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High CO performance of graphene oxide modified with CuCl by using “ion implantation” method

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Abstract

Copper (I) chloride (CuCl) modified graphene oxide with different copper (Cu) content were prepared by ‘ion implantation’ method using CuCl as Cu source. The samples were characterized by x-ray Powder Diffraction-XRD, FTIR, BET, SEM, TEM, EDS and x-ray photoelectron spectroscopy-XPS. From TEM images and EDS elemental mapping, it showed the CuCl particles of 30–50 nm with high dispersion on graphene oxide surface. From XPS result, it revealed the presence of both Cu+ and Cu2+ ions but Cu+ ion amount was predominant. CO adsorption on CuCl modified graphene oxide with different Cu content was tested. Among tested CuCl modified GO samples, 2CuCl/GO sample exhibited the highest CO gas adsorption capacity of 2.9 mmol g−1 at 20 °C which was 7.5 times higher than that of pristine GO (0.38 mmol g−1). High CO adsorption performance on CuCl modified GO can be explained by the formation of π–π complexation between CO molecules and Cu(I) ions. From CO adsorption on CuCl modified GO, it showed that the experimental data fit well with Langmuir-Freudlich model.

1. Introduction

Carbon mono-oxide (CO) is a colorless, odorless, tasteless and highly toxic gas. Carbon mono-oxide is a metabolic waste and toxic gas, which is mainly originated from the incomplete burning of fuels used in automobile engines, coals in the thermal power plants etc... [1–3]. Carbon mono-oxide is an raw material for production of chemicals, such as formic acid, methanol, ethylene glycol, fertilizer (urea) and resin [4]. However, CO gas is very toxic to humans because it reacts with hemoglobin in the blood to form carboxy-hemoglobin, which reduces the blood’s ability to carry oxygen, causing to death [5]. Therefore, CO removal has received a great attention of researchers and many efforts have been done [6]. Among the methods used for CO removal, adsorption method is widely applied due to its low-cost treatment, friendly environment and effectiveness. Adsorbents for selective CO adsorption like activated carbons, zeolite, metal oxides and metal-organic frameworks have been reported [7–9]. However, low CO adsorption selectivity of mentioned adsorbents was noted. Recently, the Cu(I) containing adsorbents for CO removal with high efficiency have been investigated and developed [10]. Thus, due to the formation of π–π complexation between CO molecules and Cu (I) ions, it makes them much more selective for CO adsorption as compared to that of adsorbents without containing CuCl which CO adsorption is mainly based on the Van der Waal force [11–13]. Recently, Xue et al [11] reported that activated carbon modified with CuCl showed much higher CO adsorption capacity as compared to that of unmodified activated carbon. Thus, CO adsorption capacity increased from 11.5 cm3 g−1 to 45.4 cm3 g−1. They explained the highly CO adsorption performance is due to the formation of π complexation bond between CO molecules and Cu(I) ions. Zhu et al [12] synthesized the porous carbon xerogels doping with CuCl and showed
the high CO adsorption capacity of 12.04 cm$^3$ g$^{-1}$ which was much higher than that of the undoped carbon xerogels. He et al.[13] prepared the Zn–Cu(1)/MCM-41 by using solid state ion exchange with CuCl and ZnCl$_2$ and these materials showed the CO adsorption capacity of 1.82 mmol g$^{-1}$ which is much higher than that of ZnCl$_2$/MCM-41 (0.26 mmol g$^{-1}$) and CuCl/MCM-41 (0.59 mmol g$^{-1}$). Gao et al.[14] prepared the CuCl supported AC and they claimed that these materials had high CO adsorption capacity (3.63 mmol g$^{-1}$). Xie et al.[15] studied zeolites modified with CuCl by ion exchange method. At low temperature, the high CO adsorption capacity of 3.7 mmol g$^{-1}$ was obtained. Hirai et al.[16] synthesized a composite including CuCl and polystyrene resin with amine groups and they showed that plastic materials containing CuCl had a CO adsorption capacity of 5.7 times higher than that of the material without containing CuCl. Graphene oxide is recognized as a promising material with many applications such as adsorbent, catalyst carrier, drug carrier etc. .[17] Graphene oxide is consisted of one or several carbon layers with high surface area and having the functional groups like hydroxyl, carbonyl, epoxy and carboxylic groups.[18] Lingam dinne et al.[19] reported the maximum CO (II) adsorption capacity of 21.28 mg g$^{-1}$ on GO and they explained the high Co(II) ions adsorption capacity of GO is due to the chemical interactions between Co (II) and surface oxygen like—C=O and C–O, and as well as the formation of the π–π bonding. Darae et al.[20] reported that composite UiO-66/GO showed the high H$_2$S adsorption capacity of 8.7 mmol g$^{-1}$ at 30 °C which was 3 times higher than that of the pristine UIO-66 and GO. They explained the improvement of H$_2$S adsorption capacity is due to the synergistic effect between UIO-66 and GO. Yi et al.[21] prepared the chitosan/graphene oxide composites and used them to adsorb aniline from aqueous solutions and cigarette smoke. Chitosan/graphene oxide composite showed the adsorption amount of aniline, phenol, pyridine and furan gases of 15.23%, 18.68%, 8.74% and 8.74%, respectively. However, to our best knowledge, CO adsorption on the GO as well as the modified GO, especially CuCl modified GO has not yet been reported. In this paper, we report the GO modified with CuCl by using ‘ion implantation’ method. The CuCl modified GO with different Cu contents were tested in the CO adsorption at different temperatures. CO adsorption capacity on CuCl-modified GO was evaluated and explained on the formation of π–π-complexation bond between CO molecules and Cu(I) ions.

2. Materials and methods

Chemicals: Copper (I) chloride (CuCl), graphite, dichlorodiphenyltrichloroethane (C$_{14}$H$_{9}$Cl$_{5}$), phosphoric acid (H$_3$PO$_4$), sulphuric acid (H$_2$SO$_4$, 98%), hydrochloric acid (HCl, 37%), hydrogen peroxide (30 wt% H$_2$O$_2$), and potassium permanganate (KMnO$_4$, 99.5%). All chemical were of analytical grade and purchased from Sigma Aldrich company. Ultra-high pure nitrogen (99.99%) was purchased from gas delivery company of Vietnam.

2.1. Synthesis of graphene oxide

Graphene oxide (GO) was synthesized by using the procedure described in reference [22]. About, 1 g expanded graphite was introduced into a container of a mixture of 150 ml concentrated H$_2$SO$_4$ and H$_2$PO$_4$, then stirred at 25 °C for 60 min. After that, 6 g of KMnO$_4$ was added slowly into the mixture. The mixture was kept at room temperature for 3 days. Further oxidation reaction was occurred by adding 3 ml H$_2$O$_2$ quenched in ice-cold water for temperature control (due to the exothermal reaction). The solid product was washed with 1 M HCl and then was washed with deionized water until pH of 7.0. The obtained graphite oxide was dried at 100 °C for 24 h. To obtain graphene oxide, graphite oxide synthesized as mentioned above was delaminated by using micro wave method.

2.2. Synthesis of CuCl/GO nanocomposite

Insertion of Cu ions into GO framework (denoted as CuCl/GO) was performed by using ‘ion implantation’ method. Ion implantation is carried out in a quartz tubular reactor. The reactor was divided into two compartments separated by a membrane of quartz fibers. A certain amount of CuCl and graphene oxide are put into each compartment. The reactor is placed in a tubular furnace and heated up 500 °C with heating rate of 20 °C/min. At 500 °C, CuCl is dissociated in Cu$^+$ and Cl$^-$ ions and with N$_2$ flow (50 ml min$^{-1}$) goes to the compartment containing the graphene oxide. At high temperature, CuCl is dissociated into Cu$^{+}$, Cl$^-$ ions and incorporated into GO matrix. After 1 h of heating at 500 °C, reactor is cooled down to the room temperature. The scheme of GO modified with CuCl by ion implantation method is shown in Scheme 1:

Graphene oxide with 1, 2 and 3 times CuCl modifying were denoted as: 1CuCl/GO, 2CuCl/GO and 3CuCl/GO.

2.3. Characterization of diatomite

The x-ray Powder Diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer-Germany using Cu K$_{α}$, as radiation source ($\lambda = 0.15406$ nm) a range of 2θ = 10°–80°. TEM image studies was
recorded on a JEOL JEM 1400 Transmission Electron Microscopy (TEM) at 100 kV acceleration voltage. The SEM images were performed on JEOL JSM 6500F (USA). EDS measurements were carried out using JEOL JED-2300 spectrometer. The FT-IR measurements were performed on a Jasco 4700 spectrometer. XPS measurements were performed on a Thermo ESCALAB spectrometer (USA) using a monochromic Al Kα source at 1486.6 eV. The surface area, pore volume and pore diameter were measured on Tristar-3000 instruments using N₂ as adsorbate.

2.4. CO gas adsorption test

Before the adsorption measurements, the products were degassed under vacuum at 150 °C for 4h. CO adsorption isotherms was carried out at 20 °C, 30 °C and 40 °C under static condition using volumetric apparatus (NOVE1000 e, Quantachrome corp., Boynton Beach, FL, USA). During the adsorption test, temperature was maintained by circulating ethane diol-water from a bath with setting temperature. Ultrahigh purity CO (99.99%) was used for CO adsorption measurement.

3. Results and discussion

3.1. Structural characterization of GO and CuCl/GO

3.1.1. X-ray powder diffraction (XRD)

XRD patterns of CuCl modified GO samples were presented in figure 1. In the XRD pattern of GO, it appeared a single diffraction peak at 2θ of 10.6° which corresponds to the (001) reflection plane [23]. In XRD patterns of xCuCl/GO the peaks appeared at 27.6°, 45.5° and 56.5° which contributed to the reflection (111), (220) and (311) of CuCl [24]. With increasing of Cu content, the increase of these peak intensity was observed. Additionally, no peaks which are characteristic of CuO and Cu₂O phase was noted, indicating the high purity of CuCl phase. In XRD patterns of CuCl modified GO materials, the characteristic peak of GO structure at 2θ of 10.6° disappeared. This can be explained by the fact that CuCl particles were intercalated within GO layers [25, 26].

3.1.2. Fourier-transform infrared spectroscopy (FTIR)

Figure 2 shows the FTIR spectra of GO and CuCl/GO with different Cu content. In the spectra of GO and CuCl/GO appeared the bands at 3418 cm⁻¹ and 1716 cm⁻¹ which assigned to the vibration of O–H groups. Bands at 1556 cm⁻¹ and 1154 cm⁻¹ which attributed to the vibration of C=O and C–O groups, respectively [27]. In the spectra of CuCl modified GO samples, an additional band at 666 cm⁻¹ appeared, which assigned to the vibration of Cu–Cl bond [28].

3.1.3. Energy-dispersive x-ray spectroscopy (EDS or EDX)

Element compositions of GO and CuCl modified GO determined by EDS are given in table 1. As seen in table 1, the main constituents of graphene oxide are C (65.75%) and O (34.25%). For CuCl modified GO samples, with increasing the CuCl content inserted into GO framework, C and O content were gradually decreased from 65.75 wt% to 44.02 wt% and 34.25 wt% to 23.59 wt%, respectively. Cu and Cl content incorporated into GO framework increased from 7.26 wt% to 22.22 wt% and 3.82 wt% to 10.17 wt%, respectively. This indicated the replace of C and O by Cu and Cl element.
Figure 1. XRD patterns of CuCl modified GO samples with different CuCl content.

Figure 2. FTIR spectra of GO and CuCl/GO samples.

Table 1. Element composition (wt%) of GO and CuCl/GO samples determined by EDS.

| Element | GO    | 1CuCl/GO | 2CuCl/GO | 3CuCl/GO |
|---------|-------|----------|----------|----------|
| C       | 65.75 | 58.38    | 51.16    | 44.02    |
| O       | 34.25 | 30.55    | 27.15    | 23.59    |
| Cu      | —     | 7.26     | 14.33    | 22.22    |
| Cl      | —     | 3.81     | 7.36     | 10.17    |
| Total   | 100   | 100      | 100      | 100      |
Figure 3. Elemental mapping by EDS of 2CuCl/GO: (a) total elements, (b) Cu element and (c) Cl element.

Figure 4. TEM images of GO (a); 1CuCl/GO (b); 2CuCl/GO (c) and 3CuCl/GO samples (d).
Morphology of CuCl/GO determined by EDS mapping was illustrated in figure 3. As seen in figure 3, a homogeneous distribution of Cu and Cl on graphene oxide surface was noted.

3.1.4. Transmission electron microscopy (TEM)

TEM-images of GO and CuCl modified GO samples were presented in figure 4. In the TEM image of 1CuCl/GO samples (figure 4(b)), aggregated particles of 60–100 nm which consisted of very small particles on GO surface were observed. In the case of 2CuCl/GO sample (figure 4(c)), aggregated particles of 30–50 nm size were noted. TEM image of 3CuCl/GO samples showed a dense zone consisted of very small CuCl particles.

3.1.5. N2 adsorption–desorption isotherms analysis (BET)

BET of GO and xCuCl/GO samples are shown in the figure 5. BET of GO and CuCl/GO samples showed a type IV according to the IUPAC classification [29]. In isotherms curve of GO, at the high P/Po of 0.5–1 appeared a hysteresis loop, which is characteristic for mesoporous materials. This is due to the capillary condensation of N2 at high P/Po. However, in comparison with GO sample, CuCl/GO samples showed smaller hysteresis loops. This can be explained by the fact that the space between GO layers is large, which facilitates the N2 capillary condensation. In the case of CuCl/GO samples, due to the deposition of CuCl particles within GO layer, it causes the narrowing of the space of GO layers, leading the limitation of the N2 capillary condensation.

Textual characteristics of GO and CuCl/GO samples are shown in table 2. As seen in table 2, it showed that the specific surface area of CuCl/GO samples material was smaller than that of GO. Thus, specific surface area decreased with increasing CuCl loading (from 297 to 159 m² g⁻¹). Also, volume and pore diameter decreased from 1.38 cm³ g⁻¹ to 0.65 cm³ g⁻¹ and from 32.22 nm to 16.50 nm, respectively. The decrease of S_BET, V_pore and D_BJH with increasing CuCl loading may be due to the deposition of CuCl particles within GO layers.

3.1.6. X-ray photoelectron Spectroscopy (XPS)

To investigate the valence states of the copper element, XPS measurements were performed. Figure 6 presented the XPS spectra of 2CuCl/GO samples including survey spectrum, spectra of Cls, O1s and Cu 2p. As seen in figure 6(A), appeared the peaks of C 1s at 285.20 eV, O 1s at 534.84 eV, Cu 2p at 936.36 eV and Cl 2p at 198.52 eV.
respectively [30–34]. In the C1s spectrum (figure 6(B)) the peaks of C 1s at 288.2 eV, 285.62 eV and 284.41 eV assigned to the bonding of O=\(\text{C}–\text{O}\), \(\text{C}–\text{O}\) and \(\text{C}–\text{C}\) in graphene oxide sheets [35]. In the O1s spectrum, the peaks of O1s at 534.3 and 531.1 eV which correspond to the bonding of \(\text{C}–\text{O}\) and \(\text{C}=\text{O}\), respectively [36]. In figure 6(D), the binding energies of Cu 2p\(_{3/2}\) appeared at 934.86 eV, 942.80 eV and 963.32 eV and binding energy of Cu 2p\(_{1/2}\) appeared at 954.66 eV. Deconvolution of Cu 2p spectrum revealed the presence of both Cu\(^+\) and Cu\(^{2+}\) ions. Characteristic peaks of Cu\(^{2+}\) ions appeared at 935 eV, 943 eV and 957 eV and characteristic peaks of Cu\(^+\) ions appeared at 934 eV, 953 eV and 963 eV [37]. The much higher peak intensities of Cu\(^+\) as compared to those of Cu\(^{2+}\) revealed the Cu\(^+\) amount was predominant.

3.2. CO adsorption on GO and CuCl modified GO

CO adsorption isotherms of GO and CuCl modified GO at 20 °C were presented in figure 7.

As seen in figure 7, CO Adsorption capacity of CuCl modified GO samples was much higher than that of pristine GO. Thus, 2CuCl modified GO samples exhibited the CO adsorption capacity of 2.9 mmol g\(^{-1}\) which was 7.5 times higher than that of the pristine GO (0.38 mmol g\(^{-1}\)). This can be explained by the fact that CO adsorption on GO is the physical adsorption by Van der Waals force while CO adsorption on CuCl modified GO is the chemical adsorption by the interaction between CO molecules and Cu\(^+\) ions to form \(\pi\)-complexation bonds [12]. As observed in figure 7, CO adsorption capacity of CuCl modified GO samples was also significantly differentiated. Among CuCl modified GO samples, 2CuCl/GO sample showed the highest CO adsorption capacity of 2.9 mmol g\(^{-1}\) while 1CuCl/GO and 3CuCl/GO samples exhibited the CO adsorption capacity of 2.21 mmol g\(^{-1}\) and 2.48 mmol g\(^{-1}\), respectively. The increase of CO adsorption capacity from 2.21 mmol g\(^{-1}\) of 1CuCl/GO to 2.9 mmol g\(^{-1}\) of 2CuCl/GO sample may be due to the increase of Cu\(^+\) amount which promoted the formation of \(\pi\)-complexation between CO and Cu\(^+\) ions. Note that the presence of Cu\(^{2+}\) ions in the sample as revealed by XPS did not contribute the formation of \(\pi\) bond, but mainly CO–Cu\(^{2+}\) bonding by the electrostatic force [38–41]. However, further increase of CuCl loading led to decrease of CO adsorption capacity. This may be due to the aggregation of CuCl particles at high CuCl loading, causing the decrease of surface area as well as the decrease of CuCl particle dispersion [11].
CO adsorption isotherms of CuCl/GO samples at 20 °C, 30 °C and 40 °C were shown in figures 8, 9 and 10. For all CuCl/modified GO samples, the decrease of CO adsorption capacity with increasing adsorption temperature was noted. It is well documented that CO adsorption is exothermic and it is thermodynamically
favored at low adsorption temperature. Therefore, the increase of adsorption temperature causes the decrease of CO adsorption capacity [42].

3.3. Langmuir-Freundlich (L-F)

Adsorption isotherms of CO on CuCl/GO were fitted by the L-F model [43]. The L-F model can be expressed as the following equation:

\[ q = q_m \frac{b \cdot p^n}{1 + b \cdot p^n} \]

Where \( q \) (mmol g\(^{-1}\)) is the adsorbed amount moles, \( p \) (kPa) is the pressure and \( q_m \) (mmol g\(^{-1}\)) is the saturation adsorbed amount, \( b \) (kPa\(^{-1}\)) is the adsorption affinity and \( n \) (dimensionless) is the corresponding deviation from the Langmuir isotherms.

Figure 11 plotted \( \ln(q) \) as a function of \( \ln(p) \) of CO adsorption on 2CuCl/GO sample. Langmuir-Freundlich fitting parameters of CO isotherms on CuCl/GO are listed in table 3.

From figure 11 and table 3, it shows that the experimental data fit well with L-F model. Thus, high \( R^2 \) values of 0.991–0.998 were obtained for all CuCl/GO samples. For all CuCl/GO samples adsorption capacity (\( q_m \)) reached the highest value at the lowest temperature (20 °C). Among 3 tested CuCl/GO samples, 2CuCl/GO sample exhibited the highest CO adsorption capacity (\( Q_m \) of 2.90 mmol g\(^{-1}\)).
4. Conclusion

Graphene oxide was modified with CuCl by using novel method ‘ion implantation’. CuCl modified GO samples were achieved by evaporation of CuCl and incorporation of Cu$^+$ ions into GO framework. CuCl modified GO with different CuCl content were characterized by XRD, FTIR, BET, TEM, EDX and XPS. XRD result revealed the presence of pure CuCl phase. From EDS elemental mapping image and TEM image, it showed the CuCl particles of 30–50 nm with uniform distribution. XPS results revealed the presence of both Cu$^+$ and Cu$^{2+}$ ion but Cu$^+$ amount was predominant. CO adsorption on GO and CuCl modified GO was tested and evaluated. Among tested CuCl modified GO samples, 2CuCl/GO sample showed the highest CO adsorption capacity of 2.90 mmol g$^{-1}$ at 20 °C which was 7.5 times higher than that of pristine GO. The high CO adsorption performance can be explained basing on the formation of π-complexation between CO molecules and Cu$^+$ ions. From GO adsorption on CuCl modified GO it showed that the experimental data fitted well with Langmuir-Freundlich model.

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Table 3. Langmuir-Freundlich fitting parameter of CO adsorption isotherms on CuCl/GO samples.

| Sample     | Temperature (°C) | qm (mmol/g) | b     | n     | R²    |
|------------|------------------|-------------|-------|-------|-------|
| GO         | 20               | 0.38        | 0.352 | 0.82  | 0.86  |
| 1CuCl/GO   | 20               | 2.21        | 0.353 | 1.032 | 0.993 |
| 30         | 2.11             | 0.350       | 1.031 | 0.994 |
| 40         | 1.90             | 0.349       | 1.032 | 0.994 |
| 2CuCl/GO   | 20               | 2.90        | 0.253 | 1.010 | 0.998 |
| 30         | 2.72             | 0.262       | 1.013 | 0.998 |
| 40         | 2.47             | 0.217       | 1.021 | 0.992 |
| 3CuCl/GO   | 20               | 2.63        | 0.210 | 1.022 | 0.991 |
| 30         | 2.36             | 0.267       | 1.014 | 0.998 |
| 40         | 2.06             | 0.264       | 1.018 | 0.996 |
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