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Tantalum (oxy)nitrides: Preparation, characterisation and enhancement of photo-Fenton-like degradation of atrazine under visible light

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ABSTRACT

Tantalum (oxy)nitrides were prepared by the nitridation of Ta_2O_5 and were added to a photo-Fenton-like system to enhance Fe^{3+} reduction and atrazine degradation under visible light. The samples were characterized by XRD, XPS, DRS and BET analyses. XPS analysis showed that the nitrogen content of the tantalum (oxy)nitride samples increased noticeably with the nitridation temperature and nitridation time but slightly with the flow rate of NH_3. XRD results showed Ta_2O_5 was first converted to TaON and then to Ta_3N_5 when the nitridation temperature increased. DRS analysis showed that the sample obtained at 800 °C displayed the strongest absorption of visible light. However, the ability of the tantalum (oxy)nitrides to reduce Fe^{3+} did not increase continuously with the nitrogen content. Sample 7 (700 °C, Q_{NH_3} = 0.3 L/ min, 6 h) showed the highest level of photocatalytic activity for Fe^{3+} reduction. This is because the photocatalytic activity of TaON for Fe^{3+} reduction is higher than that of Ta_3N_5. And a slight synergetic effect was observed between TaON and Ta_3N_5. With the addition of sample 7, H_2O_2 decomposition and atrazine degradation were significantly accelerated in a photo-Fenton-like system under visible light. The regenerated tantalum (oxy)nitrides catalyst displayed considerably stable performance for atrazine degradation.

1. Introduction

The photo-Fenton-like (Fe^{3+}/H_2O_2) and photo-Fenton (Fe^{2+}/H_2O_2) systems constitutes one kind of the most attractive advanced oxidation processes, as the materials required are relatively abundant, inexpensive, and environmentally benign. In photo-Fenton-like and photo-Fenton system, the degradation of the contaminant is based on the attack of the active hydroxyl radical (•OH), which is generated by the reaction of Fe^{2+} and H_2O_2 (Eqs. (1) and (2)). A variety of refractory organics such as chlorinated phenols, herbicides and dyes can be decomposed effectively by the photo-Fenton(-like) reactions [1–6].

In photo-Fenton(-like) reaction, the cycling of the catalyst (Fe^{2+}/Fe^{3+}) is key to the effective degradation of the contaminant. Eqs. (1) and (3) showed the cycling of iron ions driven by H_2O_2. Fe^{2+} is oxidized by H_2O_2 with a high rate constant. But the reduction of Fe^{3+} by H_2O_2 is slow and thus ineffective. In photo-Fenton(-like)processes, the efficient way to reduce Fe^{3+} is the irradiation of UV light ($\lambda < 360$ nm) (Eq. (4)) [7]. However, the industrial applicability of this process is limited since natural UV comprises only 3–5% of the solar light energy that reaches the earth.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad k_1 = 51\,M^{-1}\,s^{-1}[8] \tag{1}$$

$$^{\bullet}OH + P \xrightarrow{k_{^{\bullet}OH}} \text{intermediates} \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad k_3 = 0.001\text{–}0.01\,M^{-1}\,s^{-1}[9] \tag{3}$$

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + {}^{\bullet}OH \tag{4}$$

Many semiconductor compounds, especially TiO_2 have been used as the photocatalysts in the reactions driven by solar energy such as water splitting and photocatalytic degradation [10–13]. The modified TiO_2 such as metal-doped or/and nonmetal-doped TiO_2 possessed the photocatalytic activity under visible light [12,14–18].

Tantalum (oxy)nitrides (Ta_3N_5 and TaON) have narrow band gaps of 2.08 and 2.4 eV [19], respectively, making them suitable as visible-light driven photocatalysts. With respect to the modified TiO_2 such as Ce–N codoped TiO_2, C–N codoped TiO_2 and bimetal codoped (Bi-Co and Fe-Co) TiO_2 [12,15,17], Ta_3N_5 and TaON have relatively simple composition and structure. It has been found that TaON and Ta_3N_5 were novel photocatalysts suitable for water decomposition and pollutant degradation reactions driven by visible light [20–22]. Compared with $TiO_{2-x}N_x$ in the same size, Ta_3N_5

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Table 1
Composition, BET surface area and the ability to reduce Fe^{3+} of the tantalum (oxy)nitride samples prepared under various conditions.

No.	Conditions	Ta:O:N	Specific surface area (m^2/g)	Fe^{2+} (mg/L)	Reduction of Fe^{3+} (%)
1	600 °C, 0.1 L/min, 6 h	1:3.0:0.10	0.896	0.129	0.45
2	600 °C, 0.5 L/min, 6 h	1:2.67:0.26	1.000	0.317	1.12
3	600 °C, 0.3 L/min, 6 h	1:2.62:0.34	1.548	0.534	1.90
4	700 °C, 0.1 L/min, 6 h	1:2.18:0.66	9.014	1.489	5.31
5	700 °C, 0.3 L/min, 2 h	1:3.32:0.24	1.894	0.425	1.51
6	700 °C, 0.3 L/min, 4 h	1:2.0:0.86	9.796	1.737	6.19
7	700 °C, 0.3 L/min, 6 h	1:1.86:0.80	14.25	2.003	7.15
8	800 °C, 0.3 L/min, 2 h	1:1.88:0.94	9.433	1.586	5.65
9	800 °C, 0.3 L/min, 6 h	1:1.50:1.07	8.549	1.171	4.17
10	800 °C, 0.1 L/min, 6 h	1:1.44:1.03	9.656	1.320	4.70
11	800 °C, 0.5 L/min, 6 h	1:1.16:1.17	9.654	0.700	2.50

showed much higher photocatalytic activity for the degradation of methylene blue under visible light irradiation [20]. To improve the efficiency of photo-Fenton system under visible light irradiation, Wang et al. [23] introduced Ta_3N_5 into the photo-Fenton system and found that Ta_3N_5 was effective to promote the reduction of Fe^{3+} under visible light and thus the degradation of N,N-dimethylaniline and 2,4-dichlorophenol. The mechanism of iron ions cycling in the presence of Ta_3N_5 was also proposed. Under visible light, Ta_3N_5 is excited to form electrons in the conduction band and holes in the valence band. The photoelectrons are captured by Fe^{3+} to generate Fe^{2+}, while the generated Fe^{2+} is oxidized by H_2O_2 immediately to regenerate Fe^{3+} and thus a rapid iron ions cycling is established.

Tantalum (oxy)nitrides are usually obtained by the nitridation of Ta_2O_5 in a NH_3 flow. The nitridation reaction always leads to the formation of a mixture of TaON and Ta_3N_5 [19]. The composition of the prepared sample was affected by the nitridation temperature, the nitridation time and the flow rate of NH_3. Thus, the preparation condition should influence the photocatalytic activity of the samples. However, to the best of our knowledge, little information on the photocatalytic activity for Fe^{3+} reduction of the samples prepared under various conditions is available.

In this study, the tantalum (oxy)nitride samples were prepared by the nitridation of Ta_2O_5 at first. XPS and DRS analysis showed that increasing the nitridation temperature, the nitridation time and the flow rate of NH_3 led to the higher content of nitrogen and the stronger absorption of visible light. But it was interesting to find that the photocatalytic activity for Fe^{3+} reduction is not increased continuously with the nitrogen content. This is because the photocatalytic activity of TaON for Fe^{3+} reduction is higher than that of Ta_3N_5, confirmed by the experimental data. And a slight synergetic effect was observed between TaON and Ta_3N_5. In the photo-Fenton-like system under visible light, the degradation of atrazine was significantly accelerated by the tantalum (oxy)nitrides sample. And the regenerated catalyst was considerably stable for atrazine degradation.

2. Experimental

2.1. Materials

Ta_2O_5, $Fe_2(SO_4)_3$ and hydrogen peroxide (30%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. NH_3 (99.99%) was supplied by Special Gas Co., Ltd., Nanjing, China. Atrazine was from Tokyo Chemical Industry Co., Ltd., Japan. Deionized water was used throughout this study.

2.2. Preparation and characterisation of tantalum (oxy)nitrides

For the preparation of tantalum (oxy)nitrides, 2.0 g of Ta_2O_5 was put into a quartz tube, which was put into a tube furnace and then subjected to nitridation under a flow of NH_3 at rates ranging from 0.1 to 0.5 L/min. The nitridation temperature ranged from 600 to 800 °C, and the nitridation time was 2–6 h. After the reaction, the sample was cooled to room temperature in the flow of N_2. The detailed conditions for the preparation of each sample are summarized in Table 1.

The phase composition of the sample was characterized by X-ray diffraction (XRD) (model D/max-rA, Rigaku Co., Tokyo, Japan), using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a RBD-upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation ($h\nu$ = 1253.6 eV). Binding energies were calibrated with containment carbon (C1s = 284.6 eV). The specific surface area of the powders was determined by nitrogen absorption (BET, ASAP 2020M Analyzer, Micromeritics). UV–vis diffuse reflectance spectra (DRS) were recorded on a UV-2401 Shimadzu spectrometer.

2.3. Photocatalytic reactions and analysis

Experiments were carried out in a photoreaction apparatus, which is shown in Fig. 1. The apparatus consists of two parts. The first part is an annular quartz tube and cooling water passes through an inner thimble of the annular tube. In the axial center of the reactor, there is a 500W xenon lamp as the light source. The wavelength of the visible light is controlled through a 400 nm cut filter. The second part is a 50 mL quartz tube, which is put on a magnetic stirrer. The reaction solution in the quartz tube was stirred during the experiments. The distance between the light source and the surface of the reaction solution is 4 cm.

In the experiment, the solution of atrazine was put into the quartz tube at first, of which pH was adjusted to 2.6 with H_2SO_4 solution ($V_{H_2SO_4} : V_{\text{deionized water}} = 1 : 20$). Then Fe^{3+} stock solution (pH 2.6) and 0.03 g tantalum (oxy)nitrides were put into the tube. To achieve an adsorption/desorption equilibrium of Fe^{3+} and atrazine on the surface of the tantalum (oxy)nitrides, the suspension was kept in the dark and stirred for 30 min. After that, the stock solution of H_2O_2 was put into the tube and at the same time the lamp was turned on to initiate the photoreaction. The samples were taken out at the desired time intervals and filtered with a 0.22 μm Millipore filter to remove the catalyst. In the experiment of Fe^{3+} photoreduction, the procedure was similar except that no atrazine and H_2O_2 was added.

Analysis of atrazine was conducted on an Agilent 1120 compact HPLC system with a reversed phase C 18 column and UV detector. The UV detector wavelength was set at 235 nm. The mobile phase was 70:30 (v/v) of methanol and deionized water with a flow rate of 1.0 mL/min. The potential reaction of atrazine with hydroxyl radical was prevented by adding 1.0 mL of 1.0 M *tert*-butyl alcohol to the sample.

The concentration of Fe^{2+} was measured by the *o*-phenanthroline colorimetric method (λ = 510 nm, $\varepsilon = 1.1 \times 10^4\ M^{-1}\ cm^{-1}$) [24]. The concentration of H_2O_2 was