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The effect of pH on the U(VI) sorption on graphene oxide (GO): A theoretical study

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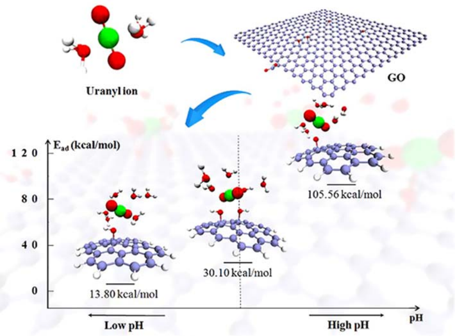
HIGHLIGHTS

- Theoretical calculations were applied to explore the interaction mechanism.
- High pH level was more favorable for the adsorption of uranyl.
- GO with bi-hydroxyl groups has the highest sorption capacity.
- A combination of E_{ad}, G_{ad}, and binding structures are crucial.

GRAPHICAL ABSTRACT



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ABSTRACT

Environmental contamination of radioactive waste water has drawn major public concerns because of its serious hazard in chemical and dynamic bio-toxicities. In present work, the interaction mechanism of the important radionuclide uranium (U) and graphene oxide (GO) under aqueous conditions with varying pH levels was scrutinized by means of high-level density functional theory (DFT) together with the implicit water model. A closer look at the bonding structures and adsorption energies of 12 GO/uranyl complexes indicated that the main adsorption sites on GO were the oxygen-containing functional groups such as epoxy group, carboxyl group, and hydroxyl group. More importantly, high pH level was more favorable for the adsorption process of uranyl species on the graphene oxide due to the stronger electrostatic interaction between negatively charged O atom and uranyl ion. This conclusion was further verified by comprehensive analysis from density of state (DOS) and charge density difference. Compared to the other forms of graphene oxide, the GO containing bi-hydroxyl groups had the highest adsorption capacity towards the uranyl species. The present theoretical view point gave supplement to the experimental observations and the proposed intrinsic mechanisms may bring new insight into the environmental management of radioactive pollution.

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1. Introduction

Nuclear energy is a clean energy of great significance to meet the demand of electricity and sustainable development of energy resources. However, discharge of radioactive nuclide into the radioactive waste water has become a serious environmental issue because of their long-term radiological and chemical toxicities [1]. The long-lived actinide uranium (U) is such kind of radionuclide which was mainly presented as the penta-coordinated $[UO_2(H_2O)_5]^{2+}$ species in aqueous solution. Excess exposure to U may cause various diseases such as thyroiditis and renal failure, increasing the incidence of cancer enormously. Therefore, how to disposal and clean up of uranyl-bearing radioactive waste water has become a growing public concern that brought plenty of studies about the removal and immobilization of uranyl from aqueous solutions [2–6]. Recently, due to the superior performance in large adsorption capacity and high adsorption efficiency, the graphene-based materials, such as graphene and graphene oxide (GO) have inspired multidisciplinary studies as possible adsorbents to remove the nuclides [7,8]. Particularly, for uranium, Zhao and co-workers [9] explored the adsorption of uranium on graphene by carrying out series of batch experiments, and a maximum adsorption of 97.5 mg/g had been obtained towards U(VI). Besides, Wu's group [10] prepared single-layered GO material to adsorb U(VI) and achieved a considerable adsorption capacity of about 299 mg/g. And Sun's group showed significant adsorption capacity of 138.89 mg/g of the GO material towards U(VI) ion [11]. Apart from these, there are also lots of correlative researches on the removing of U(VI) by GO/LDH or GO/metal-oxide complexes [12–14]. Compared with the graphene, graphene oxide (GO) is an oxygen-rich carbonaceous layered material that possessing better adsorption capacity and higher dispersion in water. Therefore, GO has potential promising as an efficient adsorbent for the removal of uranium.

Although many experimental studies focused on the adsorption of uranyl on GO, from chemical aspects, the molecular level to understand the initial bonding nature and interaction mechanism of GO/uranyl still need further clarifications, especially from a theoretical perspective. There are now more and more theoretical calculations that concerned the binding coordinates and electronic properties of uranyl ions. Adsorption of uranyl species on vanadium carbide MXene [15] and hydroxylated titanium carbide nanosheet [2] had been investigated by DFT calculations. The molecular dynamics of interaction between the humic acid and uranyl in the presence of a carbon nanotube were explored by Lan et al. [16]. Furthermore, the suitable binding sites for preferential uranyl complexation with a mesoporous terbium(III)-based MOF materials were reported by Liu et al. based on the first principle calculations [17]. Another DFT calculation by Druchok's group investigated the charge effect and three possible interaction spots for uranyl binding to a –COO functionalized CNTs [18]. Sun and coworkers [11] studied the effect of three oxygen functional groups on the adsorption of GO to uranium under neutral condition, except the carboxyl group, which was found to be most efficient in alkaline environment. On the other hand, Wu et al. [10] concluded the uranyl was more likely to combine with carboxyl and hydroxyl groups at high pH value compared with those in neutral environment by analyzing the vibration frequencies and binding energies of various GO/uranyl complexes. Therefore, the pH level was one of the most important factors in enhancing the adsorption stability and complexation of uranyl species. The knowledge of interactions between uranyl and GO under different pH conditions was crucial in the development of novel graphene-based adsorbents for removal of toxic uranium. However, to sum up, there was no systematic theoretical study about how the pH affected the adsorption behavior of uranyl on the GO and it was worthwhile to add a comprehensive comment that regarding the pH influence on GO/uranyl compounds.

Recently, our group carried out a batch of experiments to explore the sorption of U(VI) on GO in various experimental conditions, and found out that the adsorption ability of GO towards U(VI) was primarily depended on the pH values of aqueous solutions [11,19]. In conjunction with the experimental work, in this paper, DFT calculations were carried out to gain insights towards the pH-dependent behavior of uranyl adsorption at the molecular level. We selected graphene oxide modified by different kinds of oxygen functional groups to study the adsorption behavior of graphene oxide and uranyl ion in acidic, neutral and alkaline environments by inspecting variety of properties such as binding configuration, binding energy and density of states, et al. The theoretical results addressed in present work will enrich new horizon for the fundamental researches and technological application of graphene-based materials in the removing of radionuclide contaminants from aqueous environment.

2. Computational details

A finite 10 carbon ring model was chosen for graphene by comprehensive considering computational cost and accuracy [10,11,19]. This model had been successfully used in former calculations [11]. To model the GO, the epoxy oxygen, hydroxyl group (both mono- and bi-substituted) and the carboxyl group were then added on the basal plane or at the edge of the graphene surface according to the Lerf-Klinowski model [20]. While for uranyl, the penta-coordinated $[UO_2(H_2O)_5]^{2+}$ was taken in this work since it was proposed to be the most common form in water solution [21–26]. The adsorption energy was calculated as following:

$$E_{ad} = E_{(GO)} + E_{(uranyl)} - E_{(GO/uranyl)}$$

$$G_{ad} = G_{(GO)} + G_{(uranyl)} - G_{(GO/uranyl)}$$

where $E_{(GO)}(G_{(GO)})$, $E_{(uranyl)}(G_{(uranyl)})$, and $E_{(GO/uranyl)}(G_{(GO/uranyl)})$ correspond to the total electronic energy (Gibbs free energies) of the adsorbents, the penta-coordinated uranyl species, and the combined GO/uranyl system, respectively.

All the structures, energies and corresponding harmonic vibrational frequencies were obtained with Gaussian 09 software package [27]. The hybrid exchange-correlation functional PBE1PBE was employed since it had been widely prove to provide reliable geometries and energies for actinide compounds with experimental data [28–30]. The effective core potential and basis set of Stuttgart-Dresden-Bonn group [31] were chosen to describe U atom, while the cc-pVDZ was applied for describing the light atoms (C, H and O). The conductor polarizable continuum model (CPCM) [32,33] was applied to mimic the solvation effect in aqueous solution.

3. Results and discussion

The oxygen-functional groups such as –OH (pKa = 9.80), –COOH (pKa = 4.19) [34] and –O– groups were mostly like to be protonated or deprotonated under acid or alkaline condition. Scheme 1 depicted the possible protonated or deprotonated states for different oxygen-functionalized GO systems. Herein, the protonated states for epoxy group, carboxyl group, mono-hydroxyl group and bi-hydroxyl group functionalized graphene were noted as $[GO–O–H]^+$, $[GO–COOH_2]^+$, $[GO–OH_2]^+$ and $[GO–OH–OH_2]^+$, respectively. While the deprotonated states were $[GO–COO]^-$, $[GO–O]^-$ and $[GO–OH–O]^-$ for carboxyl group, mono- and bi-hydroxyl groups functionalized graphene, respectively. Similarly, their neutral forms can be described as [GO–O–], [GO–COOH], [GO–OH], [GO–OH–OH], respectively. The optimized structures of twelve GO/uranyl complexes were shown in Figs. 1 and 2, and their corresponding original GO were provided in Figs. S1 and S2. Besides, the bond lengths of all the optimized structures were summarized in Tables 1 and S1.