Preparation of Graphene Oxide (GO) and Its Composites and Study on Their Mercury Adsorption Properties - Postprint

Authors: Tian Chong (1,2); Yuxi Liu (3); Yu Xuehai (2,4); Hongbo Zeng (3); Zhao Yongchun (2); Zhang Junying (2)

Date: 2018-01-02T00:00:00+00:00

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), and nano-Ag particle-modified magnetic graphene oxide (GO-Ag and MGO-Ag). The materials were characterized and the adsorption of mercury from flue gas by graphene oxide and its composites was investigated. The results demonstrate 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, with the MGO-Ag composite adsorbent showing the best mercury adsorption capacity; MGO-Ag demonstrates excellent mercury adsorption capability at 150-200°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 Hg0 under medium-low temperature conditions, can be effectively separated from fly ash, and possesses promising industrial application prospects.

Full Text

Abstract

Nano-composites including graphene oxide (GO), ferriferrous oxide nanoparticles (Fe-NPs) loading graphene oxide (MGO), 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 adsorption in flue gas.

The results indicated that the four kinds of nano-composites can be synthesized successfully by the facile chemical methods. GO shows good Hg adsorption performance when the temperature ranges from 100℃ to 150℃. The Ag-NPs decorated GO can greatly enhance the Hg adsorption capability. MGO-Ag performs best of all the four composites on Hg adsorption. The optimum working temperature for MGO-Ag on Hg 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 serve as excellent candidates for Hg adsorption under medium-low temperatures (100-200℃). Further, the decoration of Fe-NPs helps 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

Introduction

Mercury emissions from coal-fired power stations pose serious threats to both the environment and human health [1, 2]. Although mercury exists only as a trace element in coal, its long-term and large-scale utilization 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). 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 (WFGD) systems, or selective catalytic reduction (SCR) systems. Nevertheless, 20-50% of elemental mercury still remains in coal-fired flue gas, and Hg is difficult to remove through these conventional systems. Therefore, developing effective adsorbents for Hg removal is of great significance [7].

Currently, common methods for Hg 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 turning the fly ash into a mercury sink and affecting fly ash quality. Developing efficient and economical adsorbents is therefore critically important. Among these, developing regenerable and recyclable adsorbents offers obvious advantages in reducing adsorbent costs. The greatest advantage of magnetic adsorbents is their ease of separation from fly ash. Consequently, developing magnetic adsorbents that can be easily separated from fly ash and investigating their regeneration and recycling technologies have become current research hotspots.

In recent years, carbon nanomaterials represented by graphene (G) have become a research focus for environmental experts worldwide 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 being the most stable basic unit in the material. Since its discovery in 2004, graphene has attracted intense 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. Meanwhile, GO can be easily 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 study uses GO as an adsorbent and functionally modifies it through chemical methods to prepare nano-silver decorated magnetic functional adsorbents. On one hand, we investigate the mercury adsorption capacity of GO-based adsorbents in coal-fired flue gas. On the other hand, we develop GO surface-functionalized magnetic adsorbents and examine their mercury adsorption capacity, regeneration, and recycling characteristics, laying the foundation for developing efficient, regenerable magnetic adsorbents and their industrial applications.

1.1 Experimental Raw Materials

The main raw materials for preparing GO and its composites include: graphite powder (particle size 7-10 m), concentrated sulfuric acid (H SO , 95-98 wt.%), sodium nitrate (NaNO), hydrogen peroxide (H O , 29-32% W/W aqueous solution), PVP (molecular weight 58,000); iron(III) source FeCl ·6H O, iron(II) source FeCl ·4H O; potassium permanganate (KMnO), ammonia water (29.5 wt.%), silver nitrate (AgNO), etc. All chemicals used in the experiments were of analytical grade.

1.2 Synthesis of Graphene and Composites

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 in a three-neck flask, then KMnO was slowly added, and the reaction system was stirred at high speed for 5 days. A certain amount of hydrogen peroxide was then added. Subsequently, a solution containing 500 mL deionized water/concentrated sulfuric acid (H SO , 98%)/hydrogen peroxide (H O , 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 yield fluffy graphene oxide powder (GO).

Nano-Ag decorated GO-Ag composite materials were prepared based on 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 then repeatedly washed with ethanol and deionized water and 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 and FeCl solutions (2:1 ratio) were prepared and then 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.

1.3 Characterization of Composites

The graphene-based composite samples were characterized by XRD, SEM, and TEM. XRD tests were performed using a Rigaku RU-200B X-ray diffractometer (CuK) with Cu emitter at 40 kV and 110 mA. SEM and TEM tests were completed at the University of Alberta ACSES facility. 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.

1.4 Adsorbent Mercury Removal Experiments

The Hg breakthrough experimental bench is shown in the system diagram [Figure 1: see original paper]. Before the 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, and the furnace temperature was set to meet experimental requirements. The experimental carrier gas was high-purity Ar with a flow rate of 40 ml/min. During the experiment, 200 L of mercury vapor was precisely injected using a syringe through polytetrafluoroethylene tees 1 and 2. During the experiment, Hg in the system was captured at room temperature using a gold amalgamation trap and then released at high temperature by heating. Hg monitoring was performed using a Tekran 2500 Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) detector (detection limit < 0.1 pg Hg).

2.1 XRD Characterization of Graphene and Composites

XRD tests were conducted on 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 increased compared to graphite' s interlayer spacing of 0.34 nm [11, 12], mainly due to the introduction of oxygen-containing functional groups into the lamellar structure. Comparative analysis of the differences between the XRD patterns of GO composites and GO reveals that the peak at 9.92° disappears in GO composites, primarily because some oxygen-containing functional groups may have detached during ultrasonic treatment [11]. However, this process facilitates functional modification such as nano-Ag particle decoration. GO-Ag and MGO-Ag exhibit different crystal planes at diffraction angles of 38.2°, 44.3°, 64.5°, 77.5°, and 81.6°, corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes, mainly from cubic nano-Ag particles, indicating successful decoration of nano-silver particles on the GO surface. Meanwhile, cubic phase -Fe O and Fe O appear in the XRD spectra of MGO and MGO-Ag, indicating successful preparation of magnetic graphene oxide composites through the co-precipitation method.

2.2 SEM/TEM of Graphene and Composites

The micro-morphologies of GO and its composites were characterized by SEM and TEM. The results show that GO ([Figure 3: see original paper]-a) presents as a smooth single-layer sheet 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) indicate that nano-silver particles are 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) shows 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 for MGO-Ag demonstrate that both nano-Fe and Ag particles were successfully decorated on the GO surface, and the decoration of Ag and Fe basically does not affect each other' s morphological characteristics.

2.3 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 show 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 show that the existence forms of C in GO samples decorated with nano-Ag particles do not change significantly, but there are some changes in the intensity of carbon diffraction patterns. After Ag decoration on the GO surface, diffraction peaks of Ag 3d / and Ag 3d / appear at 368.2 eV and 374.2 eV (c), consistent with the binding energy of metallic silver reported in literature [13, 14]. Fe 2p / in MGO and MGO-Ag shows a small peak at a binding energy of 718 eV (d), indicating that -Fe O and cubic Fe O coexist on the GO surface, and magnetic particles were successfully decorated on the GO surface. All XPS detection results demonstrate that GO composites and surface-modified metals were successfully synthesized.

2.4 Magnetic Hysteresis Characterization of Composite Adsorbents

Magnetic property test results for MGO and MGO-Ag ([Figure 5: see original paper]) show that MGO and MGO-Ag exhibit superparamagnetic characteristics with saturation magnetization of 14.9 emu/g (MGO-Ag) and 13.4 emu/g (MGO). Comparing the magnetism of MGO and MGO-Ag reveals that the saturation magnetization of MGO-Ag is 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 indicates that the adsorbent possesses strong magnetism, enabling effective separation from fly ash after use.

2.5.1 Mercury Removal Characteristics of GO

Test results of mercury adsorption performance of pristine GO samples ([Figure 6: see original paper]) show that GO exhibits good mercury adsorption characteristics at temperatures below 150℃. When the temperature is below 50℃, the mercury adsorption performance reaches 50%; when the temperature is between 100℃ and 150℃, GO' s mercury adsorption performance reaches 95%; however, when the temperature continues to rise above 200℃, GO samples completely lose their mercury adsorption performance.

Thermogravimetric analysis results of GO samples ([Figure 7: see original paper]) show that during temperature increase, GO weight loss mainly occurs in three intervals. When the temperature is below 50℃, adsorbed water on the GO surface is lost. This adsorbed water has a certain inhibitory effect on mercury adsorption [15]. Therefore, after this adsorbed water desorbs, more active sites are exposed on the GO surface, resulting in good mercury adsorption effects, manifested as strong mercury adsorption capacity between 100℃-150℃ [16]. Meanwhile, oxygen-containing functional groups on the GO surface such as -OH or -COOH also have certain adsorption effects on mercury. When the temperature continues to rise, oxygen-containing functional groups on the GO surface gradually lose, completely eliminating mercury adsorption capacity.

2.5.2 Mercury Removal by GO Composites

Test results of mercury removal performance of GO composites ([Figure 8: see original paper]) show that decoration of GO surface with nano-Ag or nano-Fe particles significantly promotes mercury adsorption. The strong mercury adsorption effect of GO decorated with nano-Ag particles mainly originates from Ag-Hg alloy formation [17-20]. Meanwhile, the co-decoration of Fe and Ag on the GO surface shows the most obvious effect in enhancing adsorbent performance, possibly due to Ag-Hg alloy effects and special active site chemical adsorption of Hg on magnetic iron oxide and mercury synergistic effects [20-22]. At 50℃, MGO’ s mercury breakthrough performance is about 50%, while GO-Ag and MGO-Ag exhibit 100% mercury adsorption. When the temperature is between 100℃ and 150℃, all samples show excellent mercury adsorption performance. At 200℃, GO samples have completely lost mercury adsorption capacity, while GO-Ag and MGO samples gradually lose mercury adsorption performance with mercury breakthrough reaching about 40%. When the temperature continues to rise to 250℃, all samples gradually lose mercury adsorption capacity.

2.5.3 Mercury Adsorption Performance of Adsorbents 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 show that MGO-Ag exhibits rapid adsorption capacity. At 100-200℃, 15 mg of adsorbent adsorbs about 4.5 ppm within 5 min, 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 reaches 60 µg/g (w/w) at 100-150℃, 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.

2.5.4 Adsorbent Cycling Performance Tests

To investigate the cyclic regeneration characteristics of composite adsorbents, continuous adsorption (200℃) and desorption (370℃) experiments were conducted on MGO-Ag for five cycles. The adsorbent’ s mercury adsorption performance during cycling is shown in [Figure 10: see original paper]. The results indicate that after five consecutive adsorption-desorption cycles, the adsorbent’s mercury adsorption performance shows almost no change and completely retains mercury adsorption capacity. These results demonstrate that MGO-Ag adsorbent has excellent regeneration and cycling characteristics, showing tremendous potential for practical industrial applications.

3. 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 can be successfully synthesized and characterized.
2. Pristine GO exhibits excellent Hg adsorption performance at 100-150℃. Ag-NPs decoration of GO can effectively promote mercury adsorption, and the MGO-Ag composite adsorbent shows the best mercury adsorption capacity.
3. MGO-Ag exhibits excellent mercury adsorption capacity at 150℃-200℃, and its adsorption performance remains almost unchanged after repeated cycles.
4. The renewable magnetic graphene-based composite adsorbent represented by MGO-Ag has excellent Hg adsorption performance under medium-low temperature conditions and can be effectively separated from fly ash, demonstrating good prospects for industrial application.

References

[1] Pacyna E G, Pacyna J M, Steenhuisen F, et al. Global Anthropogenic Mercury Emission Inventory for 2000 [J]. Atmospheric Environment, 2006, 40(22):4048-4063.

[2] Wang S, Zhang L, Li G, et al. Mercury Emission and Speciation of Coal-Fired Power Plants in China [J]. Atmospheric Chemistry Physics, 2010, 10(3):1183-1192.

[3] Sasmaz E, Kirchofer A, Jew A D, et al. Mercury Chemistry on Brominated Activated Carbon [J]. Fuel, 2012, 99:188-196.

[4] Baltrus J P, Granite E J, Rupp E C, et al. Effect of Palladium Dispersion on the Capture of Toxic Components from Fuel Gas by Palladium-Alumina Sorbents [J]. Fuel, 2011, 90(5):1992-1998.

[5] Wang S, Hao J. Air quality Management in China: Issues, Challenges, and Options [J]. Journal of Environmental Sciences, 2012, 24(1):2-13.

[6] Wu Y, Wang S, Streets D G, et al. Trends in Anthropogenic Mercury Emissions in China from 1995 to 2003 [J]. Environmental Science & Technology, 2006, 40(17):5312-5318.

[7] Presto A A, Granite E J. Survey of Catalysts for Oxidation of Mercury in Flue Gas [J]. Environmental Science & Technology, 2006, 40(18):5601-5609.

[8] Shen J, Hu Y, Shi M, et al. One Step Synthesis of Graphene Oxide-Magnetic

Nanoparticle Composite [J]. Journal of Physics Chemistry C, 2010, 114(3):1498-1503.

[9] Tang X Z, Li X, Cao Z, et al. Synthesis of Graphene Decorated with Silver Nanoparticles by Simultaneous Reduction of Graphene Oxide and Silver Ions with Glucose [J]. Carbon., 2013, 59:93-99.

[10] Kassaee M Z, Motamedi E, Majdi M. Magnetic Fe O -Graphene Oxide/Polystyrene: Fabrication and Characterization of a Promising Nanocomposite [J]. Chemical Engineering Journal, 2011, 172(1):540-549.

[11] Liu L, Liu J, Wang Y, et al. Facile Synthesis of Monodispersed Silver Nanoparticles on Graphene Oxide Sheets with Enhanced Antibacterial Activity [J]. New Journal Of Chemistry, 2011, 35(7):1418.

[12] Fu Y, Wang J, Liu Q, et al. Water-Dispersible Magnetic Nanoparticle-Graphene Oxide Composites for Selenium Removal [J]. Carbon, 2014, 77:710-721.

[13] Weaver J F, Hoflund G B. Surface Characterization Study of the Thermal Decomposition of Ag O. Chemistry Of Materials [J]. 1994, 6(10):1693-1699.

[14] Heister K, Zharnikov M, Grunze M. Adsorption of Alkanethiols and Biphenylthiols on Au and Ag Substrates: A High-Resolution X-Ray Photoelectron Spectroscopy Study [J]. The Journal of Physics Chemistry B. 2001, 105(19):4058-4061.

[15] Li Y H, Lee C W, Gullett B K. The Effect of Activated Carbon Surface Moisture on Low Temperature Mercury Adsorption [J]. Carbon., 2002, 40(1):65-72.

[16] Li Y H, Lee C W, Gullett B K. Importance of Activated Carbon’ s Oxygen Surface Functional Groups on Elemental Mercury Adsorption [J]. Fuel, 2003, 82(4):451-457.

[17] Liu Y, Kelly D J A, Yang H, et al. Novel Regenerable Sorbent for Mercury Capture from Flue Gases of Coal-Fired Power Plant [J]. Environmental Science & Technology, 2008, 42(16):6205-6210.

[18] Dong J, Xu Z, Kuznicki Z M. Magnetic Multi-Functional Nano Composites for Environmental Applications [J]. Advanced Functional Materials, 2009, 19(8):1268-1275.

[19] Luo G, Yao H, Xu M, et al. Carbon Nanotube-Silver Composite for Mercury Capture and Analysis [J]. Energy & Fuels, 2010, 24(1):419-426.

[20] Wilcox J, Rupp E, Ying S C, et al. Mercury Adsorption and Oxidation in Coal Combustion and Gasification Processes [J]. International Journal Of Coal Geology, 2012, 90-91:4-20.

[21] Granite E J, Pennline H W, Hargis R A, Novel Sorbents for Mercury Removal from Flue Gas [J]. Industrial & Engineering Chemistry Research, 2000,

39(4):1020-1029.

[22] Wu S, Oya N, Ozaki M, et al. Development of Iron Oxide Sorbents for Hg Removal from Coal Derived Fuel Gas: Sulfidation Characteristics of Iron Oxide Sorbents and Activity for COS Formation during Hg Removal [J]. Fuel, 2007, 86(17-18):2857-2863.

[23] Dong J, Xu Z, Kuznicki S M. Mercury Removal from Flue Gases by Novel Regenerable Magnetic Nanocomposite Sorbents [J]. Advan. Funct. Mater, 2009, 19:1268-1275.

[24] Carey T R, Richardson C F. Assessing Sorbent Injection Mercury Control Effectiveness in Flue Gas Streams [J]. Environmental Progress, 2004, 19(3):167-174.

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

Source: ChinaXiv —Machine translation. Verify with original.