

# Highly Efficient Adsorption of Copper Ions by a PVP-Reduced Graphene Oxide Based On a New Adsorptions Mechanism

Yongji Zhang<sup>1</sup>, HuiJuan Chi<sup>1</sup>, WenHui Zhang<sup>1</sup>, Youyi Sun<sup>1,2,\*</sup>, Qing Liang<sup>1</sup>, Yu Gu<sup>2,\*</sup>, Riya Jing<sup>1</sup>

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**Abstract:** Polyvinylpyrrolidone-reduced graphene oxide was prepared by modified hummers method and was used as adsorbent for removing Cu ions from wastewater. The effects of contact time and ions concentration on adsorption capacity were examined. The maximum adsorption capacity of 1689 mg/g was observed at an initial pH value of 3.5 after agitating for 10 min. It was demonstrated that polyvinylpyrrolidone-reduced graphene oxide had a huge adsorption capacity for Cu ions, which was 10 times higher than maximal value reported in previous works. The adsorption mechanism was also discussed by density functional theory. It demonstrates that Cu ions are attracted to surface of reduced graphene oxide by C atoms in reduced graphene oxide modified by polyvinylpyrrolidone through physisorption processes, which may be responsible for the higher adsorption capacity. Our results suggest that polyvinylpyrrolidone-reduced graphene oxide is an effective adsorbent for removing Cu ions in wastewater. It also provides a new way to improve the adsorption capacity of reduced graphene oxide for dealing with the heavy metal ion in wastewater.

**Keywords:** Polyvinylpyrrolidone; Graphene oxide; Cu ions; Wastewater treatment; Adsorption mechanism; Density functional theory

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## Introduction

Electroplating is a major polluting industry due to easily discharging of toxic metals in effluents [1]. Tracing amounts of some metal ions such as copper, zinc, iron and cobalt is required by organisms as cofactors with enzymatic activities. However, the excess of the heavy metal ions will cause serious potential problems on living organisms due to their high toxicity, carcinogenic and bioaccumulation [2]. The content of The World Health Organization (WHO) recommended the maximum acceptable concentration of Cu ions in drinking water is 1.5 mg/L [2]. Lots of treatment methods (such as chemical precipitation, ion exchange, electrol-

ysis, reverse osmosis, adsorption, etc.) have been investigated and applied to remove Cu ions [3-7]. Among these methods, adsorption is considered to be an economical, efficient and promising method for Cu ions treatment in wastewater [8]. Till now, a lot of adsorbents, for example, agricultural wastes, kaolinite, natural zeolites, clays, chitosan, magnetic particles, active carbon, carbon nanotubes, graphene oxide have been investigated to remove Cu ions from aqueous solution [9-17]. However, further applications of these materials are limited due to the lower adsorption capacities or efficiencies (< 200 mg/g).

Graphene was considered as a good nanomaterial for removing metal ions due to its high surface area, an-

<sup>1</sup>Research Center for Engineering Technology of Polymeric Composites of Shanxi Province, North University of China, Taiyuan 030051, P.R. China

<sup>2</sup>Department of Mechanics, Beijing Jiaotong University, Beijing 100044, P.R. China

\*Corresponding author. E-mail: syyi@mail.ustc.edu.cn (Y. Y. Sun), yugu@bjtu.edu.cn (Y. Gu)

tibacterial property and lower cytotoxicity [18-26]. In recent years, graphene nanosheets (GNSs) were fabricated by the vacuum-promoted exfoliation method at low-temperature and used to adsorb Pb ions and the adsorption capacity of about 40 mg/g was obtained [24]. Chemically reduced and functionalized graphene oxide (GO) was also prepared by refluxing of GO with ethylenediamine (ED) using dimethyl formamide (DMF) as solvent. The resulting adsorbent (ED-DMF-RGO) with amine group was used to remove Cr ions from aqueous solution and about 92.5 mg/g of adsorption capacity was found [25]. Kwang S. Kim reported the preparation of PPy-reduced GO (PPy-rGO), which has highly selective adsorption capacity for Hg ions. The results showed that the adsorption capacity was about 980 mg/g and 58 mg/g for removing Hg ions and Cu ions, respectively [26]. This value of 58 mg/g for Cu ions is relatively lower compared with those for other metal ions. How to improve the adsorption capacities for Cu ions is then becoming an important and interesting issue. Moreover, despite of many studies in this field, it can be noticed that very few and isolated fact are available on how to affect adsorption capacities of graphene materials, that is, the adsorption mechanism is less discussed.

The aim of this paper is to improve Cu ions adsorption capacity of graphene. The adsorption mechanism was also discussed. Polyvinylpyrrolidone (PVP) was chosen as the reductant and dispersant for preparing the reduced graphene oxide (rGO) by using modified hummers method.

## Experimental

### (1) Materials

Nature graphite flakes (325 mesh, 99.8%), cupric chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), hydrochloric acid (HCl), and other chemicals and reagents used in this work are all in analytical grade. Deionized water was used for preparation, dilution and analytical purpose.

### (2) Preparation of polyvinylpyrrolidone-reduced graphene oxide (PVP-rGO)

PVP-rGO was prepared from natural graphite by modifying the well-known hummers method [18]. Firstly, 5 g graphite was oxidized by 250 mL  $\text{H}_2\text{SO}_4$  (98%) in ice-water bath with stirring for 30 min. A 15 g  $\text{KMnO}_4$  was gradually added with stirring and cooling for 30 min. Subsequently, 30 g  $\text{NaNO}_3$  was added with continuous stirring at 30°C for 1 h. Then, 900 mL deionized water was added with continuous stirring at 90°C for 30 min. Finally, 30 mL  $\text{H}_2\text{O}_2$  solution (30%) was slowly added to the mixture. The color of the dispersion turned from black to yellow. The synthetic product was filtered and washed with HCl (5.0 wt%)

and deionized water for several times, respectively. The product was dried at 60°C and then the graphite oxide solid was obtained.

The GO solution with high stabilization was prepared by dispersing 0.5 g graphite oxide solid powder in 200 mL deionized water and ultrasounded under 150 W for 1 h. A 0.25 g PVP and 2.5 mL hydrazine hydrate were mixed in a 250 mL round-bottomed flask and then 100 mL above GO solution (2.5 mg/mL) was added. The mixture was gradually heated to 80°C and kept for 4 h under stirring. The color of the dispersion solution turned from yellow to black.

### (3) Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/Max-2000 diffractometer (Japan) equipped with a Cu KR radiation source ( $\lambda = 0.15418$  nm). The scanning range was from 10° to 80° and the scanning interval was 0.5°.

Morphologies of the samples were studied by a Hitachi S-4800 scanning electron microscope (SEM) (Japan). The element composition was characterized by a Horiba EX-250 X-ray energy-dispersive spectrometer (EDX) associated with SEM.

Fourier Transform Infrared (FTIR) spectra were recorded using Nicolet 5700 Infrared Spectrometer (USA) in the mid infrared range (4000 - 400  $\text{cm}^{-1}$ ).

### (4) Adsorption Experiments

The Cu ions solution (17.5 mg/mL) was prepared by dissolving 50 g cupric chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) in 1000 mL deionized water. The other solutions with various concentrations were adjusted by successive dilution. The effect of contact time on Cu ions adsorption was investigated by setting different adsorption time (from 2 to 30 min) with the dosage of 2.5 mg/mL and pH of 3.5. To evaluate the effect of initial Cu ions concentration, the experiments were conducted at initial Cu ions concentrations from 3.5 to 17.5 mg/mL at 2.5 mg/mL dosage and pH 3.5 for 10 min.

The solution was then filtered and the residual Cu ions concentration was measured using an atomic absorption spectrophotometer (GBC, Avanta) at a  $\lambda = 324.7$  nm. The amount of Cu ions adsorbed at equilibrium  $q_e$  (mg/g) was obtained from the equation,

$$q_e = (C_o - C_e)W/w \quad (1)$$

Where  $C_o$ ,  $C_e$ ,  $W$  and  $w$  represent the initial ion concentrations (mg/g), equilibrium Cu ions concentrations (mg/g), the solvent mass (g) and the adsorbent mass (g), respectively.

## Results and discussion

The X-ray diffraction results of graphite and PVP-rGO are shown in Fig. 1. The graphite appeared a strong peak at 26.4° corresponding to (002) lattice

planes [27]. However, a broad diffraction peak at  $25.8^\circ$  was observed on PVP-rGO powder, which was attributed to (002) lattice planes of the graphene [24]. The plane space  $d$  was calculated to be 0.36 nm, which was slightly larger than 0.34 nm of graphite (JCPDS No. 75-1621) [27]. These results indicate the formation of rGO prepared from nature graphite [18].

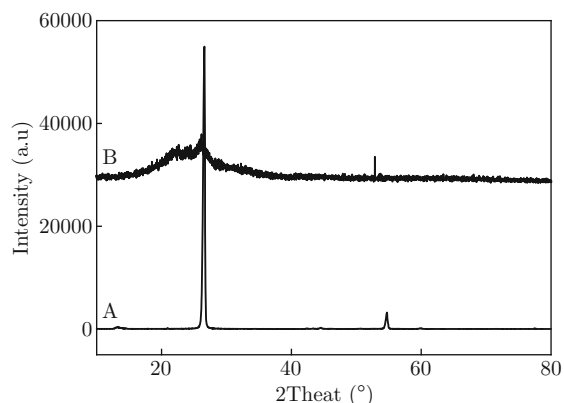


Fig. 1 XRD of (A) graphite and (B) PVP-rGO.

The FT-IR spectrum of PVP-rGO is shown in Fig. 2. The IR spectrum of rGO was also measured as a comparison, in which two absorption bands at  $1485\text{ cm}^{-1}$  and  $1160\text{ cm}^{-1}$  were ascribed to C=C conjugation and C-C vibrations in graphene skeleton [28]. Some new absorption peaks of  $1335\text{ cm}^{-1}$ ,  $1596\text{ cm}^{-1}$  and  $1237\text{ cm}^{-1}$  were observed on PVP-rGO sample, which was caused by the PVP [29]. The inset in Fig. 2 shows the snapshot of rGO and PVP-rGO aqueous solution. Both of them were ultrasonically dispersed for 10 min

in double-distilled water and then stood for 30 min. It can be seen that the PVP-rGO solution is more stable and homogeneous compared with that of rGO. This is crucial to further applications.

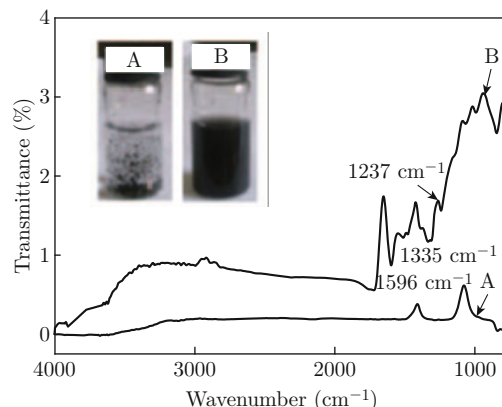


Fig. 2 FT-IR spectra of (A) rGO and (B) PVP-rGO. Inset is snapshot of (A) rGO aqueous solution and (B) PVP-rGO aqueous solution.

The SEM images of PVP-rGO adsorption results of Cu ions before and after are displayed in Fig. 3. The surface before adsorption is smooth (Fig. 3(a)), whereas, it contains many small particles after adsorption (Fig. 3(b)). EDX performed on these two samples are shown in Fig. 3(c) and 3(d). The weight fractions of elements before and after adsorption Cu ions are shown in Table 1. No Cu element was observed before adsorption, whereas, 43 wt% of Cu was measured after adsorption. The weight ratio of Cu and PVP-rGO is about 1.15.

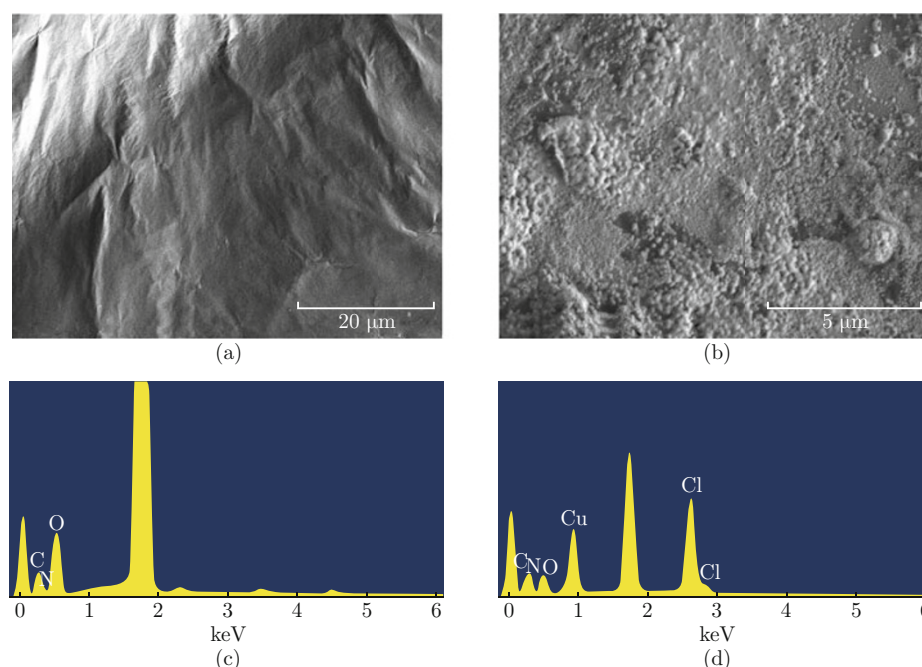


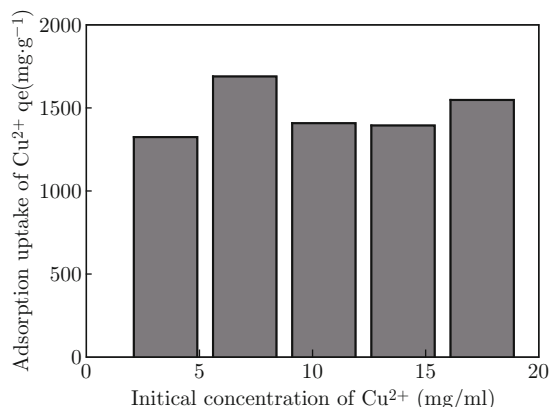
Fig. 3 SEM of (A) rGO and (B) PVP-rGO, EDX of (C) rGO and (D) PVP-rGO.

**Table 1** Element analysis of PVP-rGO before and after adsorption copper ions by EDX

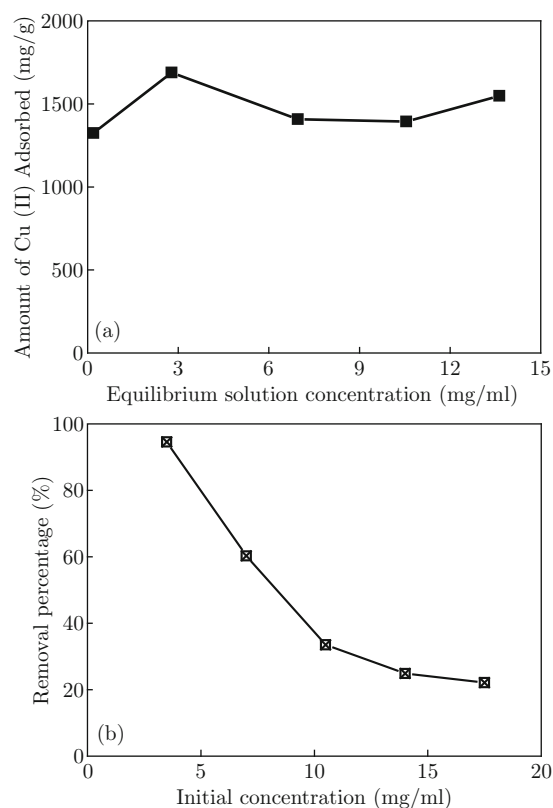
Element	C	N	O	Cu	Cl	Si
Before	43.93	1.99	7.91	—	—	46.17
After	28.87	1.29	7.34	43.27	15.36	3.88

The adsorption capacity of PVP-rGO as function of initial Cu ions concentration was investigated as shown in Fig. 4. It shows that the effect of initial concentration on adsorption capacity of PVP-rGO is slight. Generally, the adsorption capacity increased with an increase in initial Cu ions concentration in previous works [12-16]. The reason is shown as follow: when the initial concentration of Cu ions was low ( $< 0.1$  mg/mL), the adsorption sites of adsorbents were not used fully and thus the adsorption uptake was low. So, the adsorption capacity increased with the increase of initial Cu ions concentration. Here, the different result was attributed to that the adsorption sites of PVP-rGO were almost used fully at high initial concentration of 3.5 mg/mL, and so the adsorption capacity slightly increased with the increase of initial Cu ions concentration from 3.5 mg/mL to 17.5 mg/mL. In addition to this, it is also observed that the maximal adsorption capacity is about 1689 mg/g at the initial Cu ions concentration of 7.0 mg/mL. Table 2 is the comparison of adsorption capacity of PVP-rGO and other adsorbents for Cu ions. It can be seen that PVP-rGO has a relatively higher adsorption capacity of Cu ions compared with other adsorbents, and it is almost 10 times higher than maximal value reported in previous works [10-17, 26]. These results further indicate that the PVP-rGO owns high adsorption capacity of Cu ions.

Fig. 5(a) and 5(b) show the adsorption isotherms of PVP-rGO toward Cu ions and the effect of the initial concentration on the removal percentage of Cu ions by PVP-rGO using a 2.5 mg/mL adsorbent dose, respectively. As shown in Fig. 5(a), the adsorption capacity slightly increased with increasing equilibrium concentration. The result is attributed to high initial

**Fig. 4** Adsorption capacity of PVP-rGO as functions of initial Cu(II) concentration.**Table 2** Comparison of adsorption capacity and equilibrium time of various adsorbents for Cu<sup>2+</sup>

Adsorbent	Adsorption capacity (mg/g)	Equilibrium time (min)	Reference
PVP-rGO	1689.0	10	This work
PPy-rGO	58.0	20	[26]
GO	117.5	150	[16]
Fe <sub>3</sub> O <sub>4</sub> /GO	62.73	100	[10]
	18.26	20	[11]
Fe <sub>2</sub> O <sub>3</sub> nanotubes	111.11	60	[12]
Ag/carbon nanotubes	58.02	120	[13]
Dowex M-4195	110.9	300	[14]
clays	32.3	80	[15]
fly ash	221	20	[17]

**Fig. 5** (a) Adsorption isotherms of PVP-rGO toward Cu<sup>2+</sup> and (b) Effect of initial concentration of Cu(II) on removal percentage.

concentration as well. At high initial solution concentration ( $> 3.5$  mg/mL), the total available adsorption sites are limited, and so the effect of equilibrium concentration on adsorption capacity is slight. The removal percentage of Cu ions decreased with increasing initial concentration as shown in Fig. 5(b). At low initial solution concentration, the surface area and the availability of adsorption sites are relatively high. At higher initial solution concentration, the total available adsorption sites are limited, thus resulting in a decrease in the percentage removal of adsorbate.

Equilibrium time is another important parameter to heavy metals wastewater treatment process and also investigated as shown in Fig. 6. It clearly shows that the adsorption capacity of PVP-rGO slightly increases with the increase of contact time from 2 min to 10 min. When the contact time further increases, the adsorption capacity is almost with no change. The result indicates the adsorption equilibrium to be about 10 min. Table 2 also shows the comparison of equilibrium time of PVP-rGO and other adsorbents for Cu ions. It can be seen that PVP-rGO has a relatively more rapid adsorption of Cu ions compared with other adsorbents. This rapid adsorption indicated that the adsorption occurred mainly on the surface of the adsorbent, which was difficult to be observed in previous results [10-17, 26]. In addition to this, the adsorption reach equilibrium within few minutes is attributed to following two reasons. Firstly, the surface of PVP-rGO did almost not contain COOH or -OH group. So, the effect of -COOH or -OH on equilibrium time was slight. Secondly, the good stabilization and dispersion of PVP-rGO provide shorter time for the contact between adsorption sites and metal ions. As shown in inset of Fig. 6, the blue water containing Cu ions (7.0 mg/mL) change to colorless water after adsorption treatment for 2 min. These results indicate that the PVP-rGO has high adsorption rate of Cu ions, which is also very important for wastewater treatment.

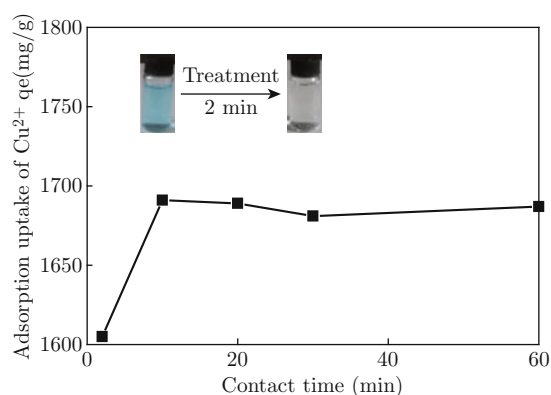


Fig. 6 Adsorption capacity of PVP-rGO as functions of contact time. The inset is snapshot of Cu ions aqueous solution after and before treatment.

## Mechanism of high efficient adsorption

On the basis of the above experimental results, it is believed that the PVP-rGO is highly efficient in adsorption of Cu ions. It is well-known that there is strong interaction between functional groups (eg. C=O and C-N) of PVP and metal ions [30-31], which provides lots of adsorption sites for removal of Cu ions. So, here the high adsorption capacity (1689 mg/g) of PVP-rGO was believed to come from the PVP coated on surface of rGO. The adsorption process was investigated by the

IR spectra of PVP-rGO after and before adsorption Cu ions as shown in Fig. 7. As shown in Fig. 7A, the absorption peaks at  $1596\text{ cm}^{-1}$  and  $1237\text{ cm}^{-1}$  are ascribed to the vibrations of C=O and C-N of PVP coated on surface of rGO. It clearly shows that these absorptions bands corresponding to C=O and C-N of PVP all disappear after the adsorption of Cu ions (in Fig. 7B). The result indicates that the PVP-rGO can adsorb the Cu ions by the interaction between functional groups (C=O and C-N) of PVP and Cu ions. The adsorption mechanism is similar to that reported in previous works [16, 26], in which the functional group (C=O, C-N and OH) on surface of adsorbents is responsible to remove Cu ions.

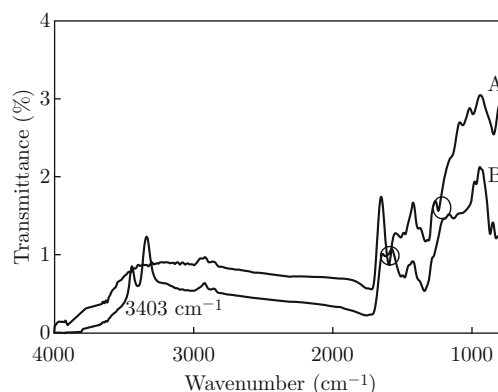


Fig. 7 IR spectra of PVP-rGO (A) before and (B) after adsorption copper ions.

However, according to the content of adsorption sites (-C=O and -C-N) of PVP coated on surface of graphene by EDX, the theory value of maximal adsorption capacity is calculated to be about 350.0 mg/g, which is far lower than experimental value of maximal adsorption capacity (1689 mg/g). In addition to this, the polypyrrole-rGO as adsorbents to remove the Cu ions from wastewater has been reported in the previous work [26]. Although there are similar chemical structure between polypyrrole and PVP, but the low adsorption capacity (ca. 58 mg/g) of polypyrrole-rGO was observed for removal of Cu ions. So, what is the possible adsorption process for the high adsorption capacity (1689 mg/g)? The traditional mechanism based on adsorption of chemical functional group coated on surface of graphene is difficult to explain it. The C atoms of graphene modified by PVP can attract Cu ions, which is possible reason for the high adsorption capacity. However, the possible adsorption process is rarely reported for removing heavy metal ions in wastewater.

To understand the high adsorption mechanism, the adsorption interaction between Cu ions and PVP-rGO were further discussions by density functional theory (DFT). The density functional theory (DFT) calculations were performed with CASTEP. In the DFT calculations, the lattice constant (a, b and c) of the

graphene were designed as 2.46 Å, 2.46 Å and 3.14 Å, respectively. At the same time, the vacuum layer with thickness of 2.0 nm was also doped into two layer graphene. And then, one Cu ion was put randomly on the  $4 \times 4$  graphene super cell, in which the initial Cu ion-to-graphene distance was ca. 2.35 Å. Furthermore, exchange-correlation interactions were approximated by the generalized gradient approximation (GGA) with PBE parameterization. In the DFT calculations, Ultra-soft-pseudo potential was used. The k-point was set to  $5 \times 5 \times 1$  for the Brillouin zone integration. A 350 eV cut-off energy for the plane-wave basis set was used in all relaxation processes. Geometry relaxations were performed with the criterion that ionic force was smaller than  $0.001 \text{ eV}\text{\AA}^{-1}$ . Several positions of Cu ions relative to the PVP-rGO were considered near the three symmetry sites on the PVP-rGO to find the most favorable adsorption configuration (Fig. 8A - 8C). For convenience, the adsorption configurations shown in Fig. 8A - 8C are referred to as hollow (H), bridge (B) and stack (T) configurations, respectively [32]. The result of optimization shows that the most stable atomic configurations for the Cu ions adsorbed on the PVP-rGO is stack. The potential energy of Cu ions/PVP-rGO system as function of distance between Cu ions and PVP-rGO was further calculated as shown in Fig. 9. Table 3 lists the potential energy and equilibrium Cu ions/PVP-rGO distance. In the Cu ions/PVP-rGO system, all configurations gave rise to a different adsorption energy ( $E_b = 0.249, 0.234$  and  $0.072$  eV for T, B and H configurations, respectively). Thus, this interaction is related to the cation- $\pi$  interaction between the Cu ions and the C-ring of the PVP-rGO. According to the contour plots for the total charge densities shown in Fig. 10, we can observe a homogeneous charge distribution in the PVP-rGO sheet and in the Cu ions without covalent or ionic bond. It indicates a physisorption between the Cu ions and C-ring of the PVP-rGO. According to Table 3, the shortest Cu ion-to-G distance ( $d = 2.13$  Å) for the stack configurations is a little shorter than that of others configurations, and the adsorption energies is larger than that of others configurations. This is a consequence of coulomb repulsion

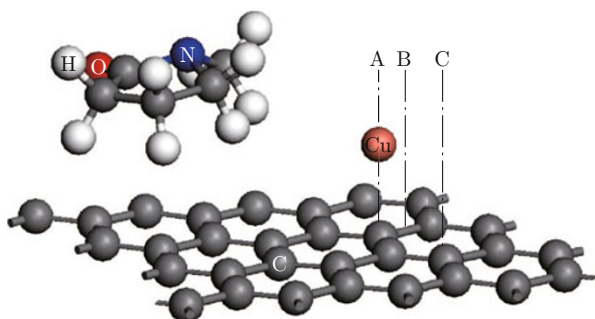


Fig. 8 Schematic view of  $\text{Cu}^{2+}$  adsorbed on PVP-rGO with different configurations: (A) stack, (B) bridge, (C) hollow.

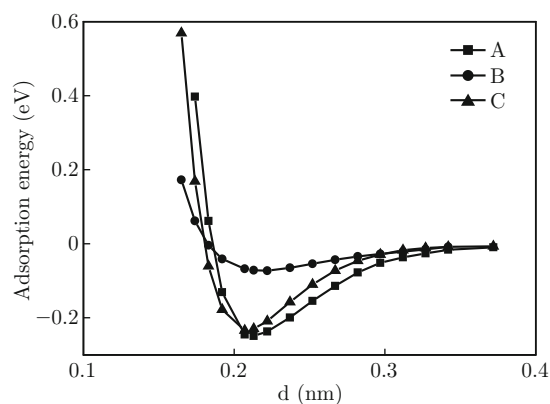


Fig. 9 Potential curve of the Cu ions and PVP-rGO with different configurations: (A) stack, (B) bridge, (C) hollow by DFT.

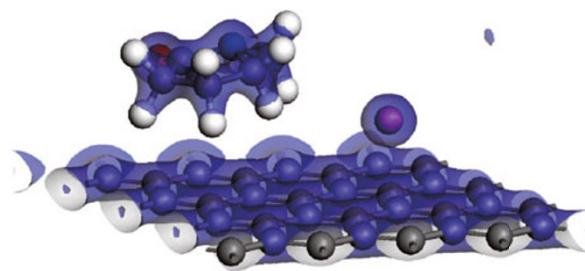


Fig. 10 Schematic view and contour plot of the total charge densities of  $\text{Cu}^{2+}$  interacting with PVP-rGO.

**Table 3 Adsorption Energy and Equilibrium  $\text{Cu}^{2+}$ /PVP-rGO distance**

	T	B	H
$E_b(\text{eV})$	0.249	0.234	0.073
$d(\text{\AA})$	2.13	2.25	2.17

between the Cu ions and the C atoms on top of the PVP-rGO. To compensate for this repulsion, the cation- $\pi$  interaction between the C-rings generates the considerable adsorption energies observed ( $0.072 \sim -0.249$  eV). These results indicate that the Cu ions can attract to the surface of PVP-rGO by the physisorption between Cu ion and C atom of graphene modified by PVP, which is the reason for the high adsorption capacity.

## Conclusions

The present study indicates that PVP-rGO can be used as an effective adsorbent material for the treatment of Cu ions due to its adsorption sites (functional group of PVP) and large surface area of rGO. The adsorption capability of PVP-rGO can reach 1689 mg/g, which is much higher than that of GO, carbon nanotubes and activated carbon. Furthermore, according to calculations of density functional theory, the Cu ions were adsorbed to the surface of PVP-rGO by

the physisorption between Cu ions and the C atoms of graphene modified by PVP. The new adsorption process is the reason for the high adsorption capacity (1689 mg/g). So, it is very interesting to obtain a more effective interaction between this Cu ions and the C atom of graphene surface by chemically/physically modifying the rGO surface. These results will be helpful to further improve adsorption capacity of graphene materials for removal of heavy metal ions in wastewater.

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