
Lirui Wu\textsuperscript{1}, Lanxin Zhang\textsuperscript{1}, Tao Meng\textsuperscript{1}, Fei Yu\textsuperscript{2,3}, Junhong Chen\textsuperscript{2,4}, Jie Ma\textsuperscript{2*}

\textsuperscript{1} School of Mechanical Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China
\textsuperscript{2} State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China
\textsuperscript{3} School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Hai Quan Road, Shanghai 201418, China
\textsuperscript{4} Department of Mechanical Engineering, University of Wisconsin–Milwaukee, Milwaukee, WI 53211, USA

ABSTRACT

Amino-functional graphene-sponge composites decorated by graphene nanodots (G-GND/S) were synthesized. The preparation technology prevents the loss of nano-materials and reduces the amount of graphene addition. G-GND/S was used as adsorbents to remove formaldehyde, and then their performances for formaldehyde adsorption were evaluated by dynamic adsorption experiment. The adsorption properties of three different materials: sponge, graphene-sponge, and G-GND/S, the breakthrough time and adsorption capacity had been compared, the results showed G-GND/S had better formaldehyde adsorption properties with longer breakthrough time (~2137 min/g) and adsorption ability of formaldehyde (22.8 mg/g). Large amounts of amine groups were the most important factor for the strength enhancement of the adsorption efficiency.

Keywords: Graphene; Sponge; Nanodot; Formaldehyde.

INTRODUCTION

Indoor air pollution has recently become a major concern, among the indoor volatile organic compounds (VOCs), formaldehyde is the most abundant airborne carbonyl chemical (Yu et al., 2013; Zhou et al., 2013). Formaldehyde can cause watery eyes burning sensations in the eyes and throat, nausea and difficulty in breathing in some people exposed at elevated levels (above 0.1 ppm). Environment Protection Agency (USEPA) reported that exposing to formaldehyde chronically may cause cancer (Lee et al., 2013). Therefore, it is strongly necessary to develop an effective method to remove formaldehyde. Up to now, many methods, such as photo-catalyst (Liang et al., 2012), enzymes (Sigawi et al., 2011), plasma (Saultich and Müller, 2013) and adsorption (Rengga et al., 2012) etc. have been reported to remove the formaldehyde. The adsorption method is commonly and effectively used in the elimination of formaldehyde due to its simplicity, less energy consumption, and without generating secondary pollutants (Lee and Kim, 2012; Beheshtian et al., 2013). Activated carbons (AC) were used as adsorbents most frequently to remove formaldehyde. Wen et al. (2011) used activated carbon derived from sewage sludge to remove formaldehyde, but the adsorption capacity just was 7.62 mg/g at a low concentration of formaldehyde (about 0.41 mg/m\textsuperscript{3}). Ma et al. (2011) studied the removal of low-concentration formaldehyde using activated carbon modified by hexamethylene diamine and found that modification significantly improved the adsorption performance of AC (form 0.08 to 3.8 mg/g). The nitrogen-containing functional groups played an important role in increasing formaldehyde adsorption ability, as also described elsewhere. Lee et al. (2013) found that activated carbons with higher nitrogen content greatly improved the adsorption capacity and the breakthrough time. Though the modified activated carbon has been greatly improved, as an important adsorption material, it is still less than the expectation. The use of activated carbon for removing formaldehyde was currently caught in a bottleneck for the small adsorption capacity and short breakthrough time. Graphene have attracted considerable interests for its unique physicochemical properties, such as high surface area, excellent conductivity, high mechanical strength, ease of functionalization (Shao et al., 2010). Carbon nanomaterials can be applied to remove formaldehyde and volatile organic compounds (VOCs) ((Lee and Kim, 2012). Lee found that graphite is a porous
The carbon material and its specific surface area and pore volume can be expanded by using the shape modification process. On the other hand, the adsorption of formaldehyde on graphene was also investigated to design high sensitivity sensors for detection of formaldehyde (Majidi and Karami, 2014). However, there are still some obstacles for graphene to be well used as an efficient adsorbent of formaldehyde: 1) the complex synthesis process and high cost; 2) a poor adsorption capacity for formaldehyde (Lee and Kim, 2012); 3) being powdered form and separated with difficulty, leading to the second environmental pollution.

In this study, in order to apply graphene to enhance the removal efficiency of formaldehyde, three-dimensional carbon nanoarchitect, which contribute to prevent the loss of nano-materials and reduce the amount of graphene, were synthesized based on the low-cost sponge. To enhance the removal properties of formaldehyde, the graphene-sponge composites were decorated using graphene nanodots and functionalized by ethylenediamine (EDA). And then the amino-functional graphene-sponge composites decorated by graphene nanodots were used as adsorbents to remove the indoor formaldehyde, presenting the enhanced formaldehyde adsorption and removal performance than previous reports.

**METHODS**

**Materials**

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) in analytical purity and used in the experiments directly without any further purification. All solutions were prepared using deionized water. Sponge is bought from Yongkang Runde Commerce and Trade Co., Ltd.

**Preparation of Graphene Oxide**

Graphite oxide was prepared using a modified Hummer’s method (Hummers Jr and Offeman, 1958; Hirata et al., 2004; Ma et al., 2014). Graphite oxide was dispersed in deionized water and sonicated in an ultrasound bath for 12 h. The sonicated dispersion was centrifuged for 20 min at 4000 r.p.m. to remove unexfoliated graphite oxide particles from the supernatant. The obtained suspension of graphite oxide (GO) was then processed by freeze-drying to obtain GO powders.

**Preparation of Graphene Nanodots**

Graphene nanodots was prepared using the method described in literature (Zhou et al., 2012) using photo-Fenton reactions. GO (150 mg) was dispersed in 75 mL water followed by sonication for 6 h. Add 5 ml hydrochloric acid (1 mol/L) and 2 mL FeCl₃ (0.5 mol/L) solution to the prepared GO solution, mixed thoroughly and transfer the solution to a quartz reactor. The reactor were placed on a light box with a 1000 W UV lamp (365 nm). The reactors worked for 2 h under vigorous stirring and the UV light. A peristaltic pump was used to inject 300 ml H₂O₂ (2 mol/L) to the quartz reactor at a pumping rate of 5 mL/min.

**Preparation of G-GND/S**

GO (50 mg) was dispersed in 25 mL water followed by sonication for 2 h. Upon addition of 530 μL EDA, 130 μL ammonia (30% w/v) and different usages of 1mg, 5mg and 10mg graphene nanodots to the preparation GO solution, the sponges (18 mm × 18 mm × 18 mm) were placed in the sufficiently stirred mixtures. The solution was then quickly heated to 95°C and maintained at the constant temperature in a water bath for 12 h to form hydrogels and introduce amino-group on the GO surface. The hydrogels were taken out and freeze-dried to obtain G-GND/S-1, G-GND/S-5 and G-GND/S-10, corresponding to the graphene nanodots amount of 1mg, 5mg and 10mg.

**Adsorption Experiment**

G-GND/S was used to adsorb formaldehyde in the experimental apparatus as shown in Schematic 1. This consists of two main parts: (i) Formaldehyde gas generator; (ii) Adsorption and detector equipment of formaldehyde. The 3.6 ppm standard formaldehyde gas without the interference of water vapor was generated by flowing nitrogen gas at the flow rate of 400 mL/min through the diffuse tube. The outlet concentration of formaldehyde was detected by a PPM formaldehyde analysis instrument (PPM Technology Ltd, UK). According to the guideline value of the WHO, 0.08 ppm formaldehyde was generally recognized as a safety threshold. Thus, the breakthrough time was defined at the output concentration reached 0.08 ppm. The average weight of G-GND/S was around ~70 mg. The experiments were stopped when the output concentration (C) reached 80% of the inlet concentration (C₀).

![Schematic 1. Schematic diagram of the adsorption experiment of formaldehyde.](image-url)
**Characterization Methods**

The microstructure and morphology of the Sponge, G/S, G-GND/S were analyzed by scanning electron microscopy (SEM, JSM-6400F, Japan). The microstructure and morphology of the G-GND were analyzed by transmission electron microscopy (TEM, JEOL 2100, Japan). X-Ray photoelectron spectroscopy (XPS) analysis was carried out in a Kratos Axis Ultra DLD spectrometer, using monochromated Al Ka X-rays, at a base pressure of $1 \times 10^{-9}$ Torr. Survey scans determined between 1100 and 0 eV revealed the overall elemental compositions of the sample and regional scans for specific elements were performed. The peak energies were calibrated by placing the major C1s peak at 284.6 eV. Samples were prepared identically to those of the batch experiments. Fourier transform infrared spectra (FT-IR) of powder samples were recorded on a Tensor 27 FTIR spectrometer (Bruker Optics, Inc.).

The total amount ($W$) of formaldehyde adsorption for each sample was calculated according to the following equation:

$$W = \frac{P \times M}{R \times T} \times C \times V$$  \hspace{1cm} (1)

C is the concentration (ppm).

T is the temperature (K).

P is the atmospheric pressure (kPa).

M is the molar mass (30.01 for HCHO) of the gas (g/mol).

R is the ideal gas constant (8.314 JK/mol).

V is volume of adsorbed formaldehyde: breakthrough time $\times$ flow rate (0.4 L/min).

**RESULTS AND DISCUSSION**

The SEM images and photograph of sponge and G-GND/S-5 were shown in Figs. 1(a) and 1(b). SEM images show that the sponge possesses an interconnected porous framework with skeleton (Fig. 1(a)). Graphene were distributed in the porous three-dimensional interconnected structure, as shown in Figs. 1(b) and 1(b1). The TEM images of G-GND decorated by graphene nanodots were shown in Figs. 1(c) and 1(d). Fig. 1(c) shows layered graphene with folded edges, and its surface is not perfectly flat due to the presence of a few wrinkles. In Fig. 1(d), graphene sheets were decorated by some graphene nanodots with the diameter of ~5 nm. After the process of freeze-drying for the hydrogel, the sponge was used as a skeleton to ensure the complete contact of adsorbent materials and formaldehyde gas due to the prominent contacting.

FT-IR spectra of GO and G-GND are shown in Fig. 2. The characteristic peaks of GO appear at 1727 cm$^{-1}$ (C=O in carboxyl group), 1619 cm$^{-1}$ (C-C in the aromatic ring), 1398 cm$^{-1}$ (C-OH group) and 1051 cm$^{-1}$ (C-O-C in the epoxide group). The bands at 2887 cm$^{-1}$ and 2944 cm$^{-1}$ are attributed to -CH$_2$ stretching vibration of the EDA chain. Compared the FT-IR spectra of G-GND with GO, the doublet at 2887 cm$^{-1}$ and 2944 cm$^{-1}$ appeared G-GND due to stretching vibration of N-H (in the C-NH group) and C-N (in the -C-NH-C- group) (Srisuda and Virote, 2008), which indicated the nucleophilic substitution reaction of the amine groups with the epoxide groups of GO was prepared successfully. As far as we know, surface specific area, pore volume, surface functional groups and pore size distribution were the most important factors that affect the adsorption capacity of the material. The addition of graphene nanodots had little impact on the surface specific area (data not shown), pore volume, and pore size distribution of the sample since the sponge pore size was far larger than that of the graphene nanodots, the pore dimension of sponge was about 100 μm while the dimension of the graphene nanodots was about only 5 nm, as shown in Fig. 1(d).

![Fig. 1. SEM images and photograph of sponge (a, a1, a2) and G-GND/S (b, b1, b2), TEM images (c, d) of G-GND.](image-url)
The composition of the G and G-GND is strongly supported by the XPS analysis, as shown in Figs. 2(b)–2(d). Figs. 2(b)–2(d) shows the XPS survey scans and typical N1s spectra of G and G-GND. It was worthy of note that the sponge was removed to prevent the impact of sponge on the XPS analysis results. The N1s peak at 399.7 eV is attributed to the nitrogen in -C(ON), while the peak at 400.3 eV correspond to the nitrogen in -NH2 (Jansen and Vanbekkum, 1995). XPS data for G and G-GND are given in Table 1. After the addition of graphene nanodots, the content of nitrogen in the modified G-GND samples was higher than that of G. The respective percentages of these two kinds of nitrogen in G and G-GND are compared to clarify the bonding state of the amino-group in the GO structure. The nitrogen content of the C(ON) bonds in G is 80%, which is much larger than that of 20% in the -NH2 bonds; This maybe indicates that the majority of EDA have both their amino ends covalently attached to the GO surface in G-NH2. However, in G-GND, the proportion of -NH2 bonds (30%) was much higher than that of G (20%), indicating the efficient amination of G-GND.

Fig. 3 shows the breakthrough curves and adsorption amount of formaldehyde adsorption for G/S, G-GND/S and sponge. The sponge has little adsorption capacity for formaldehyde, as shown in Fig. 3(a). Compared G/S with sponge, G/S showed better formaldehyde adsorption properties with longer breakthrough time (~915 min/g). To achieve the best adsorption effect, G-GND/S decorated with different amount of graphene nanodots of 1 mg, 5 mg and 10 mg were tested. For G-GND/S-1, its breakthrough time for formaldehyde increased by twice than G/S. Decorated with 5 mg graphene nanodots, its removal ability against formaldehyde increased astonishingly with longer breakthrough time (~2137 min/g). The breakthrough time of G-GND/S presented a rising trend with the adding quantity of graphene nanodots from 1 to 5 mg, whereas decreased slightly with the adding quantity of graphene nanodots from 5 to 10 mg. It is shown that G-GND/S-5 presented better formaldehyde adsorption properties with longer breakthrough time (~2137 min/g). Fig. 3(b) represents the adsorption amount of formaldehyde for G/S, G-GND/S and sponge until the breakthrough time. As mentioned before, the sponge was just a role as a skeleton supporting without contribution to adsorption amount and the mass of the sponge was excluded from the sample when calculating the adsorption capacity (Fig. 3(b)). The experimental results showed that the adsorption ability of formaldehyde was as high as ~22.8 mg/g for G-GND (5.5 mg/g, calculated with the mass of sponge), with more excellent adsorption capacity than previously reported work (Carter et al., 2011; Ma et al., 2011; Wen et al., 2011; Zhang et al., 2011; Chen et al., 2014).

According to Eq. (2), it is showed that the -NH2 bonds on the surface of G/S and G-GND/S has been considered the main reasons for the adsorption of formaldehyde (Rong et al., 2010). For the graphene nanodots, there were a relatively
little content of carboxyl group contained on the surface of graphene nanodot, which resulting more effective amino were reserved in reaction procedure with ethylenediamine, as shown in Fig. 4. The addition of graphene nanodot can greatly enhance their removal capacity for formaldehyde because of the increased chemical interaction between amino groups and formaldehyde molecules. Based on Fig. 3 and Table 1, it can be concluded that graphene nanodot was one of the most important factors to improve the adsorption properties of the G-GND/S for the removal of formaldehyde.
To obtain a stable micro-structure, the graphene were designed as aerogel poly-composite which make the graphene sheets adhere to the skeleton of the sponge uniformly and tightly. The amino-functional graphene composite has larger specific surface area for the excellent dispersion degree. Considering the high cost of graphene, we make the quantity of graphene decreased dramatically by adding trace amount of graphene nanodots. After decoration with graphene nanodots, the chemisorption contribute more for the removal of formaldehyde and then the removal property of the composite for formaldehyde has been improved remarkably. On the other hand, the preparation process of graphene were used in this paper is mild and simple which also helps to reduce the cost of adsorbents. According to the several aspects stated above, the 3D amino-functional graphene-sponge composite has huge potential for its practical value in environmental protection field.

CONCLUSIONS

Amino-functional graphene-sponge composites were decorated with graphene nanodots, and then their performances for formaldehyde adsorption were evaluated by dynamic adsorption experiment. The adsorption properties of three different materials, the breakthrough time and adsorption capacity, had been compared, G-GND/S-5 showed the best adsorption performance. As mentioned before, large amounts of amine groups were the most important factor for the strength developing of the adsorption efficiency. The above results show that the addition of graphene nanodots greatly enhances the quantity of amine groups and the adsorption properties of formaldehyde.

ACKNOWLEDGMENTS

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REFERENCES


Table 1. Surface element composition of G and G-GND by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s (atom%)</th>
<th>N1s (atom%)</th>
<th>N1s (-C(O)N) (atom%)</th>
<th>N1s (NH₂) (atom%)</th>
<th>O1s (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>41.23</td>
<td>10.76</td>
<td>8.61 (80%)</td>
<td>2.15 (20%)</td>
<td>48.01</td>
</tr>
<tr>
<td>G-GND</td>
<td>66.87</td>
<td>13.51</td>
<td>9.46 (70%)</td>
<td>4.05 (30%)</td>
<td>19.62</td>
</tr>
</tbody>
</table>


