4-loaded graphene composite (MGO), nano-Ag particle-modified graphene oxide (GO-Ag), and nano-Ag particle-modified magnetic graphene oxide (MGO-Ag). The materials were characterized and the adsorption of mercury in flue gas by graphene oxide and its composites was investigated. The study demonstrates that the four graphene-based adsorbents can be successfully synthesized and characterized; GO exhibits excellent adsorption performance for Hg0 at 100-150°C, Ag-NPs modification of GO can effectively enhance the adsorption capacity for mercury, and the MGO-Ag composite adsorbent shows the best adsorption capacity for mercury; MGO-Ag exhibits excellent mercury adsorption capacity at 150°C-200°C, with almost no change in adsorption performance after repeated cycling; the renewable magnetic graphene-based composite adsorbent, represented by MGO-Ag, exhibits excellent adsorption performance for Hgo under medium-low temperature conditions, can be effectively separated from fly ash, and demonstrates promising industrial application prospects.

Full Text

Fabrication of Graphene Oxide (GO) Based Nanocomposites and Their Applications in Hg^0 Adsorption

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Abstract

Nano-composites including graphene oxide (GO), ferroferrous oxide nanoparticles (Fe-NPs) loaded graphene oxide (MGO), and nano silver particles (Ag-NPs) decorated GO and MGO (GO-Ag/MGO-Ag) were fabricated via facile chemical methods. All four kinds of nano-composites were well characterized by advanced instruments and tested for their capability of Hg^0 adsorption in flue gas.

The results indicated that the four kinds of nano-composites can be successfully synthesized by the facile chemical methods. GO shows good Hg^0 adsorption performance when the temperature ranges from 100℃ to 150℃. The Ag-NPs decorated GO can greatly enhance the Hg^0 adsorption capability. MGO-Ag performs best of all the four composites on Hg^0 adsorption. The optimum working temperature for MGO-Ag on Hg^0 adsorption is about 150℃-200℃, and the MGO-Ag can be recycled after successive adsorption and desorption without any significant loss in adsorption performance. The recyclable nano-composites of MGO-Ag can be served as excellent candidates for Hg^0 adsorption under medium-low temperatures (100-200℃). Further, the decoration of Fe-NPs helps for the separation of the materials and the fly ash in a real case of coal-fired power plants, which provides great advantages in practical applications.

Keywords: Graphene oxide; Hg adsorption; Magnetic; Ag Nano Particles; Recyclable

1. Introduction

Mercury emissions from coal-fired power plants pose serious threats to both the living environment and human health [1, 2]. Although mercury exists only as a trace element in coal, its long-term and large-scale use inevitably leads to cumulative effects of mercury emissions [1-6]. The mercury content in Chinese coal is approximately 0.2 g/g, and the mercury concentration in coal-fired flue gas is generally 1-20 g/m^3. During coal combustion, mercury is initially released in elemental form (Hg^0). However, due to thermochemical reactions in high-temperature flue gas, a portion of elemental mercury can be oxidized to Hg^{2+}, and some mercury can be captured by fly ash particles to form particulate mercury (Hg). Hg^{2+} is water-soluble, and Hg can be removed by electrostatic precipitators (ESP), wet flue gas desulfurization (FGD) systems, or selective

catalytic reduction (SCR) systems. Nevertheless, 20-50% of elemental mercury still remains in the flue gas, and Hg^0 is difficult to remove through these conventional systems, making the development of effective adsorbents for Hg^0 removal critically important [7].

Currently, common methods for Hg^0 control include SCR oxidation combined with WFGD absorption of Hg^{2+}, and sorbent injection. Sorbents used include carbon-based materials (such as activated carbon) and non-carbon-based materials (such as minerals). However, activated carbon adsorbents are too costly and cannot be recycled. Moreover, after injection, the adsorbents are difficult to separate from fly ash, ultimately making the fly ash a mercury sink and affecting fly ash quality. Therefore, developing efficient and economical adsorbents is of great significance. In particular, developing regenerable and recyclable adsorbents offers obvious advantages in reducing adsorbent costs. The greatest advantage of magnetic adsorbents is their easy separation from fly ash. Consequently, developing magnetic adsorbents that can be readily separated from fly ash and investigating their regeneration and reuse technologies have become current research hotspots.

In recent years, carbon nanomaterials represented by graphene (G) have attracted worldwide attention from environmental researchers due to their large specific surface area and strong adsorption capacity. Graphene has a strict two-dimensional honeycomb structure in which carbon atoms are arranged in a six-fold symmetric two-dimensional plane, with the benzene hexagon ring as the basic unit and the most stable structure in the material. Since its discovery in 2004, graphene has sparked a wave of research interest and has been widely applied in various fields due to its outstanding physicochemical properties. Graphene derivative graphene oxide (GO) possesses good water solubility and easily modifiable chemical activity, making it a unique adsorption material. Moreover, GO can be readily surface-modified, facilitating physical and chemical modification. Current research indicates that studies on GO' s mercury adsorption performance in coal-fired flue gas are not yet comprehensive.

This paper uses GO as an adsorbent and functionally modifies GO through chemical methods to prepare nano-silver-modified magnetic functional adsorbents. The study investigates both the mercury adsorption capability of GO-based adsorbents in coal-fired flue gas and the adsorption capacity, regeneration, and recycling characteristics of functionalized magnetic GO adsorbents, laying a foundation for developing efficient, regenerable magnetic adsorbents and their industrial applications.

2. Experimental Section

2.1 Raw Materials

The main raw materials for preparing GO and its composites include: graphite powder (particle size 7-10 m), concentrated sulfuric acid (H_2SO_4, 95-98 wt.%), sodium nitrate ($NaNO_3$), hydrogen peroxide (H_2O_2, 29-32% W/W aq.), PVP

(molecular weight 58000); iron(III) source $FeCl_3 \cdot 6H_2O$, iron(II) source $FeCl_2 \cdot 4H_2O$; potassium permanganate ($KMnO_4$), ammonia water (29.5 wt.%), silver nitrate ($AgNO_3$), etc. All chemicals used in the experiments were of analytical grade.

2.2 Synthesis of Graphene and Composite Materials

Graphene oxide (GO) was prepared through an improved Hummers method [8]. Under ice bath conditions, sulfuric acid (98%) was mixed with graphite powder and $NaNO_3$ in a three-neck flask. $KMnO_4$ was then slowly added, and the reaction system was stirred at high speed for 5 days. A certain amount of hydrogen peroxide was subsequently added. Then, a solution containing 500 mL deionized water/concentrated sulfuric acid (H_2SO_4, 98%)/hydrogen peroxide (H_2O_2, 30 wt.%) was added dropwise to the reaction system, at which point the suspension color changed to bright blue. After centrifugation, the suspension was repeatedly washed with deionized water and subjected to ion dialysis in 2 L deionized water. Finally, the obtained brown powder was freeze-dried to obtain fluffy graphene oxide powder (GO).

Nano-Ag decorated GO-Ag composites were prepared according to the silver mirror reaction principle [9]. A homogeneous GO solution (0.5 mg/mL) was ultrasonically exfoliated for 45 min. Under vigorous stirring, PVP (4 mg/mL) and glucose were gradually added to the reaction system. Then, silver ammonia solution was added to the reaction system, the reaction temperature was adjusted to 60℃ and maintained for 7 min. The GO-Ag composite was subsequently washed repeatedly with ethanol and deionized water, then freeze-dried to obtain a gray-brown GO-Ag powder sample.

Magnetic graphene oxide-based composite adsorbents were prepared using a co-precipitation method [10]. $FeCl_3$ and $FeCl_2$ solutions (2:1 ratio) were prepared and slowly added to a homogeneous GO solution that had been ultrasonicated for 45 min. The reaction temperature was adjusted to 90℃, and the pH of the reaction system was adjusted to 10 by adding 30% ammonia water. After vigorous stirring for 40 min, the reaction system was cooled to room temperature. The black powder in the suspension was separated from the solution using a magnet, repeatedly washed with deionized water, and dried to obtain the MGO sample. The preparation of MGO-Ag repeated the GO-Ag preparation procedure.

2.3 Characterization of Composites

Graphene-based composite samples were characterized by XRD, SEM, and TEM tests. XRD tests were performed using a Rigaku RU-200B X-ray diffractometer (CuKα) with Cu as the emission source at 40 kV and 110 mA. SEM and TEM tests were completed at the ACSES facility of the University of Alberta. SEM was performed on a JEOL JAMP 9500F Auger Microscope, and TEM was performed on a Philips (FEI) CM 20 TEM at an operating voltage of 200 kV.

2.4 Mercury Adsorption Experiments

The Hg^0 breakthrough experimental setup is shown in [Figure 1: see original paper].

Before each experiment, 30 mg of adsorbent was accurately weighed and placed in a U-shaped tube, which was plugged with quartz wool. The U-shaped tube was placed in a heating furnace with the temperature set according to experimental requirements. The carrier gas was high-purity Ar at a flow rate of 40 ml/min. During the experiment, 200 L of mercury vapor was precisely injected through polytetrafluoroethylene tees 1 and 2 using a syringe. Hg^0 in the system was captured by a gold amalgamation trap at room temperature and subsequently released at high temperature. Hg^0 monitoring was performed using a Tekran 2500 Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) detector (detection limit < 0.1 pg Hg^0).

3. Results and Discussion

3.1 XRD Characterization of Graphene and Composites

XRD tests were conducted to analyze the crystal phase composition of the prepared graphene oxide and its composites, with results shown in [Figure 2: see original paper].

GO exhibited a distinct diffraction peak at a diffraction angle of 9.92°. Through Bragg' s equation calculation, the GO interlayer spacing was determined to be 0.89 nm, which is larger than the 0.34 nm interlayer spacing of graphite [11, 12], mainly due to the introduction of oxygen-containing functional groups on the lamellar structure. Comparative analysis of the differences between the XRD patterns of GO composites and GO revealed that the peak at 9.92° disappeared in the GO composites, primarily because some oxygen-containing functional groups may have detached during the ultrasonic treatment process [11]. However, this process facilitates functional modification by nano-Ag particles and other functional groups. GO-Ag and MGO-Ag exhibited different crystal planes at diffraction angles of 38.2°, 44.3°, 64.5°, 77.5°, and 81.6°, corresponding to (111), (200), (220), (311), and (222) planes, mainly from cubic nano-Ag particles, indicating that nano-silver particles were successfully decorated on the GO surface. Meanwhile, cubic phase γ-Fe_2O_3 and Fe_3O_4 appeared in the XRD spectra of MGO and MGO-Ag, indicating that magnetic graphene oxide composites were successfully prepared through the co-precipitation method.

3.2 SEM/TEM Analysis of Graphene and Composites

The micro-morphologies of GO and its composites were characterized by SEM and TEM. The results showed that GO ([Figure 3: see original paper]-a) presented as a smooth single-layer structure with some wrinkles, not completely flat in one plane. The possible reason is that when the material size is reduced

to a single or few atomic layers with surface functional groups, the material exhibits certain wrinkles.

Micro-morphology observations of GO-Ag ([Figure 3: see original paper]-b/c) indicated that nano-silver particles were uniformly distributed on the GO surface with Ag particle sizes of about 50 nm. The micro-morphology of MGO ([Figure 3: see original paper]-d) demonstrated that magnetic nano-Fe particles were successfully decorated on the GO surface through the co-precipitation method, with uniform distribution and particle sizes of about 10 nm. Micro-morphology test results of MGO-Ag showed that both nano-Fe and Ag particles were successfully decorated on the GO surface, and the decoration of Ag and Fe had basically no effect on their respective morphological characteristics.

3.3 XPS Characterization of Composite Adsorbents

XPS characterization results of GO and its composites are shown in [Figure 4: see original paper]. The C1s spectra of GO (a) and GO-Ag (b) after fitting showed that carbon in GO mainly exists in five forms: 284.6 eV (C=C/C-C), 285.5 eV (C-OH), 286.9 eV (C-O-C), 287.8 eV (C=O), and 288.9 eV (COOH), indicating that oxygen-containing functional groups were successfully intercalated into the single-layer G surface.

The carbon spectra results of GO-Ag and GO showed that the existence forms of C did not change significantly after nano-Ag particle decoration, but there were some changes in the intensity of carbon diffraction patterns. After Ag decoration on the GO surface, diffraction peaks of Ag $3d_5/_2$ and Ag $3d_3/_2$ appeared at 368.2 eV and 374.2 eV (c), consistent with the binding energy of metallic silver reported in literature [13, 14]. Fe $2p_3/_2$ in MGO and MGO-Ag showed a small peak at a binding energy of 718 eV (d), indicating that γ-Fe_2O_3 and cubic Fe_3O_4 coexisted on the GO surface, and magnetic particles were successfully decorated on the GO surface. All XPS detection results confirmed that GO composites and surface-modified metals were successfully synthesized.

3.4 Magnetic Hysteresis Characterization of Composite Adsorbents

Magnetic property test results for MGO and MGO-Ag ([Figure 5: see original paper]) showed that MGO and MGO-Ag exhibited superparamagnetic characteristics with saturation magnetizations of 14.9 emu/g (MGO-Ag) and 13.4 emu/g (MGO). Comparing the magnetism of MGO and MGO-Ag, the saturation magnetization of MGO-Ag was slightly higher than that of MGO, most likely due to dipole interactions between Fe and Ag nanoparticles.

The successful loading of magnetic particles on the adsorbent surface demonstrated that the adsorbent possesses strong magnetism, enabling effective separation from fly ash after use.

3.5 Mercury Adsorption Performance

3.5.1 Mercury Removal Characteristics of GO Mercury adsorption performance tests on pristine GO samples showed ([Figure 6: see original paper]) that GO exhibited good mercury adsorption characteristics at temperatures below 150℃. When the temperature was below 50℃, the mercury adsorption performance reached 50%; when the temperature was between 100℃ and 150℃, GO' s mercury adsorption performance reached 95%; however, when the temperature continued to rise above 200℃, the GO sample completely lost its mercury adsorption capability.

Thermogravimetric analysis results of GO samples are shown in [Figure 7: see original paper]. The results indicated that during temperature increase, GO weight loss mainly occurred in three intervals. When the temperature was below 50℃, adsorbed water on the GO surface was lost. This adsorbed water had some inhibitory effect on mercury adsorption [15]; therefore, after this water desorbed, more active sites were exposed on the GO surface, resulting in good mercury adsorption effects, manifested as strong mercury adsorption capability between 100℃-150℃ [16]. Meanwhile, oxygen-containing functional groups on the GO surface such as -OH or -COOH also had certain adsorption effects on mercury. When the temperature continued to rise, oxygen-containing functional groups on the GO surface gradually lost, completely eliminating mercury adsorption capability.

3.5.2 Mercury Removal by GO Composites Mercury removal performance test results of GO composites ([Figure 8: see original paper]) showed that decoration of GO surface with nano-Ag or nano-Fe particles both significantly promoted mercury adsorption. The strong mercury adsorption effect of nano-Ag particle-decorated GO mainly originated from Ag-Hg alloy formation [17-20]. Meanwhile, the co-decoration of Fe and Ag on the GO surface showed the most obvious effect in enhancing adsorbent performance, possibly due to Ag-Hg alloy formation and special active site chemical adsorption of Hg^0 on magnetic iron oxide and mercury synergistic effects [20-22]. At 50℃, MGO' s mercury breakthrough performance was about 50%, while GO-Ag and MGO-Ag exhibited 100% mercury adsorption. When the temperature was between 100℃ and 150℃, all samples showed excellent mercury adsorption performance. At 200℃, the GO sample had completely lost mercury adsorption capability, while GO-Ag and MGO samples began to gradually lose mercury adsorption performance with mercury breakthrough reaching about 40%. When the temperature continued to rise to 250℃, all samples gradually lost mercury adsorption capability.

3.5.3 Mercury Adsorption Performance Under Simulated Flue Gas Conditions The MGO-Ag sample, which contains magnetic particles and shows optimal mercury adsorption performance, was tested under simulated flue gas conditions. The results showed that MGO-Ag exhibited rapid adsorp-

tion capability, with 15 mg of adsorbent adsorbing about 4.5 ppm within 5 min at 100-200℃, showing significantly superior performance compared to Ag-decorated chabazite (0.14 μg/g) and Ag-decorated magnetic zeolite (0.03 μg/g) [17, 23]. MGO-Ag' s mercury adsorption capacity reached 60 μg/g (w/w) under 100-150℃ conditions, which is superior to fly ash (10-30 μg/g at 135℃) [24] and magnetic silver-decorated zeolite (13.3-40 μg/g at 150℃) [18] reported in literature.

The test results of MGO-Ag' s mercury adsorption capacity under simulated flue gas conditions at different temperatures for 5 min (a) and 30 min (b) are shown in [Figure 9: see original paper]. Simulated flue gas components: 4% O_2 + 12% CO_2 + 400 ppm SO_2 + 300 ppm NO + 75 g/g Hg vapor + 15 mg adsorbent.

3.5.4 Adsorbent Cyclic Performance Tests To investigate the cyclic regeneration characteristics of composite adsorbents, MGO-Ag was subjected to five consecutive cycles of adsorption (200℃) and desorption (370℃). The adsorbent' s mercury adsorption performance during the cycling process is shown in [Figure 10: see original paper]. The results demonstrated that after five consecutive adsorption-desorption cycles, the adsorbent' s mercury adsorption performance remained almost unchanged, with no loss of mercury adsorption capability. These findings indicate that MGO-Ag adsorbent possesses excellent regeneration and cycling characteristics, demonstrating tremendous potential for practical industrial applications.

4. Conclusions

Graphene-based magnetic materials were prepared through chemical methods and applied to mercury adsorption in coal-fired flue gas, and the feasibility of adsorbent regeneration and recycling was investigated. The following conclusions were obtained:

1. Four types of graphene-based adsorbents were successfully synthesized and characterized.
2. Pristine GO exhibited excellent Hg^0 adsorption performance at 100-150℃. Ag-NPs decoration of GO effectively promoted the adsorbent' s mercury adsorption capability, with the MGO-Ag composite adsorbent showing the best mercury adsorption capacity.
3. MGO-Ag demonstrated excellent mercury adsorption capability at 150℃-200℃, with almost no change in adsorption performance after repeated cycling.
4. The regenerable magnetic graphene-based composite adsorbent represented by MGO-Ag exhibits excellent Hg^0 adsorption performance under medium-low temperature conditions and can be effectively separated from fly ash, showing good prospects for industrial application.

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Note: Figure translations are in progress. See original paper for figures.