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Rationally designed core-shell and yolk-shell magnetic titanate nanosheets for efficient U(VI) adsorption performance[☆]

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ABSTRACT

The hierarchical core-shell and yolk-shell magnetic titanate nanosheets (Fe_3O_4@TNS) were successfully synthesized by employing magnetic nanoparticles (NPs) as interior core and intercrossed titanate nanostructures (NSs) as exterior shell. The as-prepared magnetic Fe_3O_4@TNS nanosheets had high specific areas ($114.9\ m^2\ g^{-1}$ for core-shell Fe_3O_4@TNS and $130.1\ m^2\ g^{-1}$ for yolk-shell Fe_3O_4@TNS). Taking advantage of the unique multilayer structure, the nanosheets were suitable for eliminating U(VI) from polluted water environment. The sorption was strongly affected by pH values and weakly influenced by ionic strength, suggesting that the sorption of U(VI) on Fe_3O_4@TNS was mainly dominated by ion exchange and outer-sphere surface complexion. The maximum sorption capacities (Q_{max}) calculated from the Langmuir model were 68.59, 121.36 and $264.55\ mg\ g^{-1}$ for core-shell Fe_3O_4@TNS and 82.85, 173.01 and $283.29\ mg\ g^{-1}$ for yolk-shell Fe_3O_4@TNS, at 298 K, 313 K and 328 K, respectively. Thermodynamic parameters (ΔH^0, ΔS^0 and ΔG^0) demonstrated that the sorption process was endothermic and spontaneous. Based on X-ray photoelectron spectroscopy (XPS) analyses, the sorption mechanism was confirmed to be cation-exchange between interlayered Na^+ and UO_2^{2+}. The yolk-shell Fe_3O_4@TNS had more extraordinary sorption efficiency than core-shell Fe_3O_4@TNS since the yolk-shell structure provided internal void space inside the titanate shell to accommodate more exchangeable active sites. The flexible recollection and high efficient sorption capacity made core-shell and yolk-shell Fe_3O_4@TNS nanosheets promising materials to eliminate U(VI) or other actinides in wastewater cleanup applications.

1. Introduction

The elimination of long-lived radionuclides arising from fossil fuel depletion has become an issue of mounting concern because of their deleterious effects to human health and environmental pollution management (Zhang et al., 2015; Wang et al., 2017b). Among all the radionuclides, uranium as a typically actinide element, can produce a large quantity of radioactive daughter substances and pose a profound threat to environmental safety and ecological systems (Zhao et al., 2014a; Burns et al., 2012; Craft et al., 2004; Kahouli, 2011). In other words, uranium can damage to human biological functions like brain, kidney and DNA structure of organisms (Cheng et al., 2015; Zhu et al., 2017; Li et al., 2017). Hence, the development of advanced approaches to eliminate and recover U(VI) from aqueous solutions is of urgent importance (Ding et al., 2014). Generally, hexavalent uranium (UO_2^{2+}) can dissolve easily in water and presents as negatively charged species in water and soil media, which increases the concentration of uranium by several orders of magnitude (Gui et al., 2009; Shi et al., 2014). The mobility of U(VI) in aqueous solution can be considered as the principal factor for the adsorption efficiency at solid-water interfaces (Sun et al., 2015). In the past decade, many techniques for U(VI) elimination have been widely investigated such as chemical

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precipitation (Liu et al., 2014), coagulation (Li et al., 2010; Tan et al., 2018), electrochemical extraction (Liu et al., 2017a; Renock et al., 2013), photochemical catalysis (Lu et al., 2016, 2017), sorption (Sun et al., 2015; Wang et al., 2017a; Yao et al., 2018) and so on. In virtue of uranium can be immobilized on highly efficient engineered materials, sorption has been extensively applied for attenuating radionuclide concentration from contaminated wastewater owing to its low-cost, high flexibility and wide adaptability (Hu et al., 2016). In addition, the sorption of radionuclides has been widely investigated on minerals (Xiao et al., 2013), resins (Ogden et al., 2017), layered double hydroxides (Yang et al., 2017; Chen et al., 2018), polycrystalline layered metal chalcogenides (Manos and kanatzidis, 2009; Sarma et al., 2016), MOFs (Li et al., 2018; Zhang et al., 2017; Yuan et al., 2018) and inorganic nanomaterials (Jung et al., 2014; Subramaniam et al., 2017). Unfortunately, the majority of ion exchangers suffered from the limited tolerance to high intensity of radiation, low sorption capacity and separation from aqueous solutions difficultly, which greatly hindered their practical applications (Hu et al., 2014; Liu et al., 2017b).

In recent years, titanates have been considered as ideal ion exchangers for water treatment and radionuclides' elimination owing to their unique layered structural features and high activity (Habiba et al., 2016; López-Muñoz et al., 2016). Titanate nanomaterials can be synthesized by a simple hydrothermal reaction, which possess large surface area and abundant surface hydroxyl groups in outer-sphere and exhibited extraordinary sorption capacities for Cs(I), Sr(II), Eu(III), and U(VI) (Liu et al., 2015; Sharaf El-Deen et al., 2016; Wen et al., 2016a; Sheng et al., 2015; Lu et al., 2015; Wang et al., 2015). According to recent publications, the potential of titanate nanowires was demonstrated by its significant sorption capacity of 358 mg g^{-1} as well as its excellent recycling performance (Yin et al., 2017). Sheng et al. explored the sorption behaviors of Eu(III) onto hydrous alumina using batch and extended X-ray absorption fine structure (EXAFS) techniques, and the results specified that the sorption was mainly dominated by outer-sphere and inner-sphere surface complexation at different pH-range (Sheng et al., 2012). Wen et al. found that the flexible free-standing titanate nanobelt membranes showed amazing adsorption capacities of 63.79 mg g^{-1} for $^{137}Cs^{+}$ and 238.33 mg g^{-1} for $^{90}Sr^{2+}$ (Wen et al., 2016a; b). Considering the easy separation and recycling of titanates, the fabrication of magnetic functionalized titanate can meet the demand for reutilization in real radioactive wastewater treatment. Furthermore, the bare magnetite faced with possibility of aggregation when dispersed in aqueous solutions and corrosion under acidic conditions. To compensate the drawbacks of Fe_3O_4 NPs, many researchers bend themselves to modify the surface properties by surface coating with other inorganic or organic functional materials (Zheng et al., 2017; Xie et al., 2017b).

Taking into account of the ion exchange properties and cyclic utilization of adsorbent conveniently, we rationally designed the core-shell and yolk-shell Fe_3O_4@$Na_2Ti_3O_7$ (Fe_3O_4@TNS) nanosheets for efficient uptake of U(VI) ions from aqueous solutions. The different core-shell and yolk-shell Fe_3O_4@TNS nanostructures were synthesized through hydrothermal reaction between NaOH solution and amorphous titanium hydroxide coated Fe_3O_4 and Fe_3O_4@SiO_2 owing to the lamellar sodium titanate structure shaped from the intercalation of TiO_6 octahedral layers (Cao et al., 2013). Three-dimensional (3D) hierarchical Fe_3O_4@TNS provided large specific surface area and broad contract area with target adsorbate, and the ion exchange was thought to be the primary mechanism with exchangeable Na^{+}/H^{+} ions in the interlayers of $Na_2Ti_3O_7$ (Xie et al., 2017a). The main objectives of this work are: (1) to rationally design and synthesis of core-shell and yolk-shell 3D Fe_3O_4@TNS; (2) to characterize the as-prepared Fe_3O_4@TNS samples by X-ray diffraction (XRD) patterns, scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transformed infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and magnetic hysteresis loops; (3) to investigate and compare the sorption behaviors of U(VI) on core-shell and yolk-shell Fe_3O_4@TNS. This work highlighted the interaction mechanism between the as-prepared Fe_3O_4@TNS and U(VI) ions and explored the practical application of magnetic functionalized titanates in the remediation of radionuclides' polluted water.

2. Experimental

2.1. Synthesis of Fe_3O_4 and Fe_3O_4@SiO_2 nanospheres

Typically, Fe_3O_4 NPs and core-shell Fe_3O_4@SiO_2 nanospheres were prepared according to previous reports (Wang et al., 2016). The detailed procedure was described in Supporting Information. The obtained products were collected and finally dispersed into a mixture of ethanol and water for further use.

2.2. Synthesis of Fe_3O_4@$Ti(OH)_x$ and Fe_3O_4@SiO_2@$Ti(OH)_x$ nanospheres

The core-shell Fe_3O_4@$Ti(OH)_x$ and hierarchically multishelled Fe_3O_4@SiO_2@$Ti(OH)_x$ nanospheres were fabricated by a modified sol-gel method.[39] Firstly, 0.8 g of Fe_3O_4 or Fe_3O_4@SiO_2 was dispersed in 240 mL of ethanol and 2.4 mL of water under ultrasonication. Then, 0.6 g of hydroxypropyl cellulose (average Mw = ~80,000, Sigma-Aldrich) was added into the above suspension under stirring for 30 min (marked as solution A); 8 mL of titanium butoxide (Sigma-Aldrich) was added into 20 mL of ethanol (marked as solution B). Then the solution B was mixed with solution A dropwise in the condition of vigorous stirring and maintained at 80 °C. After stirring for 100 min, the obtained Fe_3O_4@$Ti(OH)_x$ and Fe_3O_4@SiO_2@$Ti(OH)_x$ were collected by magnetic separation and washed with ethanol for several times. The precipitates were dried in vacuum at 60 °C for 12 h.

2.3. Synthesis of core-shell and yolk-shell Fe_3O_4@TNS

0.4 g of Fe_3O_4@$Ti(OH)_x$ or Fe_3O_4@SiO_2@$Ti(OH)_x$ was dissolved in 36 mL of Milli-Q water, subsequently 4 mL of 5 M NaOH aqueous solution was added. The suspension was subjected to hydrothermal reaction at 140 °C in a Teflon-lined autoclave for 6 h and allowed to cool down until reaching the room temperature. Finally, the final products of core-shell and yolk-shell Fe_3O_4@TNS were collected by magnetic separation and washed with Milli-Q water and ethanol for three times. Notably, the $Na_2Ti_3O_7$ ultrathin nanosheets were synthesized by hydrothermal reaction in which sodium cations can insert into TiO_6 octahedral layers to form a lamellar sodium titanate structure. During the alkaline hydrothermal process, the SiO_2 shell coated on the surface of Fe_3O_4 was removed to form yolk-shell Fe_3O_4@TNS structure. The fabrication of Fe_3O_4@TNS with different structures was schematically illustrated in Fig. 1.

2.4. Characterization

To characterize the morphology of various samples, the SEM images were conducted by using a field emission scanning electron microscope (FEI-JSM 6320F). The TEM images were obtained by a transmission electron microscope (JEM-2010) operating at 200 kV. More detailed characterizations of Fe_3O_4@TNS were confirmed by XRD, FT-IR, XPS, Brunauer-Emmett-Teller (BET) surface area and Zeta potential. FT-IR spectrum was performed on a Bruker Tensor 27 FTIR spectrophotometer over a range from 4000 to 400 cm^{-1} using the KBr disc technique. The XPS survey was measured on a