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Photocatalytic reduction elimination of UO_2^{2+} pollutant under visible light with metal-free sulfur doped g-C_3N_4 photocatalyst

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ABSTRACT

Reduction of soluble U(VI) to insoluble U(IV) oxide has been considered as an important approach to eliminate radioactive pollution and recycle uranium resource. The technology is hindered by the high cost, consumption of chemicals, and parallel generation of toxic wastes which are severe challenges today. In this paper, the photocatalytic reduction technology was utilized to eliminate UO_2^{2+} pollutant by constructing the highly efficient metal-free photocatalysts. Doping sulfur for substituting the lattice nitrogen of g-C_3N_4 (S-g-C_3N_4) modifies the electronic structure of g-C_3N_4 that displays the narrowed band-gap with the tuned conduction band and valence band levels as well as a good ability of electron-hole separation and carrier mobility. The photoreactivity of UO_2^{2+} reduction for S-g-C_3N_4 is 1.86 and 32 times of that for pristine g-C_3N_4 and N-TiO_2 under visible light irradiation. The substitution of sulfur for lattice nitrogen was experimentally and theoretically identified as the cause of this unique electronic structure and, consequently, the excellent photoreactivity of S-g-C_3N_4 in the reduction of UO_2^{2+}. The results may shed light on improving the reduction technology to eliminate U(VI) pollutant by doping strategies to design potentially efficient photocatalysts.

1. Introduction

With the rapid development of nuclear industry, much attention has been given to the harm of nuclear waste released from uranium mining, milling, and processing [1,2]. Study has confirmed that a long-term exposure to uranium would cause serious health problems (e.g., severe liver damage, kidney damage and eventually death) [3]. Therefore, how to eliminate uranium pollution is an important issue in the protection of environment and alleviation of the nuclear material resource [4,5]. It is seen that uranium species exist in several chemical states (e.g., U(0), U(III), U(IV), and U(VI)), in which the predominant chemical states in the ambient environment are soluble U(VI) and slightly soluble U(IV) [6–9]. Therefore, reduction of soluble U(VI) to insoluble U(IV) oxide has been proposed as an important approach to eliminate radioactive pollution and reuse uranium resource [8,10–13]. However, most of reported reduction strategies are expensive and involve a high consumption of chemicals, generating parallel toxic wastes [14]. Semiconductor photocatalysis, a green strategy that can reductively remove harmful heavy metals using semiconductor photocatalysts under sun light irradiation, provides a new option to address the above challenges [15–20]. For example, TiO_2 particles were employed as photocatalysts for photo-induced reduction of U(VI) under UV with the aid of humic acid, formic acid, and 2-propanol [14,17–19]. TiO_2 is undoubtedly the most studied semiconductor photocatalyst with its low cost, high activity and stability. However, due to its wide band gap (3.2 eV), TiO_2 cannot be activated by the visible light. In order to make full use of solar energy for photocatalytically reducing U(VI) to U(IV), it is desirable to develop efficient visible light-responsive metal/metal oxides semiconductor photocatalysts or even metal-free photocatalysts.

Recently, graphitic carbon nitride (g-C_3N_4) has attracted intensive interest for its promising applications in photo-splitting water, photo-decomposition of organic pollutants, and photosynthesis under visible light, because this material shows good visible light response (up to 455 nm), high thermal, and chemical stability

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[21–40]. Study has revealed that the conduction band position of pristine g-C_3N_4 is at around −1.23 V (vs. SHE at pH 7) [26], which is more negative than the reduction potential of UO_2^{2+}/U^{4+} (0.267 V), UO_2^{2+}/UO_2 (0.411 V), and U_4O_9/UO_2 (0.456 V). Accordingly, it will be very meaningful to investigate photocatalytic reduction of UO_2^{2+} with metal-free g-C_3N_4 as photocatalyst. However, the photocatalytic activity of the g-C_3N_4 is usually restricted by low efficiency due to the insufficient sunlight absorption and the fast recombination of photo-induced electron-hole pairs. It is known that, doping, especially anion doping, is an effective strategy to modulate absorbance, redox potentials, and mobility of photo-induced charge carriers [41–52]. However, some key issues such as the origin of non-metal doping-induced visible light absorption, the nature of the chemical states created, and the locations of the dopants are not yet well understood. Based on first-principle calculations for elements doping [53], we consider that two rules should be followed for anion dopant: one is that the electronegativity of the anion dopant must be lower than that of the substituted lattice atom; the other is that dopant anion should have a radius comparable to that of the substituted lattice atom. In this work, to demonstrate the above considerations, sulfur, which has a smaller electronegativity and larger radius than nitrogen (2.58 vs 3.04, 1.09 vs 0.75 Å), was chosen as dopant into g-C_3N_4 for the photocatalytic reduction of U(VI). The desirable electronic structural properties of the sulfur-doped g-C_3N_4 were revealed by spectroscopy characterizations. The remarkable electronic structure exhibits potency in achieving high photo-reduction activity for the reduction of U(VI). The origin of the unique electronic structure and, consequently, the excellent photo-reduction performance of the S-g-C_3N_4 are explored both experimentally and theoretically, suggesting doping strategies to design potentially efficient photocatalysts for photocatalytic reduction elimination of U(VI) pollutants.

2. Experimental

2.1. Photocatalyst preparation

All of the chemical reagents were of analytic grade without further purification. In detail, 10 g of urea or thiourea powder were heated to 520 °C in air at a heating rate of 2.5 °C/min. The temperature was kept at 520 °C for 2 h and then cooled to room temperature. The as-prepared samples prepared with urea or thiourea were labeled as g-C_3N_4 or S_1-g-C_3N_4, respectively. It is reported that the sulfur doping into g-C_3N_4 with a tuned content is not an easy process and sublimed sulfur can mediate polymerization of the g-C_3N_4 [29], and therefore CS_2 was further selected as sulfur source and sublimed sulfur was used to improve the doping of sulfur from CS_2 precursor into g-C_3N_4 or S_1-g-C_3N_4. 0.005 g sulfur powder was dissolved into 8 ml of CS_2, and then 25 ml aqueous solution including 10 g of urea or thiourea was added into the sulfur solution and ultrasonicated for 25 min, and the mixture was agitated at 40 °C for 0.5 h. Afterwards, the obtained solids were heated to 520 °C at a heating rate of 2.5 °C/min and kept at the temperature for 2 h. The obtained samples were denoted as S_2-g-C_3N_4 and S_3-g-C_3N_4 corresponding to urea and thiourea as precursors.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were performed on a D/Max-RB X-ray diffractometer (Rigaku) using Cu *Kα* radiation at a scanning rate (2θ) of 0.05° s^{-1}. The morphology was observed by transmission electron microscope (TEM, JEOL-JEM-1005 at 100 kV), and high resolution TEM (HRTEM, JEM2010 at 200 kV). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB250xi spectrometer (Thermon Scientific). The binding energy (BE) was referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. Micromeritics ASAP2020 nitrogen adsorption apparatus (USA) was used to record Brunauer–Emmett–Teller (BET) specific surface area of photocatalysts and all of the samples were degassed at 180 °C before analysis. The pore size distributions were evaluated using desorption data with Barret–Joyner–Halender (BJH) method. The BET surface area was determined by a multipoint BET method to analyze the adsorption data in the relative pressure (P/P_0) range from 0.05 to 0.25. UV–vis diffuse reflection spectra (DRS) were obtained by using a dry-pressed disk sample with a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan), and $BaSO_4$ is used as reflectance standard. Photoluminescence (PL) spectra were obtained on a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan) at room temperature. The Photo Multiplier Tube voltage was 700 V, the scanning speed was 1200 nm/min, and the excitation wave-length was 380 nm. The widths used for the excitation and emission slit were both 1.0 nm. Photocurrent measurements were performed using an electrochemical analyzer (CHI 660D electrochemical workstation, Chenhua Instrument, Shanghai, China) in a conventional three-electrode configuration with working electrode, counter electrode, and reference electrode. The working electrodes prepared with samples have an active area of 0.5 cm^2, and a Pt wire and Ag/AgCl (saturating KCl) were used as the counter electrode and reference electrode, respectively. A 300 W Xe arc lamp equipped with an ultraviolet cutoff filter ($\lambda > 400$ nm) was utilized as the visible light source. The integrated visible light intensity measured with a visible light radiometer was 25 mW/cm^2, and Na_2SO_4 aqueous solution (1 M) was used as the electrolyte.

2.3. Photocatalytic tests

The as-prepared g-C_3N_4 samples were used as photocatalysts for the photocatalytic reduction of UO_2^{2+} solutions under the visible light irradiation. In the catalytic process, 0.10 g of the g-C_3N_4 samples was added into 200 ml of 0.12 mM UO_2^{2+} solution which was prepared by dissolving uranyl nitrate ($UO_2(NO_3)_2{\cdot}6H_2O$) into mixture of deionized water and methanol (5 ml). A 350 W Xe lamp with a 420 nm cutoff filter was used as the visible light source. Before irradiation, the reduction reaction system was bubbled with nitrogen for 60 min to remove oxygen, which ensures that the reaction system was under anaerobic condition. And then, the mixed solution was magnetically stirred in the dark for 2 h to ensure the adsorption-desorption equilibrium. After illumination for a certain time, the absorbance of UO_2^{2+} was analyzed by UVmini-1240 using Arsenazo III Spectrophotometric method at wavelength of 650 nm. The absorbance intensity at different illumination time was transformed to the reduction ratio of UO_2^{2+}, which is calculated with the following expression:

Reduction ratio of UO_2^{2+}: $C/C_0 = (A_0 - A_t)/A_0 \times 100\%$, where A_0 and A_t are the absorbance intensities at 0 (after the dark adsorption) and t min, respectively. UO_2^{2+} solution without photocatalysts was also irradiated under visible light for 40 min.

2.4. Computational details

Density functional theory (DFT) calculations were performed using Perdew-Burke-Ernzerhof functionals with the combined basis sets of 3-21G* (C, H, N and S) and LanL2DZ (U). The atomic structures of the pristine and the sulfur-doped g-C_3N_4 were modeled by a truncated unit with three melems, in which two possible cases of nitrogen substituted by sulfur were considered. The peripheral C/N atoms were saturated with hydrogen atoms in order to avoid the boundary effect. U(VI) ion was encapsulated into the center of the g-C_3N_4 and S-g-C_3N_4 to investigate the binding