



Immobilization of uranium(VI) by niobate/titanate nanoflakes heterojunction through combined adsorption and solar-light-driven photocatalytic reduction

Xiaona Liu^{a,b}, Penghui Du^c, Weiyi Pan^d, Chenyuan Dang^c, Tianwei Qian^a, Hongfang Liu^a, Wen Liu^{c,**}, Dongye Zhao^{a,b,*}

^a Institute of Environmental Science, Taiyuan University of Science and Technology, Taiyuan, Shanxi 030024, PR China

^b Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL 36849, United States

^c The Key Laboratory of Water and Sediment Sciences, Ministry of Education, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, PR China

^d Department of Energy, Environmental, and Chemical Engineering, Washington University, St. Louis, MO 63130, United States

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ABSTRACT

A niobate/titanate nanoflakes (Nb/TiNFs) composite was synthesized through a one-step hydrothermal method. Nb/TiNFs displayed a heterojunction structure owing to deposition of a small fraction of niobate onto tri-titanate nanoflakes. Tri-titanate ($\text{Na}_{1.6}\text{H}_{0.4}\text{Ti}_3\text{O}_7 \cdot 1.7\text{H}_2\text{O}$) was the primary crystal phase, and the molar ratio of niobate ($\text{Na}_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}$) to titanate was determined to be 1:15.9. Nb/TiNFs showed rapid adsorption kinetics and high adsorption capacity for U(VI) (Langmuir $Q_{\text{max}} = 298.5 \text{ mg/g}$). Ion-exchange and surface complexation were the key mechanisms for U(VI) uptake, and the adsorption was further enhanced by the unique tunnel lattice structure of the heterojunction. Moreover, Nb/TiNFs were able to convert U(VI) into its immobile form, $\text{UO}_2(\text{s})$ under solar light through photocatalytic reduction. More than 89.3% of (VI) was transformed into U(IV) after 4 h of solar irradiation (initial U(VI) = 20 mg/L, pH = 5.0). Diffuse reflectance UV–vis absorption spectra and Mott-Schottky plots indicated a narrowed band gap energy of Nb/TiNFs compared to neat TNTs. Density functional theory (DFT) calculation on band structure and density of states further confirmed the heterojunction architecture of niobate and titanate, resulting in offset of the conduction bands for the two phases in the composite material. Therefore, transfer of photo-excited electrons from titanate to niobate leads to inhibition of re-combination of the electron-hole pairs. In addition, the trapping of uranium in the tunnel lattice of titanate and niobate heterojunction prevents re-oxidation of U(IV) to U(VI), thus achieving long-term immobilization of uranium. Remobilization tests indicated that only 18.7% of U(VI) was re-oxidized to U(VI) and almost no U dissolved into the aqueous phase when exposed air for 90 days. The new material is promising for separation and safe disposal of high strength radionuclides in water.

1. Introduction

Uranium (U) is a common radionuclide in soil and groundwater associated with nuclear materials mining, nuclear energy, nuclear weapon testing, and radioactive material disposal [1]. ^{238}U is the primary uranium isotope, which has a half-life of 4.5×10^9 years [2]. Uranium has been known to pose widespread and lingering threat to the eco-systems and human health due to its radioactivity and carcinogenic effect [3,4].

The environmental fate and mobility of U is strongly related to its speciation and redox conditions of the matrix [1,5]. Under typical

environmental conditions, U(VI) and U(IV) are the most predominant species. U(VI), usually existing as UO_2^{2+} cations, is soluble and much more mobile in the environment, and thus is more likely to invade into the food chain [5,6]. In contrast, U(IV), mainly as UO_2 , is only sparingly soluble ($K_{\text{sp}} = -52.0$) and much less mobile [7], and thus is less likely to reach the food web [6,8]. Although adsorption has been widely studied for removal of U(VI) in contaminated water for its simplicity [9–12], reductive transformation of U(VI) to U(IV) precipitate is considered more viable as the reduced form of U(IV) is much more resistant to remobilization than the adsorbed U(VI). To this end, zero-valent iron and iron sulfide (FeS) have been the most studied materials for

* Corresponding author at: Environmental Engineering Program, Department of Civil Engineering, Auburn University, Auburn, AL 36849, United States.

** Corresponding author at: College of Environmental Sciences and Engineering, Peking University, Beijing 100871, PR China

E-mail addresses: wen.liu@pku.edu.cn (W. Liu), zhaodon@auburn.edu, dzhao@eng.auburn.edu (D. Zhao).

reductive immobilization of U(VI) [13–19].

Photocatalytic reduction is a promising technique considering its high efficiency, reusability of photocatalysts, no reducing agent consumption, low energy input if solar light is used, and environment-friendliness. However, photocatalytic transformation of U(VI) to U(IV) is hard to occur under normal oxic environmental conditions due to the low redox potential (0.411 V) of $\text{UO}_2^{2+}/\text{UO}_2$ [20–22], where U(IV) can be easily re-oxidized to U(VI). Therefore, various photocatalysts, such as $\text{TiO}_2/\text{Fe}_3\text{O}_4$ composite and sulfur doped $\text{g-C}_3\text{N}_4$ [23,24], were developed to enhance the photo-reduction under specific conditions.

In recent years, titanate nanomaterials, especially titanate nanotubes (TNTs), have drawn great research interests due to their uniform structure in nanoscale, good ion-exchange property, surface and interface effect, and quantum size effect [25,26]. Both TNTs and titanate nanowires were reported to offer effective adsorption for U(VI) [12,27–29]. Moreover, metal-doped/deposited titanate or titanate composites have been shown to be highly effective photo-catalysts under visible/solar light [30–32]. Therefore, titanate may be used as a primary material for synthesizing new photocatalysts, which can combine the excellent ion-exchange/adsorption capacity and solar-light-driven photocatalytic activity upon proper tailoring of the material. Niobate exhibits similar ion-exchange properties to titanate, and has been shown to be effective adsorbents for radionuclides [33,34]. Moreover, incorporation of niobium or niobate into titanate may lead to a new electron donor level (valence band) and a heterojunction structure, which can enhance the photocatalytic activity in the visible light range [35,36]. Therefore, there is a great application potential of niobate/titanate heterojunction composite for photo-transformation of U(VI) to U(IV).

In this study, a new titanate/niobate nanocomposite (Nb/TiNFs) with a heterojunction structure was synthesized, and tested for immobilization of $^{238}\text{U(VI)}$ through initial adsorption and subsequent photocatalytic reduction. The main objectives of this study were to: 1) develop a novel nanocomposite with titanate as the primary material and niobate as a photo-reaction facilitator; 2) test the U(VI) adsorption capacity and the photo-reduction efficiency by Nb/TiNFs under solar light; 3) elucidate the underlying adsorption mechanism and the effect of initial adsorption on subsequent photocatalysis; 4) explore the mechanisms on enhanced photocatalytic activity of the titanate/niobate composite by means of computational chemistry analysis, and 5) test the re-oxidation and long-term stability of immobilized U.

2. Experimental

2.1. Chemicals

All chemicals used in this study were of analytical grade or higher. Nano- TiO_2 (P25, ~80% anatase and ~20% rutile) was obtained from Degussa (now Evonik) of Germany. NaOH, HCl, NaHCO_3 , Na_2CO_3 , methanol (HPLC grade) and absolute ethanol were purchased from Acros Organics (Fair Lawn, NJ, USA). Nb_2O_5 (99.5%) was acquired from Alfa Aesar of USA. Deionized (DI) water (Millipore Co., 18.2 M Ω cm) was used to prepare all solutions. A stock solution of U(VI) (1000 mg/L) was prepared by dissolving 2.11 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (International Bio-Analytical Industrial Inc., FL, USA, U in ^{238}U) in 1000 mL DI water.

2.2. Preparation and characterization of Nb/TiNFs

Nb/TiNFs were synthesized through a one-step hydrothermal treatment based on the method for TNTs preparation [37,38]. Typically, 1.2 g of TiO_2 and 0.1 g Nb_2O_5 were mixed and dispersed into 80 mL of a 10 M NaOH solution. After magnetically stirred for 12 h, the mixture was transferred into a Teflon reactor with stainless steel coating, and allowed to react for 72 h at 130 °C. Afterwards, the white precipitate was washed with deionized water till pH ~9, and then

oven-dried at 105 °C for 4 h.

The material morphology was examined using a Tecnai30 FEG transmission electron microscopy (TEM, FEI, USA) operated at 300 kV. The crystal phase of the material was analyzed using a Dmax/2400 XRD (Rigaku, Japan) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and at a scan rate (2 θ) of 4°/min. AXIS-Ultra X-ray photoelectron spectroscopy (XPS, Kratos, England) analysis was performed to determine the elemental compositions and oxidation states of Nb/TiNFs before and after reacting with U using Al K α X-ray at 15 kV and 15 mA. The standard C 1s peak (Binding energy, $E_b = 284.80 \text{ eV}$) was used to eliminate the static charge effects. The Brunauer-Emmett-Teller (BET) surface area was measured on an ASAP 2010 BET surface area analyzer (Micromeritics, USA) in the relative pressure range of 0.06–0.20. Pore size distribution was obtained following the Barrett-Joyner-Halenda method. The nitrogen adsorption volume at the relative pressure of 0.99 was used to determine the pore volume and the average pore diameter. Diffuse reflectance UV–vis absorption spectra (UV-DRS) of the materials were obtained using a UV-2400 spectrophotometer (Shimadzu, Japan), and the band gap energy (E_g) was calculated through the Kubelka-Munk function. The pH of point of zero charge (pH_{PZC}) was obtained using a Nano-ZS90 Zetasizer (Malvern Instruments, UK) by measuring the zeta potentials at various pH values. The Mott-Schottky analysis method is described in Text S1 of the Supplementary Data.

2.3. Adsorption of U(VI) by Nb/TiNFs

Batch adsorption experiments were carried out in the dark and at room temperature ($25 \pm 0.5 \text{ }^\circ\text{C}$) using 100 mL polyethylene bottles. In all cases, U solution was first purged with nitrogen (99.7%) for 1 h to remove dissolved oxygen. The kinetic tests were conducted at two levels of initial U(VI) concentrations (50 and 100 mg/L) and a Nb/TiNFs dosage of 0.2 g/L and solution pH of 5.0. The solution pH was adjusted by diluted HCl and NaOH. The reaction was initiated by adding 0.02 g of Nb/TiNFs into 100 mL of the deoxygenated U(VI) solution. The mixture was then shaken at 200 rpm and the adsorption rate was followed for 360 min. Samples were taken at predetermined time intervals and immediately filtered through a 0.22 μm polyethersulfone (PES) membrane, and U(VI) concentration in the filtrate was determined on an inductively coupled plasma-optical emission spectroscopy (ICP-OES, 710-ES, Varian, USA). Isotherm tests were carried out in a similar manner, where 0.2 g/L of Nb/TiNFs was mixed with U(VI) solutions at a range of initial concentrations (10 – 200 mg/L) and at pH 5.0. The mixtures were equilibrated under shaking for 240 min to reach adsorption equilibrium. Control tests indicated no adsorption loss of U(VI) by the bottles and the membrane filtration.

The equilibrium U(VI) uptake (q_e , mg/g) and removal efficiency (R , %) are calculated by:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of U(VI) in the aqueous phase, respectively; V (L) is the solution volume and m (g) is the mass of Nb/TiNFs.

2.4. Photocatalytic reduction of U(VI) by Nb/TiNFs under simulated solar light

Batch photocatalytic reduction experiments were conducted in a sealed glass photo-reactor (volume = 250 mL) with a quartz cover (Fig. S1 in Supplementary Data). Cooling water was circulated around the reactor to maintain the system temperature of ($25 \pm 0.2 \text{ }^\circ\text{C}$). An Oriel Sol 1A solar simulator (Newport, USA) with a 450 W xenon lamp was used as the source of solar light, which has a light intensity in the

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