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In situ carbothermal reduction synthesis of Fe nanocrystals embedded into N-doped carbon nanospheres for highly efficient U(VI) adsorption and reduction

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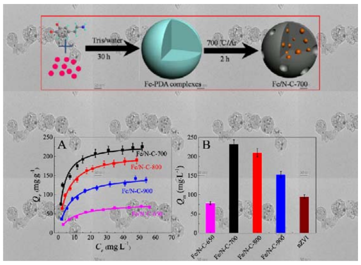
GRAPHICAL ABSTRACT

U(VI) adsorption and reduction by Fe nanocrystals embedded into N-doped carbon nanospheres.



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ABSTRACT

In this work, magnetic porous nitrogen doped carbon structures containing well-dispersed active Fe nanocrystals (Fe/N-C) are fabricated conveniently *via* Fe^{3+}-mediated polymerization of dopamine as precursor combined with in situ post carbonization process, thus allowing the entire encapsulation of active Fe nanocrystals in the interior. The obtained functional hybrid materials at 700 °C (Fe/N-C-700) show spherical structure, high proportion of metallic Fe nanocrystals, ultrahigh surface area, and easy magnetic separation property, affording excellent U(VI) removal capability (232.54 mg·g^{-1}), surpassing the Fe/N-C samples pyrolyzed at different temperatures and nano zero-valent iron. During the adsorption process, effects of water chemistries (*i.e.*, reaction time, pH, carbonates concentration and temperature) on U(VI) adsorption on Fe/N-C-700 are full explored, and the well-dispersed Fe nanocrystals play important role in reducing into U(IV). Meanwhile, nitrogen dopant could make function well in the electrostatic interaction and partial reduction of U(VI). The present study demonstrates that Fe/N-C-700 nanospheres derived from Fe-PDA have potential application for the preconcentration and immobilization of U(VI).

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1. Introduction

Uranium, one of the primary nuclear materials as well as a highly poisonous component in nuclear wastes, exceedingly threatens natural water resource and human health worldwide [1–4]. Hence, it is an extremely indispensable task to find effective treatments in reducing uranium contamination. Currently, considerable efforts have been made for developing novel functional materials which are capable of integrating chemical reduction and adsorption process for U(VI) uptake from water [5–8]. Among of which, nano zero-valent iron (NZVI) attracts much more attention due to its large surface area, high surface energy and reaction activity. However, unmodified NZVI particles suffer poor air stability and easy agglomeration due to their intrinsically high surface energy [9–11]. To overcome these limitations, loading metallic nanoparticles on natural and synthetic supports is a powerful method to improve their reaction performance [12–18]. Following this, it is encouraging and important to study the hybrid materials for better control of the NZVI particle aggregation and further optimize their reactivity and stability.

Nowadays, porous carbon materials have been widely used as the support substrates for metallic nanoparticles due to their high adsorption capacity, chemical stability and low cost [19–21]. In particular, embedding active metallic nanoparticles into porous carbon materials (M-C) can efficaciously avoid the conglomeration and augment the stability of thermodynamics [22–25]. Compared to the post-growth of active metallic nanoparticles on pre-synthesized porous carbon, high temperature thermal treatment is a more straightforward route to convert metal and carbon-based compounds/composites into M-C hybrid materials [26–29]. Along with the carbonization of organic/polymeric segments at high temperature, the metallic species will be converted into active metallic particles by synchronous carbothermic reduction and firmly attached into porous carbon substrates simultaneously. Such process provides a robust and scalable approach for the mass production of metal-carbon hybrid materials.

Dopamine, a synthetic mimic of an essential component of mussel adhesive proteins as well as, can easily self-polymerize at room temperature to form polydopamine (PDA), and it is also an outstanding carbon source which can yield thin carbon coatings [24,30–32]. In addition, dopamine possesses reduction ability and contains chelating -OH groups which can “capture” metal ions (*i.e.*, Fe, Ni, Co) during one-pot synthesis of transition metal ion-PDA complexes [33]. Making better use of the distinct reactivity and thermal stability, metal ion-PDA complexes can serve as desirable precursors to embed metallic nanoparticles into N-doped carbon nanostructures (M/N-C) through direct pyrolysis. More recently, Fe/N-C hybrid materials have attracted enhanced attention in the contaminant remediation, in which well-dispersed active Fe nanoparticles exhibit excellent oxygen reduction reaction catalytic activity and nitrogen dopant can endow Fe/N-C abundant function groups on the surface [22,23,26,34,35]. Meanwhile, Fe/N-C hybrid materials possess highly porous structure with manageable chemical properties and conveniently magnetic separation [36,37].

Motivated by all these, it can be expected to synthesize Fe/N-C hybrid materials derived from Fe-PDA complexes to achieve concurrent reduction and adsorptive removal of U(VI). Herein, we report a rational and scalable synthetic method to prepare magnetic porous Fe/N-C hybrid materials *via* simply introducing Fe^{3+} ions into tris aqueous solutions of self-polymerizable dopamine as precursor, followed by in situ activation-graphitization process (Fig. 1). Under one-pot oxidative polymerization process, highly uniform-sized Fe-PDA nanospheres are firstly synthesized. Then, the obtained Fe-PDA nanospheres experience heat-treatment under an Ar atmosphere to convert Fe-PDA complexes into Fe/N-C hybrid materials. The epoxy and hydroxyl groups in the Fe-PDA complexes explosively decompose to release a large amount of H_2O, CO, and CO_2 gases during the heat-treatment process, which leads to the production of abundant voids due to the volume shrinking at high temperature [22]. In addition, the existence of stable carbon matrix could efficiently avoid Fe nanocrystals aggregation and afford high specific surface area [29]. The local structure and chemical functions of Fe/N-C hybrid materials can be optimized by changing the pyrolysis temperature [34], as well the U(VI) removal efficiency of Fe/N-C composites could be affected. Notably, novel composites comprising similar compositions but different morphologies manifest substantially distinct catalytic activities [38]. In this study, the engineered Fe/N-C hybrid nanospheres obtained at 700 °C are found to show the impressive U(VI) removal capacity. The physical and chemical characterization of the synthesized Fe/N-C-700 (for Fe/N-C-*T*, in which *T* represents the heat-treatment temperature) is conducted systematically. The adsorption behavior of Fe/N-C-700 is further investigated under different water chemistry conditions (*e.g.*, contact time, pH, carbonates concentration, and temperature). And the adsorption and reduction mechanisms are discussed in detail. Fe/N-C-700 clearly manifests great expectation for U(VI) removal by concurrent adsorption and reduction.

2. Experimental section

2.1. Chemicals

All common chemicals were purchased from Sigma-Aldrich and used without further purification. U(VI) stock solution containing $240\ mg{\cdot}L^{-1}$ was prepared by dissolving an appropriate amount of $UO_2(NO_3)_2{\cdot}6H_2O$ in Milli-Q water.

2.2. Preparation of Fe/N-C

Fe-PDA nanospheres were prepared according to the previous reports [39]. Typically, 1.0 g of dopamine was dissolved in 1000 mL of Milli-Q water. Then, 1.76 mmol of $FeCl_3{\cdot}6H_2O$ was added. After 10 min, 10 mmol of Tris was added to adjust the pH and the reaction mixture was stirred for 30 h. The obtained Fe(III)-PDA complexes were separated from the solutions by centrifugation, washed with Milli-Q water, and then freeze-dried for 24 h. Finally, to get Fe/N-C hybrid materials, the obtained Fe(III)-PDA complexes were calcined at 650, 700, 800 and 900 °C for 2 h under an argon atmosphere, with the $5\ {}^{\circ}C{\cdot}min^{-1}$ temperature ramp rate. For comparison, NZVI particles were synthesized according the former reports [40]. N-doped carbon spheres derived from PDA spheres without adding $FeCl_3{\cdot}6H_2O$, were prepared through the same calcination process with Fe/N-C-700. (See in Supporting content)

2.3. Batch adsorption experiments

The whole experiments were carried out in 10 mL polyethylene tubes by batch technique. In brief, the suspension of adsorbent and background electrolyte solution ($0.001\ mol{\cdot}L^{-1}$ Na_2CO_3) were pre-equilibrated for 24 h, and then U(VI) stock solution were added to obtain the desired concentrations. The desired pH was adjusted by adding negligible volumes of $0.1–0.01\ mol{\cdot}L^{-1}$ HCl or NaOH. The effect of carbonate ions was investigated with different concentration of Na_2CO_3 at pH 6.0. The above suspensions were oscillated for the appropriate time and then centrifuged at 9000 rpm for 20 min. The concentration of residual U(VI) was determined with an Arsenazo-III spectrophotometer method at 650 nm [41].

Characterization methods, data analysis model and are presented in the Supporting content.

3. Results and discussion

3.1. Characterization of Fe/N-C

The phase and composition of all the derived Fe/N-C composites were investigated by means of X-ray powder diffraction, which