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Synthesis, Photophysical and Photocatalytic Properties of N-Doped Sodium Niobate Sensitized by Carbon Nitride

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The N-doped NaNbO₃ samples sensitized by carbon nitrides are synthesized via heating the mixture of NaNbO₃ powders and urea at different weight ratios, and their photocatalytic activities are evaluated by the photodegradation of Rhodamine B under full arc Xe lamp irradiation. These samples are characterized by X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, UV-vis diffuse reflectance spectroscopy and scanning electron microscope. These investigations reveal that the samples contain N-doped NaNbO₃ and sensitizer of carbon nitride. In comparison with pristine NaNbO₃, the sample prepared at the weight ratio of NaNbO₃ to urea of 1:60 shows a significantly enhanced photocatalytic activity. These results demonstrate that the metal-free carbon nitride could work as a photosensitizer, leading to an enhancement of photocatalytic activity due to the more light harvesting and efficient electron transfer between the N-doped NaNbO₃ and carbon nitride.

1. Introduction

Development of highly efficient photocatalysts becomes a hot topic in the field of photocatalysis.^{1–3} Many approaches have been adopted to develop efficient photocatalysts by modifying the bulk and surface properties.^{4–13} Among them, extending the light absorption of UV-active photocatalyst is one of the main approaches. Doping with various ions, photosensitizing with suitable dye and metal complexes, and developing new materials have been reported to be effective methods to extend the light response of photocatalysts.

Perovskite alkaline niobates represent a particularly interesting class of materials that exhibit various properties, such as ferroelectric, piezoelectric, ionic conductive, photorefractive and photocatalytic properties.^{14,15} As for the last property, recently, it was reported that NaNbO₃ was a photocatalyst for hydrogen evolution from water under UV light irradiation¹⁶ and its thin film showed photoinduced hydrophilicity.¹⁷ In view of environmental kindness and better utilization of solar light and indoor illumination, we expected to synthesize NaNbO₃-based photocatalyst with the highly efficient activity for removing organic contaminants.

Nitrogen doping is an effective method of modifying the light absorption behavior. In the case of TiO₂, various nitrogen-doping methods have been reported, such as the sputtering of TiO₂ in an N₂–Ar atmosphere,⁶ the heating of TiO₂ powders in an ammonia atmosphere at high temperature,¹⁸ the hydrolysis of organic and inorganic titanium compounds with ammonia–water followed by heating of the resultant precipitates,¹⁹ and the heating of TiO₂ powders with urea.²⁰ Among them, in the last one, the nitrogen doping was postulated to occur by ammonia being liberated during the thermal decomposition of urea and decomposition products.²⁰ Because the above procedure is manipulative and controlled easily, in this paper, we synthesized the samples via heating the mixture of NaNbO₃ powders and urea at different weight ratios, but much more excess amount of urea was used. Interestingly, we obtained the sample

containing N-doped NaNbO₃ and sensitizer of carbon nitrides, which shows higher activities for the degradation of Rhodamine B (RhB) in comparison with pristine NaNbO₃. The mechanism for the enhancement of photocatalytic activity was discussed.

2. Experimental Section

2.1. Sample Preparation. The pristine NaNbO₃ was prepared by hydrothermal method as reported previously.¹⁶ The N-doped NaNbO₃ samples sensitized by carbon nitrides were obtained by heating the well-ground mixtures of NaNbO₃ powders and urea with different weight ratios ($m_{\text{NaNbO}_3}:m_{\text{urea}} = 1:20, 1:40$ and $1:60$) at 600 °C for 0.5 h in a furnace. Typically, the weight of NaNbO₃ is 1 g. Hereafter, the samples at weight ratios of 1:20, 1:40 and 1:60 were denoted as A(20), B(40) and C(60), respectively. To investigate the extent of urea decomposition, the weight of sample after calcination was measured. And the weight loss was defined as the difference between the weight of sample after calcination and that of initial NaNbO₃.

2.2. Characterization. The crystal structures of samples were determined by an X-ray diffractometer (DX-2500 diffractometer, Fangyuan) with Cu K α radiation ($\lambda = 0.154145$ nm). Raman scattering spectrum was measured using a laser Raman spectrophotometer (RM-1000, Renishaw). Fourier transform infrared spectroscopy (FTIR) was taken with a BIO-RAD (TFS-135) spectrophotometer. The morphology was observed by using a scanning electron microscope (SEM, JSM 5600LV, JEOL Ltd.). In the case of X-ray photoelectron spectroscopy (XPS) (AXIS ULTRA), an Al anode with a monochromator was used to significantly reduce the background signal. The binding energy was referenced to the C 1s peak taken at 284.8 eV. The diffuse reflectance spectrum was recorded with a UV-vis spectrophotometer (Varian Cary 5000) and transformed to the absorption spectra according to the Kubelka–Munk relationship.

Photocatalytic activity was estimated from the photodegradation of RhB under light irradiation, which was emitted from a 500 W Xe lamp (CHF XM500W, Beijing Trusttech Co. Ltd.). The photocatalytic reaction was carried out with 0.1 g powder sample suspended in a 100 mL RhB solution in a glass cell.

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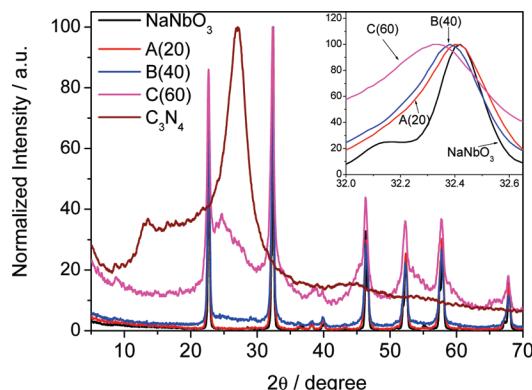


Figure 1. Normalized X-ray diffraction patterns of samples prepared at the different weight ratios of NaNbO₃ to urea. The inset is the enlarged view from 31.7 to 32.7°.

TABLE 1: Lattice Parameter of NaNbO₃, A(20), B(40) and C(60)

sample	a/Å	b/Å	c/Å
NaNbO ₃	5.553(7)	5.527(1)	15.550(1)
A(20)	5.541(5)	5.510(5)	15.587(9)
B(40)	5.553(0)	5.517(7)	15.591(1)
C(60)	5.544(1)	5.517(2)	15.594(4)

The initial concentration of RhB solution was about 5 mg L⁻¹. The concentration of RhB was detected by measuring the absorption intensity at a wavelength of 554 nm. The absorption intensity was converted to the RhB concentration referring to a standard curve which shows a linear relationship between the concentration and the absorption intensity. The rate of degradation was calculated from the difference in concentration of before and after one-hour light irradiation.

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of samples prepared at different weight ratios of NaNbO₃ powders to urea. The product of urea decomposition could be indexed as the carbon nitride of C₃N₄.²¹ All the prepared samples keep the same orthorhombic structure as NaNbO₃ with the space group of *Pbcn*. Moreover, the first strongest peak slightly shifted to lower diffraction angle direction with increasing amount of urea, as shown in the inset. Moreover, from Table 1, the lattice constant along the *c* axis increases with increasing amount of urea. These indicate that some N incorporates into the lattice of NaNbO₃ and the increased lattice constant is due to the ionic radius of N being larger than that of O. At the present step, the exact position of N atom in the structure is still unclear. Moreover, the strongest peak at 32.4° was broadened with the

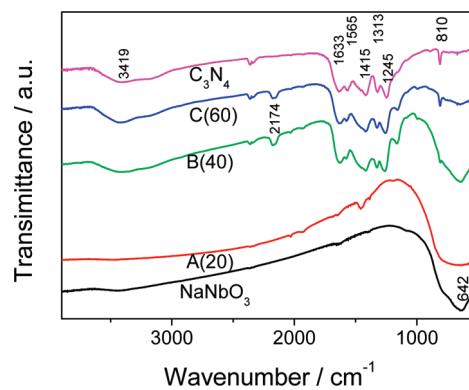


Figure 3. FTIR spectra of samples with the different weight ratios of NaNbO₃ to urea.

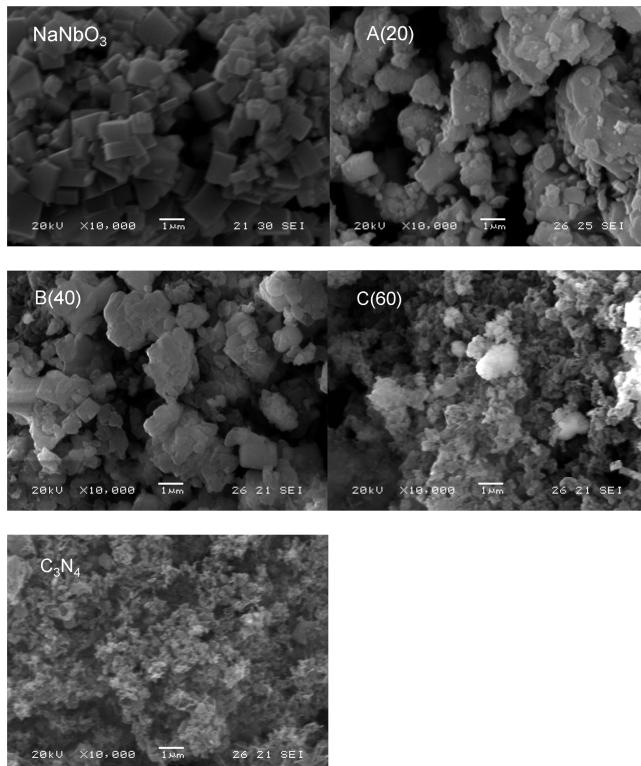


Figure 4. SEM images of samples prepared at different weight ratios of NaNbO₃ to urea.

increase in the amount of urea, as shown in the inset of Figure 1, indicating that the crystallinity is decreased in the N-doped NaNbO₃ samples in comparison with that of nondoped NaNbO₃. In addition, the weight loss for A(20) is negative, but it is positive for B(40) and C(60), implying that residual products of urea decomposition exist in B(40) and C(60) samples.

Figure 2 displays the Raman spectra of NaNbO₃ (bottom) and A(20) (top) from 400 to 800 cm⁻¹. The Raman spectrum of A(20) has the same profile as that of NaNbO₃, and no new peak was found in the spectrum of A(20), indicating that the sample has the same crystal structure as NaNbO₃, which is in good agreement with the XRD result. Moreover, the Raman peak near 600 cm⁻¹ corresponded to the stretching model of NbO octahedron shifts to higher wavenumber.²² Recently, Shiratori et al.²³ reported that these Raman bands of NaNbO₃ shift toward higher wavenumber with an increase in particle size. However, the particle size of A(20), in our case, is similar to that of NaNbO₃ (as shown in SEM images later), thus the change of particle size is not responsible for the shift of the

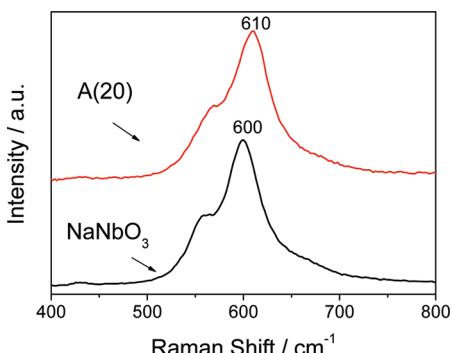


Figure 2. Raman spectra of NaNbO₃ (bottom) and A(20) (top).

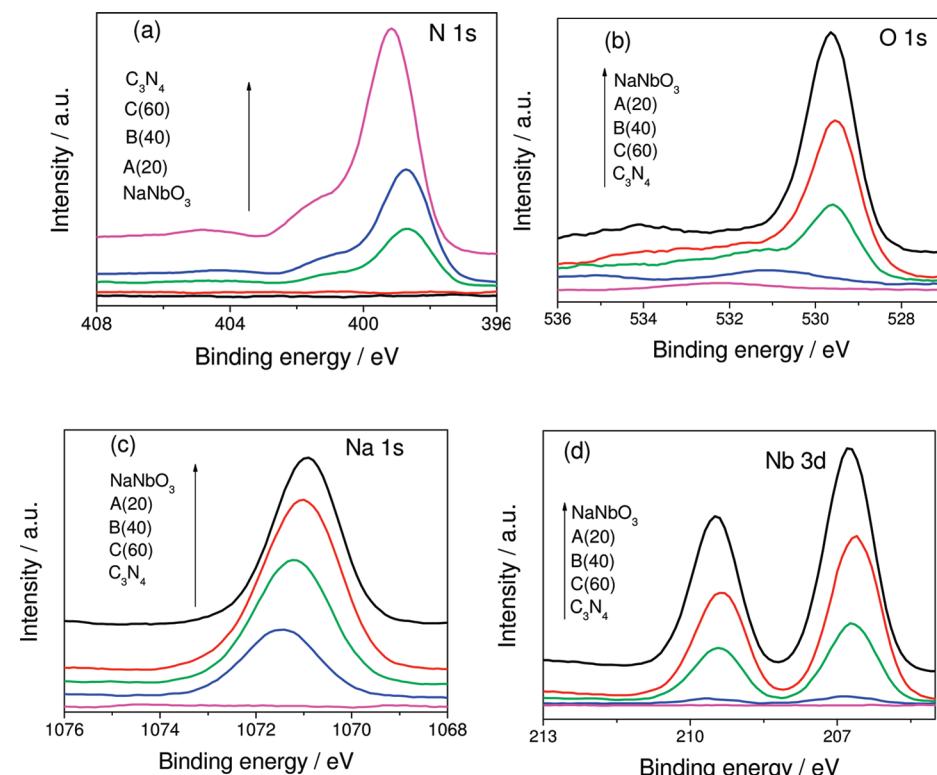


Figure 5. N 1s (a), O 1s (b), Na 1s (c) and Nb 3d (d) XPS lines of samples with different weight ratios of NaNbO₃ to urea.

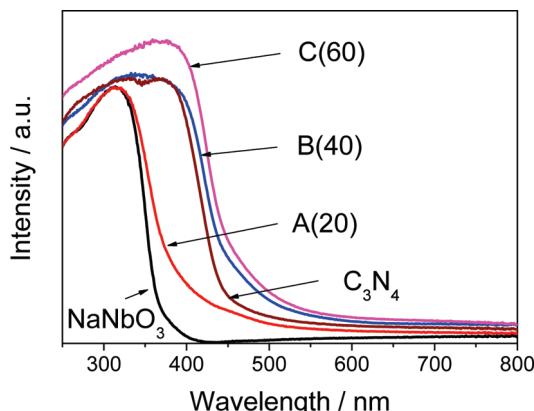


Figure 6. UV-vis diffuse reflection spectra of samples prepared by different weight ratios of NaNbO₃ to urea. The spectra of NaNbO₃ and C₃N₄ are plotted for comparison.

Raman peak at 600 cm⁻¹. According to the XRD results, the shift possibly results from the change of bond length in the NbO octahedron due to the substitution of N atoms for O atoms. It should be mentioned that no Raman band was observed in other samples, which is possibly caused by the carbon nitrides covered on the surface.

FTIR is more sensitive to carbon nitrides in comparison with X-ray diffraction.^{24,25} Figure 3 illustrates the FTIR spectra of samples prepared at the different weight ratios of NaNbO₃ powders to urea. The IR spectrum of the residual product of urea decomposition (C₃N₄) presents three main bands: (1) broadened band near 3419 cm⁻¹ is consistent with modes involving N-H stretching vibrations; (2) a series of strong bands in the 1000–1700 cm⁻¹ range are typical for molecules that contain CN heterocycles and are generally associated with the skeletal stretching vibrations of these aromatic rings; (3) another one centered at 810 cm⁻¹ is characteristic of out-of-plane bending modes of the CN heterocycles.^{24,25} The IR spectrum

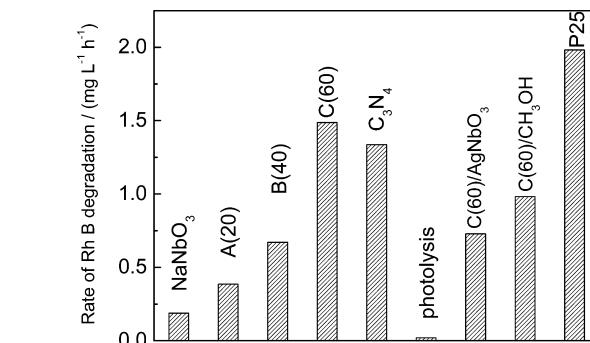


Figure 7. Photocatalytic degradation of RhB over various photocatalysts under full arc Xe lamp irradiation. The concentration of AgNO₃ is 5 mmol/L, and the ratio of methanol to water is 1:3 in volume. As references, photocatalytic activity of P25 and photolysis were investigated and shown in the figure under the same conditions.

of NaNbO₃ shows one band near 642 cm⁻¹. The IR spectrum of A(20) is similar to that of NaNbO₃ except for the peak at 1415 cm⁻¹, indicating that a small amount of C₃N₄ covered on the surface. The IR spectra of B(40) and C(60) are similar to that of C₃N₄ except for the peak at 2174 cm⁻¹, suggesting that most of the surface was covered by C₃N₄. The peak at 2174 cm⁻¹ possibly originated from the C≡N triple bonds, implying that a small amount of unknown carbon nitride existed on the surface.

In previous research, controlling the decomposition of urea to synthesize N-doped TiO₂,^{26,27} ZnO²⁸ and niobate acid²⁹ has been reported, whereas the carbon nitride was not observed, which was possibly because the amount of urea used in these works was not enough. Zhang et al. reported that the sensitizer of thiocyanuric acid was observed on the surface of ZnS when much more thiourea was used during synthesis.³⁰ Consequently, in the present case, on the basis of the results of XRD, Raman and IR spectra, we could draw a conclusion that the A(20), B(40)

and C(60) samples are N-doped NaNbO₃ covered by carbon nitrides (C₃N₄).

Figure 4 displays the SEM images of samples. The surface morphology of NaNbO₃ is of rectangle prism same as that reported previously.¹⁶ With the increase in amount of urea, the well-defined shape turns ambiguous and the particle size seems to decrease. These observations could be caused by the carbon nitride covered on the surface. The surface composition was investigated by XPS, as shown in Figure 5. From Figure 5a, it is seen that the intensity of the peak belonging to carbon nitride increases with increasing the initial amount of urea, and the reverse phenomenon is observed in the O 1s XPS line as displayed in Figure 5b, implying that the amount of carbon nitride on the surface increases with the rise in amount of urea. The N 1s spectrum can be deconvoluted into three lines centered at 398.7, 400.6, and 404.4 eV, respectively, using the Gaussian function (see Figure S1 in the Supporting Information). The contribution at 398.7 eV corresponds to sp³ C—N bond, and the one at 400.6 eV is assigned to sp² C=N. For the peak at 404.4 eV, in previous research, it was found in powder samples, but it was not in thin films.^{24,31–33} Moreover, Colaux et al. reported that it is attributed to nitrogen gas molecules,³¹ while Foy et al. thought it is due to the π electron delocalization in C₃N₃ heterocycles.³² Judging from the increase in the intensity with the rise in amount of urea, we thought it originated from the π electron delocalization in C₃N₃ heterocycles. In Figure 5c, the peak of Na 1s of NaNbO₃ is located at 1071.4 eV, which is well in agreement with the previous result.³⁴ Obviously, the peak of Na 1s shifts to high binding energy gradually with increasing the initial amount of urea, suggesting that the chemical environment of Na atom in the structure is changed due to N incorporation. In addition, the peak intensities of Na 1s and Nb 3d decrease with increasing amount of urea. This reveals that the amount of carbon nitride increases with the rise in the amount of urea. The above observations are in good agreement with XRD and IR results.

UV-vis diffuse reflection spectra could offer the light absorption information of samples, as shown in Figure 6. Compared with that of NaNbO₃, the absorption edges of the other samples shift to longer wavelength with increasing amount of urea, indicating that the light absorption property is improved. The C₃N₄ could absorb visible light due to the band gap of 2.7 eV.²¹ In the case of TiO₂, the absorption spectra after N-doping by different methods always show a combination of a main absorption edge similar to that of TiO₂ and an absorption tail from 400 nm to longer wavelength.^{6,18–20} Sample A(20) exhibits similar light absorption behavior with N-doped TiO₂, whereas the other two samples show obvious red-shift of the absorption edge. ZnS sensitized by thiocyanuric acid also shows an apparent red-shift of the absorption edge which is not affected by the initial amount of thiourea.³⁰ Therefore, the remarkable extendibility to visible light region for B(40) and C(60) could be mainly ascribed to carbon nitrides on the surface.

Photocatalytic activities of samples were investigated from the RhB degradation under light irradiation. The rates of RhB degradation are plotted in Figure 7. NaNbO₃ shows a relative low activity for RhB degradation, which is in agreement with the feature of low oxidation capacity.¹⁷ C₃N₄ shows a quite high activity compared to NaNbO₃. However, the N-doped NaNbO₃ samples covered by carbon nitrides exhibit significantly increasing activities with the rise in the initial amount of urea and the sample of C(60) has the highest rate of RhB degradation. For N-doped TiO₂, the visible light activity was often enhanced, but the activity in UV light or sunlight was reduced.^{18,35} For

metal complex photosensitization system, the similar phenomenon is usually observed.¹³ In our case, the photocatalytic activity of N-doped NaNbO₃ sensitized by carbon nitrides under the full arc Xe lamp irradiation is enhanced in comparison with NaNbO₃. On the basis of the above results, we ascribe the enhancement in the photocatalytic activity of C(60) to the increased capabilities of light absorption and charge transfer between N-doped NaNbO₃ and carbon nitrides. As above mentioned, C(60) contains the N-doped NaNbO₃ and carbon nitrides, possibly forming a photosensitization system in which the carbon nitrides work as photosensitizers of N-doped NaNbO₃, of which the function is possibly similar to that of H₆PtCl₆ in the H₆PtCl₆/Ag_{0.7}Na_{0.4}NbO₃ system.³⁶

To investigate the contribution of photogenerated electrons and holes to RhB degradation, some sacrificial reagents, namely methanol as hole sacrifice and AgNO₃ as electron sacrifice, were added to the system, forming similar systems with photocatalytic hydrogen evolution and oxygen evolution.^{16,27,37} The rate of RhB degradation was also shown in Figure 7. When both kinds of sacrificial reagents were added, the rates of RhB degradation decreased, indicating that both photogenerated electrons and holes contribute to the RhB degradation, which is similar to the results observed on N-doped niobate acid.²⁹

4. Conclusion

N-doped NaNbO₃ samples sensitized by carbon nitrides were synthesized by heating mixture of NaNbO₃ powders and urea at different weight ratios. In comparison with NaNbO₃, the prepared samples exhibit enhanced photocatalytic activity. The sample prepared at the weight ratio of NaNbO₃ to urea of 1:60 shows the highest photocatalytic activity for RhB degradation due to more light harvesting and efficient electron transfer. These results demonstrate that the metal-free carbon nitride could work as a photosensitizer, leading to an enhancement of photocatalytic activity.

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Supporting Information Available: Deconvoluted spectra of N 1s XPS lines of C₃N₄ and C(60). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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