Colloids and Surfaces A: Physicochem. Eng. Aspects 482 (2015) 258–266

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

# Surface functionalization graphene oxide by polydopamine for high affinity of radionuclides

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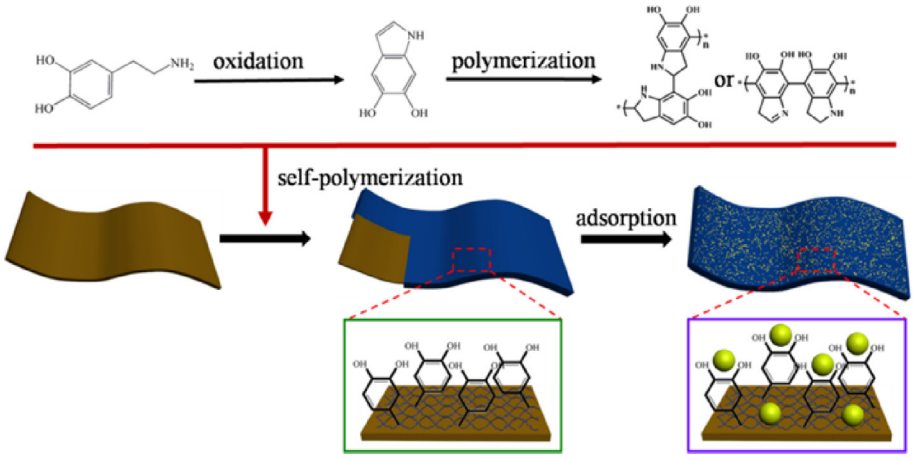
## HIGHLIGHTS

- PD/GO composites were synthesized by the oxidative self-polymerization of dopamine on the surface of GO.
- Abundant functional groups were exposed to capture uranium.
- The enhanced adsorption activity was attributed to the synergistic effect of PD and GO.
- The PD/GO composites sample can support long-term use in nuclear waste management.

## GRAPHICAL ABSTRACT

The synergistic effect of GO (high surface area) and PD (abundant functional groups) leads to an effective uranium adsorption.




## ARTICLE INFO

*Article history:*
Received 5 January 2015
Received in revised form 22 May 2015
Accepted 24 May 2015
Available online 27 May 2015

*Keywords:*
Polydopamine/graphene oxide (PD/GO)
U(VI)
Adsorption

## ABSTRACT

The utilization of nuclear energy plays an important role in our energy system; however, the leaking of radionuclides has potential threat to human health. In this paper, two-dimensional polydopamine/graphene oxide (PD/GO) composites were synthesized through a simple bio-inspired surface functionalization process by self-polymerization of dopamine monomers on GO surface. To evaluate the adsorption performance of PD/GO composites, the adsorbent was applied to remove uranium(VI) from aqueous solutions. Based on the Langmuir's equation, the maximum adsorption capacity was calculated to be 145.39 mg · $g^{-1}$ by PD/GO composites, which is higher than that of pure PD (34.21 mg · $g^{-1}$) and GO (75.71 mg · $g^{-1}$). The enhanced adsorption capacity was mainly ascribed to the synergistic effect of PD with multifunctional groups and GO with high surface area. The adsorption process fitted well with the Langmuir adsorption isotherm and a pseudo-second order kinetics. Moreover, adsorption and regeneration experiment proved the samples can support long-term use in nuclear waste management. This work provides a convenient and promising materials for the removal of U(VI) from polluted water.



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http://dx.doi.org/10.1016/j.colsurfa.2015.05.020
0927-7757/

## 1. Introduction

With the increasing worldwide energy demand, nuclear industry developed rapidly and nuclear power has been cited as one of the cleanest energy sources. Meanwhile, approximately 2300 tons of spent nuclear fuel are created during this process and this radionuclides such as 90-$Sr^{2+}$, 137-$Cs^{+}$, and $UO_2^{2+}$, will pose a long-time threat to human living environment [1]. The safe treatment and disposal of radionuclides produced is a worldwide environmental concern, especially for uranium, which is the key element for nuclear energy [2,3]. A lot of uranium and its isotopes were released to the environment from nuclear manufacturing and processing, which posed a great threat to our living conditions due to their toxicity and radioactivity. To prevent radionuclide migration, various methods have been proposed to capture or concentrate these radionuclides, including adsorption [4–7], ion exchange [1,8–10], filtration [11,12], *etc*. Among these techniques, adsorption has been considered as one of the most promising methods due to its versatility, simplicity, low-cost and high efficiency [13,14].

Graphene oxide (GO), with abundant oxygen-containing functional groups on the surfaces, has been widely employed as a promising material for the removal of heavy metals due to its high surface area and light weight. The oxygen-containing groups, such as epoxy (C—O—C), hydroxyl (—OH) and carboxyl (—COOH) groups on both basal planes and edges, allowed GO to form homogeneous suspensions in water and introduced negative charges for the adsorption of positively charged heavy metal irons *via* electrostatic interaction [15]. For example, Romanchuk et al. [16] found that the maximum sorption capacity of GO for Eu(III) and U(VI) removal were 0.76 and 0.12 mmol $\cdot g^{-1}$, respectively. However, the limited sorption capacity of native GO is still limited in their practical applications to remove radionuclides and heavy mental ions from large volumes of aqueous solutions. Therefore, more works on GO decoration is still urgently needed to enhance its adsorption performance. A simple method is to modify GO surface by introducing versatile functional groups to facilitate electrostatic interactions between GO and the heavy metal ions [17–20].

Dopamine, as a mussel adhesive protein, can be self-polymerized in Tris–HCl solutions to form polydopamine (PD) films over material surfaces [21]. Recently, it attracted great attention and applied in a broad range of fields, including drug delivery [22], biosensors [21,23], catalysts [24], energy storage [25], and environmental science [26], due to its remarkable adhesion performances onto almost any solid surfaces without any requirements for surface treatment. Moreover, PD had abundant functional groups of catechols and amines, which provided active sites to interact with heavy metal ions and organic compounds. However, PD also suffered from serious aggregation to form irregular micro or nanometer clusters, which lowered the solubility of PD in water, reduced the surface areas and restricted its applications. Therefore, many researches have focused on how to expose functional groups on outer surface and to increase the specific surface area, involving the surface coating of PD on the materials with high surface area and hydrophilicity to form thin films or nano-layers [27].

In this work, we proposed the fabrication of PD coated 2D graphene oxide composites *via* a facile and environmentally friendly method by combining both merits of GO (high surface area) and PD (abundant functional groups). The as-prepared 2D PD/GO composites were used for the removal of $UO_2^{2+}$ from wastewater. GO and PD were also synthesized to compare the adsorption efficiencies toward U(VI). As expected, PD/GO composites exhibited higher adsorption capacity than either PD or GO, indicating PD/GO composites as an outstanding material to efficiently remove $UO_2^{2+}$ from aqueous solution.

## 2. Experimental section

### 2.1. Materials

All the chemicals were of analytical grade and used as received. Graphite flakes (99.9995%, 325 mesh) was purchased from Alfa Aesar (Ward Hill, MA). $P_2O_5$, $KMnO_4$, 98% $H_2SO_4$, 30% $H_2O_2$, NaOH, dopamine, $NaNO_3$, 68% $HNO_3$ and tris(hydroxymethyl) aminomethane were obtained from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. The preparation of polydopamine and graphene oxide composites (PD/GO)

GO was synthesized by the modified Hummers method [28,29]. Generally, the pre-oxidized graphite powder was obtained as follows: the mixed solution comprised of graphite flake (3.0 g), $K_2S_2O_8$ (2.5 g), $P_2O_5$ (2.5 g) and 12 mL concentrated $H_2SO_4$ was stirred at 80 °C for 4.5 h. After dried for 12 h, the pre-oxidized graphite powder was added to a three-neck flask with concentrated $H_2SO_4$ (120 mL) and $KMnO_4$ (15.0 g). The resulting mixture was transferred to a water bath and stirred at 35 °C for 2 h before it was poured into the mixture of ice (250 mL) and 30% $H_2O_2$ (20 mL), The solid was collected by centrifugation and rinsed thoroughly with HCl (1:10, V/V). After filtration, the solid was washed with Milli-Q water until neutral, and dried at ambient temperature to produce the desired graphene oxide, which was used to prepare PD/GO composite.

To synthesis PD/GO composites, 0.15 g GO was dispersed in 25 mL Tris–HCl solution through ultrasonication to form a homogeneous suspension. 50 mg dopamine was added in the solution and stirred for 20 h. The black product was collected by repeated centrifugation at 12000 rpm and washed with Milli-Q water until the supernatant was transparent. For comparison, PD microspheres were obtained under the same conditions without the addition of GO.

### 2.3. Characterization

The sample morphologies and structures were observed by scanning electron microscopy (SEM, JEOL JSM-6330F, 15.0 kV), transmission electron microscopic (TEM, JEOL-2010). The X-ray diffraction (XRD) patterns were carried out with Philips X'Pert Pro Super X-ray diffractometer using Cu-Kα radiation (λ = 1.54178 Å). The Barrett-Emmett-Teller (BET) specific surface area of samples were calculated using $N_2$ adsorption/desorption isotherms, which were performed with a Micromeritics ASAP 2010 system at 77 K.A VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers was used to measure X-ray photoelectron spectroscopy (XPS). Fourier transformed infrared (FT-IR) spectra was carried out on a Nicolet Magana-IR 750 spectrometer over a range from 400 to 4000 $cm^{-1}$. The zeta-potential was achieved by a ZETASIZER 3000HSA system.

### 2.4. Adsorption experiments

To compare U(VI) adsorption performances among PD, GO and PD/GO composites, parallel adsorption experiments were carried out in 0.01 M $NaNO_3$ solution at pH 4.0 ± 0.1 in a 10 mL polyethylene test tubes. The adsorbents were stored in the suspension (3 g $\cdot L^{-1}$) with Milli-Q water and the initial U(VI) concentration was set as 200 mg $\cdot L^{-1}$. The desired pH of the suspension solutions was adjusted by adding negligible volumes of 0.01 or 0.1 M $HNO_3$ or NaOH solution. In the adsorption isotherm studies, the mixture was oscillated for 24 h and subsequently the solution was separated from the solids by centrifugation. The concentration of U(VI) was