



Hydrothermal carbon superstructures enriched with carboxyl groups for highly efficient uranium removal

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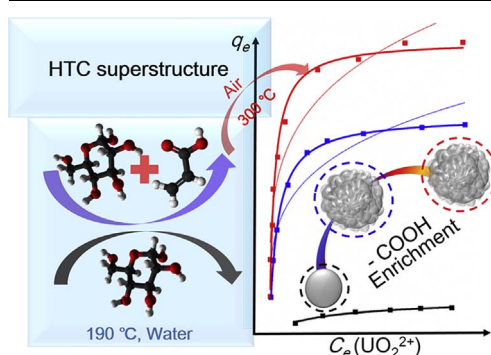
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HIGHLIGHTS

- 2-D graphitized nanosheets assembled carbon superstructures were fabricated.
- The acrylic acid modification and thermal treatment enriched the carboxyl group.
- The carbon superstructures exhibited high adsorption capacity towards U(VI).
- The carbon superstructures showed excellent recycling performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon superstructures with graphitized lamellar microstructures were fabricated through a modified hydrothermal method. The dual oxidation process combining acrylic acid functionalization and air thermal treatment introduced plentiful carboxyl groups on the surface of the carbon superstructures. Adsorption capacity of U(VI) on the as prepared carbon superparticles reached 197.7 mg g^{-1} , which was 9-fold higher than that of raw glucose-derived hydrothermal carbon microspheres. The thermo-dynamic and kinetic studies demonstrated that the uptake of uranyl ions was a spontaneous and endothermic chemisorption dominated process with the abundant carboxyl groups acting as main binding sites. Impressively, the carbon superstructure adsorbents showed excellent recycling performance. To sum up, this paper proposed a novel high-performance U(VI) adsorbent from hydrothermal carbon, which exhibited potential in real application due to their outstanding reusability and scale-up capability.

1. Introduction

The increasingly serious energy shortage has led to great progress of nuclear industry. Along with the production of nuclear energy,

radioactive waste could pose severe threats to ecosystem and living entities [1–3]. Especially, uranium-bearing contaminants are among major pollutants with great urgency to be removed from waters [4]. Compared with traditional liquid-liquid extraction techniques used for

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the recovery of uranium, solid-phase extractant based adsorption technique takes the advantages of rapid-response, low cost, easy-operation, high removal efficiency and designable functionality. Therefore, the last decade has witnessed the efforts dedicated to the development of advanced materials with highly efficient adsorption performance [5–10].

In addition to traditional adsorbents including minerals [11,12], inorganic oxides [13], and activated carbon materials [14], functional carbon-based nanomaterials with novel structures have shown great potential in the adsorption removal of radionuclides due to their high specific surface area and enriched binding sites [7,15–19]. For example, one-dimensional (1-D) pristine carbon nanotube (CNT) presented adsorption capacity of 5.0 mmol g^{-1} [20]. Two-dimensional (2-D) graphene oxide (GO) exhibited adsorption capacity of 245.14 mg g^{-1} towards U(VI) in aqueous solution ($\text{pH} = 3.0$, $T = 298 \text{ K}$) [21]. Recent studies focused on improving the adsorption properties by either increasing the amount of U(VI)-binding functional groups or fabricating CNT/GO based composites with optimized synergistic effects [17,22,23]. However, the tedious and expensive synthetic procedure, high energy consumption and their easy-aggregation nature have significantly restricted the scale-up production of CNT/GO based nanomaterials, which block their real application [24]. Therefore, it's imperative to achieve facile synthesis of functional carbon-based adsorbents with superior adsorption properties and excellent recycling performance.

With the advantages of cost effective precursors, mild and eco-friendly synthetic process, hydrothermal carbon (HTC) materials have aroused great attention over the past few decades in fields of catalysis [25], energy storage [26] and conversion [27] and water purification [28–30]. Especially, the outstanding thermal stability, pronounced acid–base resistance have made functionalized HTC materials the potential matrix in the uptake of uranium in real application. However, considering the fact that raw HTC materials are lacking in surface binding sites, much attention has been paid to introduce large amount of functional groups on the HTC matrix [29,31].

Carboxyl groups are very effective functional groups towards the adsorption of uranyl ions. To functionalize carbon materials with carboxyl groups, the widely used methods consist of multistep post-grafting relying on the covalent, hydrogen, and electrostatic binding interactions [32] or concentrated HNO_3 oxidation treatment [33,34]. Highly efficient, environmental friendly and facile methods are urgent to be developed. Titirici and co-workers showed that existence of acrylic acid could enriching carboxyl groups on HTC surface upon the hydrothermal process [28]. Su and co-workers also proved that both the concentration and thermo stability of the carboxyl groups on HTC could be increased through treatment at $300 \text{ }^\circ\text{C}$ in air in a muffle furnace [25]. The carboxyl-enriched HTC materials achieved through dual chemical modification and thermal treatment showed very high catalysis selectivity and efficiency. But it has never been utilized for the adsorption of U(VI). Herein, we have fabricated functionalized carbon superstructures which are composed of 2-D graphitized nanoflakes based on a facile and cost-effective dual oxidation method combining acrylic acid modified hydrothermal process and air thermal treatment. Experimental results from FT-IR, XPS test and Boehm titration have qualitatively and quantitatively verified the impressively increased content of carboxyl groups on the modified HTC materials, which is among the highest in carboxyl-enriched glucose derived carbon samples. Batch adsorption experiments further confirm that the carbon superstructures possess excellent U(VI) uptake performance with high U(VI) adsorption capacity and superior regeneration and recycling capability. Our work indicates the potential application of the HTC superstructures enriched with carboxyl groups in clean-up of aqueous U(VI) pollutions in real contaminated waters.

2. Experimental

2.1. Materials and reagents

Uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was achieved from Sigma Aldrich. D-Glucose and acrylic acid were purchased from Alfa Aesar. Sodium hydroxide (NaOH) and nitric acid (HNO_3) were bought from Sinopharm. All chemicals were used as received without further purification.

2.2. Characterization

Morphology information of the products were achieved using scanning electron microscopy (SEM) (Hitachi SU8220) and transmission electron microscopy (TEM, Tecnai G2 20 STWIN). X-ray diffraction (XRD) patterns were measured with D/max-TTRIII. Data of Fourier transform infrared spectra (FT-IR) were achieved on a PerkinElmer Spectrum One ranging from 4000 to 500 cm^{-1} . X-ray photoelectron spectroscopy (XPS) results were collected on a Thermo Scientific Escalab 250Xi. Raman spectra were obtained by a LabRam HR Raman spectrometer. Surface area information were determined by N_2 adsorption-desorption isotherms which were obtained on a Micromeritics ASAP 2010 (USA). Surface charge information were analyzed from Zeta potential results recorded on a Malvern Zetasizer Nano ZS.

2.3. Synthesis of hydrothermal carbon microspheres enriched with oxygenated groups

HTC superstructures with large amount of carboxyl groups were synthesized through a modified hydrothermal method. In details, 3 g glucose and 3 g acrylic acid were dissolved in 30 mL deionized water. The solution was then sealed in a 50 mL Teflon inlet and heated in an oven at $190 \text{ }^\circ\text{C}$ for 8 h . The carbon samples were washed with ethanol through 4 times of centrifugation and redispersion process. Then the samples were dried at $80 \text{ }^\circ\text{C}$ overnight. The achieved brown products were marked as HTC-10AA. In comparison, raw HTC microspheres were prepared following the above method without addition of acrylic acid. Furthermore, HTC-10AA was calcined in a muffle furnace ($300 \text{ }^\circ\text{C}$, 5 h). The achieved sample was marked as HTC-10AA-300M.

2.4. Uranium adsorption experiments

The adsorption properties of as prepared carbon materials towards U(VI) were investigated through batch experiments. Deionized water for preparation of aqueous solution was obtained from the Millipore water system. Three kind of carbon samples (HTC, HTC-10AA and HTC-10AA-300M) were dispersed in deionized water to form adsorbent stock solution (1.2 g L^{-1}). U(VI) stock solution (0.2 g L^{-1}) was prepared by dissolving uranyl nitrate in 0.01 M HNO_3 solution. Specific volume of sorbent stock solution, U(VI) stock solution and 0.3 M NaNO_3 stock solution were mixed and diluted by deionized water to form 6 mL of adsorption suspension under desired conditions. For sorbent, the mass/volume ratio is 0.20 g L^{-1} . The solution pH was tuned by adding trace amount of HNO_3 or NaOH and placed in a rotary shaker to reach adsorption equilibrium. The adsorption maximum of each sample was determined from adsorption isotherms conducted at $\text{pH} = 4.5$ with U(VI) concentrations in the range of $5\text{--}80 \text{ mg L}^{-1}$ at different temperatures. The influence of cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) and anions (Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-}) on the adsorption efficiency of HTC-based materials was also investigated. Especially, removal efficiency of U(VI) on HTC-10AA-300M was tested in real seawater (East China Sea) and simulated industrial effluent. The pH, composition and related ion concentrations of simulated industrial effluent were determined from previous studies (Table S1) [35,36]. The concentration ratio between coexisted ion and U(VI) was similar to the references. The effect of HTC-10AA-300M dosage on its adsorption performance in simulated

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