

Contents lists available at ScienceDirect

Applied Catalysis A: General

CATALYSIS

journal homepage: www.elsevier.com/locate/apcata

Preparation of nitrogen doped $K_2Nb_4O_{11}$ with high photocatalytic activity for degradation of organic pollutants

Yongfu Qiu^a, Lei Wang^{a,b,c}, Chi-fai Leung^{a,b}, Guijian Liu^{b,c}, Shihe Yang^d, Tai-Chu Lau^{a,b,*}

^a State Key Laboratory in Marine Pollution and Department of Biology and Chemistry,, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
^b Advanced Laboratory of Environmental Research and Technology (ALERT), Joint Advanced Research Center, USTC-CityU, Suzhou, Jiangsu 215123, China
^c CAS Key Laboratory of Crust-Mantle Materials and the Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China

^a CAS Key Laboratory of Crust-Mantie Materials and the Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hejel, Annul 230026, China ^a Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

ARTICLE INFO

Article history: Received 20 February 2011 Received in revised form 4 April 2011 Accepted 11 April 2011 Available online 16 April 2011

Keywords: Photodegradation Niobate Nitrogen-doped Organic pollutants

ABSTRACT

Nitrogen doped K₂Nb₄O₁₁ (K₂Nb₄O₁₁-N) has been prepared by solid state reaction between K₂Nb₄O₁₁ and urea at 400 °C. K₂Nb₄O₁₁-N has been characterized by XRD, SEM, XPS and UV/vis diffuse reflectance. The photodegradation of various organic pollutants in water by this material, including Orange G (OG), bisphenol A (BPA) and pentachlorophenol (PCP) have been studied at λ > 330 nm and >399 nm. The results show that the photocatalytic activity of K₂Nb₄O₁₁-N at >399 nm is higher than those of K₂Nb₄O₁₁ and Degussa TiO₂ P25, indicating the activating effect of nitrogen doping. A mechanism for the photodegradation of organic substrates by K₂Nb₄O₁₁-N is proposed.

© 2011 Published by Elsevier B.V.

1. Introduction

Organic pollutants in water have been causing serious environmental problems. Photocatalytic degradation of these pollutants using sunlight is an attractive solution to this global problem. Semiconductors have been used as highly active photocatalysts, such as ZnO [1], TiO₂ [2-4], BiWO₆ [5], CdS [6], Fe₂O₃ [7], and HNbO₃ [8]. These semiconductors, however, can only be excited by UV light due to their large band gaps. For better utilization of sunlight and indoor illumination, Nb-based photocatalyts have recently been studied because the layered perovskite type niobates can be excited by visible light [8-11]. In 1981, Dion reported the family of layered perovskite type niobates, generally formulated as $AM_2Nb_3O_{10}$ (A = K, Rb, Cs; M = La, Ca, etc.), which show noticeable photocatalytic activity [9]. Soon after, Yoshimura reported a layered perovskite type niobate, RbPb₂Nb₃O₁₀, that could photocatalytically generate H₂ from water by visible light [10]. Recently, Wu reported the high photoactivity of $K_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ and their protonated derivatives for water splitting under visible light [11]. However, the use of the layered perovskite type niobates as

* Corresponding author at: State Key Laboratory in Marine Pollution and Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China. Tel.: +852 2788 7811; fax: +852 2788 7811.

E-mail address: bhtchlau@cityu.edu.hk (T.-C. Lau).

photocatalysts for the degradation of organic pollutant has received little attention until very recently, when Ye reported efficient photodegradation of Rhodamine B under visible-light irradiation using nitrogen-doped lamellar niobic acid [8]. Although the layered perovskite type niobates and their protonated derivatives show high photoactivity under visible-light irradiation, these photocatalyts are generally not very stable because the layered structure is susceptible to collapse and is easily hydrated after protonation even under atmospheric conditions [8–11].

We are interested in the use of non-layered niobate salts as photocatalysts as we anticipate that they would be more robust than the layered niobates. A suitable candidate is $K_2Nb_4O_{11}$, which is constructed from NbO₆ octahedra and has a tetragonal tungsten bronze (TB) crystal structure with triangle, quadrilateral and pentagonal tunnels. The pentagonal and quadrilateral tunnels are occupied by K cations and the triangle tunnels by Nb cations [12]. It has been reported that Cu-doping of $K_2Nb_4O_{11}$ results in increased photocatalytic activity for the degradation of acid red G under UV irradiation [13].

In this paper we attempt to prepare a highly active photocatalyst by doping $K_2Nb_4O_{11}$ with nitrogen (denoted as $K_2Nb_4O_{11}$ -N). The efficiency of $K_2Nb_4O_{11}$ -N for the photodegradation of organic pollutants at >399 nm irradiation has been investigated by using Orange G (OG), bisphenol A (BPA) and pentachlorophenol (PCP) as substrates. OG, a synthetic azo dye with formula $C_{16}H_{10}N_2Na_2O_7S_2$ (7-hydroxy-8-phenlyazo-1,

 $^{0926\}text{-}860X/\$$ – see front matter © 2011 Published by Elsevier B.V. doi:10.1016/j.apcata.2011.04.015

3-naphthalenedisulfonic acid disodium salt), is an endocrine disruptor [14]. It is a common reagent in molecular biology and is used in histology in many staining formulations. Bisphenol A is also a known endocrine disruptor, which has been widely used for the production of polycarbonate (PC) and epoxy resins used in food containers [15–17]. Its concentration in wastewaters is increasing worldwide [17]. Another common toxic pollutant in aquatic environment is pentachlorophenol (PCP). PCP has a relatively long life-time in water; hence a rapid method for its decomposition is necessary [18,19]. Our results show that the K₂Nb₄O₁₁-N photocatalyst has a much higher photoactivity than pure K₂Nb₄O₁₁ or Nb₂O₅. It is also more active than Degussa P25 TiO₂ at >399 nm. This indicates that the photoactivity of K₂Nb₄O₁₁ has been greatly enhanced by nitrogen doping.

2. Experimental

2.1. Synthesis

 $K_2Nb_4O_{11}$ was prepared by heating a mixture of $0.40 \text{ g } Nb_2O_5$ and $1.60 K_2CO_3$ at 900 °C for 24 h. For nitrogen doping, 1.0 g of $K_2Nb_4O_{11}$ was finely ground with 10.0 g urea, and the mixture was then heated at 400 °C for 4 h to give a yellow product. TiO₂ P25 was purchased from German Degussa Corporation.

2.2. Characterization

The materials were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), UV/vis diffuse reflectance and photoluminescence spectroscopy (PL). The XRD analysis was performed on a Rigaku D-max X-ray diffractometer with Cu Kα irradiation $(\lambda = 1.5406 \text{ Å})$ at a scanning speed of 0.025° /s over the 2 θ range of 20–70°. The morphologies were directly examined by a Philips XL30 environmental scanning electron microscope (ESEM) at an accelerating voltage of 10 kV. The catalyst surface analysis was done by X-ray photoelectron spectroscopy using a Leybold Heraeus-Shengyang SKL-12 electron spectrometer equipped with a VG CLAM 4 MCD electron energy analyzer, with Al-K α as the excitation source. UV/vis diffuse reflectance was performed on a Perkin Elmer Lambda 750 UV/vis Spectrophotometer. Photoluminescence (PL) spectra were measured using a FluoroMax-3 spectrofluorimeter equipped with a pulsed xenon lamp as light source.

2.3. Photocatalytic degradation experiments

A 200W xenon arc lamp (Newport, Model 71232) was used as the light source. OG, BPA or PCP aqueous solution (30 mL, 20 mg/L) and photocatalyst (10 mg) were put in a quartz tube reactor (12 mm in diameter and 200 mm in length) and the mixture was sonicated for 5 min to disperse the catalyst in the aqueous solution. The distance between the liquid surface and the light source was about 11 cm. Before irradiation, the suspension was stirred in the dark for one hour so as to allow adsorption–desorption equilibrium to be established. The Infrared and UV light emitted from the Xe-lamp was filtered by a water jacket and a composited cutoff filter (Scott AG KV 399). Samples were collected at regular time intervals and centrifuged before analysis. The concentrations of substrates were determined spectrophotometrically using a Shimadzu UV-1700 UV/vis spectrophotometer.

2.4. Analysis of photodegradation intermediates and products

The intermediates and products formed during the degradation of bisphenol A were identified by LC/MS and LC/MS/MS using an



Fig. 1. XRD pattern of: (A) $K_2Nb_4O_{11}$ (B) $K_2Nb_4O_{11}\text{-}N$ and (C) standard $K_2Nb_4O_{11}$ (JCPDS 31-1059).

Agilent 1200 series liquid chromatograph equipped with an Agilent C18 column, a UV detector and a API 2000 mass spectrometer (electrospray ionization). The mass spectrometer was operated at the anionic mode in the m/z range 50–500 for LC/MS and 50–300 for LC/MS. Aliquots were withdrawn at various time intervals and centrifuged before analysis.

3. Results and discussion

3.1. X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) shows nearly identical patterns for all the samples prepared. Typical XRD patterns of $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N are shown in Fig. 1A and B, respectively. For $K_2Nb_4O_{11}$ (Fig. 1A), all the diffraction peaks can be indexed as a tetragonal tungsten bronze structure with lattice constants of a = 0.126 nm and c = 0.398 nm, which together with the intensity distribution are consistent with those of the standard card for the $K_2Nb_4O_{11}$ crystal (Joint Committee on Powder Diffraction Standard, JCPDS 31-1059). When doped with nitrogen, the XRD pattern is unchanged, as shown in Fig. 1B, indicating that there is no effect of nitrogen doping on the crystal structure of $K_2Nb_4O_{11}$, this suggests that doping occurs only on the surface.

3.2. SEM

The SEM photographs of $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N are shown in Fig. 2A and B, respectively. From Fig. 2A, the sizes and shapes of particles are inhomogeneous and the surface is clean. When $K_2Nb_4O_{11}$ was heated with urea at 400 °C for 4 h, the surface of the sample became flock-like, but the sizes and shapes of the particles were not significantly changed. The SEM and XRD results together indicate that the morphology and crystal structure of $K_2Nb_4O_{11}$ are not affected by nitrogen doping, but the surface of the sample becomes rough, suggesting that nitrogen doping may have occurred on the surface of the sample.



Fig. 2. SEM images of: (A) K₂Nb₄O₁₁ and (B) K₂Nb₄O₁₁-N.

3.3. XPS

The X-ray photoelectron spectra (XPS) of $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N in wide energy range are shown in Fig. 3. No significant contamination, besides carbon, is found in the spectra. The binding energy was determined by reference to C 1s line at 284.8 eV. In the whole energy range spectrum the elements K, Nb and O can



Fig. 3. XPS spectrum in the whole energy range. (A) K₂Nb₄O₁₁ and (B) K₂Nb₄O₁₁-N.

be observed in $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N. However, N can only be seen in $K_2Nb_4O_{11}$ -N, indicating the successful doping of N onto the surface of $K_2Nb_4O_{11}$. The N concentration is calculated to be 3.9 atom% using the equation,

$$C_{\rm N} = \frac{I_{\rm N}/S_{\rm N}}{\sum_i I_i/S_i}$$

where C_N is the nitrogen concentration, I_N and I_i are the peak intensities of nitrogen and other elements, respectively; S_N and S_i are the relative sensitivity factors of nitrogen and other elements, respectively.

To further determine the chemical states of the elements, core level XPS spectra of Nb, O and N in $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N have been obtained and are shown in Fig. 4. Fig. 4A1 and B1 shows that the binding energies of Nb $3d_{5/2}$ for $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N are 206.8 and 206.9 eV, respectively; which are consistent with the reported values [20]. The chemical shifts of the binding energies of Nb $3d_{5/2}$ in these two materials are small. However, the full widths at half maximum (FWHM) of the Nb $3d_{5/2}$ peaks are different. The FWHM of Nb $3d_{5/2}$ for $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N are 1.7 and 1.9 eV, respectively. The broadening of the Nb $3d_{5/2}$ peak indicates that the electron density on the Nb atoms in $K_2Nb_4O_{11}$ -N



Fig. 4. XPS spectra of the elements in $K_2Nb_4O_{11}$ (A) and $K_2Nb_4O_{11}$ -N (B). 1, 2 and 3 refer to Nb, O and N, respectively.



Fig. 5. (A) UV-vis diffuse reflectance spectra of $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N; (B) The curve deduced from A according to the equation $(\alpha h \upsilon)^2 = A (h \upsilon - E_g)$.

is higher than that in K₂Nb₄O₁₁ [21]. The main O 1s peak at 530.8 and 530.6 eV in Fig. 4A2 and B2 are assigned to lattice oxygen of K₂Nb₄O₁₁ and K₂Nb₄O₁₁-N, respectively [22–24]. A higher binding energy shoulder is found for both samples at about 532.6 eV, this is assigned to a mixture of surface hydroxyl and carbonate groups [21]. Nitrogen is found only on K₂Nb₄O₁₁-N and the core-level N 1s XPS is shown in Fig. 4B3. The N 1s spectrum is deconvoluted into two components with peak energies of 398.7 and 400.8 eV, which are assigned to be (N)_i or (NO)₀ and (NO)_i or (NO₂)₀, respectively [22]. (N)_i represents N in the interstitial space, (NO)₀ denotes NO sitting at the site for the lattice O. Similarly, (NO)_i and (NO₂)₀ designate the interstitial NO and substitutional NO₂ for the lattice O, respectively.

3.4. UV/vis diffuse reflectance

The light absorption of the samples can be measured by using UV/vis diffuse reflectance spectroscopy [25]. Fig. 5 shows the UV/vis diffuse reflectance spectra of $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N. It is known that the optical absorption coefficient near the band edge follows the equation $(\alpha h \upsilon)^2 = A (h \upsilon - E_g)$ for a direct-band gap material; where α , h, υ , E_g and A are the absorption coefficient, Planck constant, light frequency, band gap, and a constant, respectively [25]. This relationship gives the band gaps (E_g) by extrapolating the straight portion of $(\alpha h \upsilon)^2$ against $h \upsilon$ plots to the point $\alpha = 0$, which are 3.27 eV and 3.12 eV for $K_2Nb_4O_{11}$ and $K_2Nb_4O_{11}$ -N, respectively. The absorption edge of $K_2Nb_4O_{11}$ -N shifts to longer wavelength compared with that of the undoped one, indicating that nitrogen-doping has a narrowing effect on the band gap of the material on the surface [25].



Fig. 6. (A) Plot of C/C_0 (*C* is the concentration at time *t*, C_0 is the initial concentration) versus time for the photo-degradation of OG using 330 nm cut off filter; (B) Plot of C/C_0 versus time for photo-degradation of OG using 399 nm cut off filter; (a) $K_2Nb_4O_{11}$, (b) TiO₂ P25 and (c) $K_2Nb_4O_{11}$ -N.

3.5. Photocatalytic degradation of orange G

The photodegradation of OG with 330 nm cutoff filter using K₂Nb₄O₁₁ and K₂Nb₄O₁₁-N as photocatalysts was investigated and results are shown in Fig. 6A. The degradation of OG was negligible after 4 h when K₂Nb₄O₁₁ was used as the photocatalyst. On the other hand, when K₂Nb₄O₁₁-N was used, nearly 90% OG was degraded after 2h of irradiation, indicating nitrogen doping greatly enhances the photocatalytic activity of the K₂Nb₄O₁₁. Control experiments show that both light and the photocatalyst are required for the degradation of OG. The degradation of OG by K₂Nb₄O₁₁-N is only slightly less efficient than TiO₂ P25 when 330 nm cutoff filter is used. On the other hand, when 399 nm cutoff filter was used, the photocatalytic activity of K₂Nb₄O₁₁-N is higher than that of TiO₂ P25. As shown in Fig. 6B, nearly 90% of OG is degraded over the K₂Nb₄O₁₁-N after 12 h of irradiation when a 399 nm cutoff filter is used, while only 46% is degraded over TiO₂ P25.

Fig. 7A shows the spectral changes of OG during irradiation using 399 nm cutoff filter with $K_2Nb_4O_{11}$ -N. The main absorption band of OG is at around 478 nm, which decreases with time upon irradiation, but λ_{max} remains at around 478 nm, indicating that the photodegradation does not occur by a dye self-photosensitized oxidative mechanism [26]. Apart from the peak at 478 nm, the photodegradation of OG by $K_2Nb_4O_{11}$ -N also results in the disappearance of the peak at 330 nm, indicating that both the OG chromophores and the aromatic rings have been destroyed [8]. Also the total organic carbon (TOC) value of the solution decreases



Fig. 7. (A) Spectral changes of OG during irradiation using 399 nm cutoff filter with $K_2Nb_4O_{11}$ -N; (B) Plot of (TOC)/(TOC)_o [(TOC) is the total organic carbon at time *t*, (TOC)_o is the initial total organic carbon] versus time for photo-degradation of OG using a 399 nm cut off filter with $K_2Nb_4O_{11}$ -N.

by approximately 25% at 90% OG conversion after 12 h of irradiation (see Fig. 7B). We conclude that the OG is mainly degraded to aliphatic organic compounds and is only partially mineralized to CO_2 and/or CO.

To assess the stability of the photocatalyst, a sample of $K_2Nb_4O_{11}$ -N was aged at atmospheric ambient conditions for six months and its photocatalytic activity was then tested. As shown in Fig. S2, the photocatalytic activity of the aged $K_2Nb_4O_{11}$ -N sample decreases by about 6% compared with the freshly prepared sample. This shows that that $K_2Nb_4O_{11}$ -N photocatalyst is reasonably stable when stored under ambient conditions.

3.6. Photocatalytic degradation of BPA and PCP

It has been suggested by several authors that the photocatalytic degradation of dyes under visible light may be induced by light absorbed by the dye rather than by the catalyst [27,28]. In order to understand the photoactivity of $K_2Nb_4O_{11}$ -N under visible light, bisphenol A (BPA) and pentachlorophenol (PCP), which do not absorb in the visible region and are emerging pollutants in water, were selected as substrates. For comparison, Nb₂O₅, pure $K_2Nb_4O_{11}$ and Degussa TiO₂ P25 were also used as photocatalysts and results are shown in Fig. 8. In the absence of photocatalyst, the concentration of BPA and PCP remained virtually unchanged even after 20 h of visible light irradiation (399 nm cutoff). Also, BPA and PCP were not degraded by the photocatalysts in the dark. However, upon visible-light irradiation in the presence of $K_2Nb_4O_{11}$ -N, 90% of



Fig. 8. (A) Plot of C/C_o (*C* is the concentration at time *t*, C_o is the initial concentration) versus time for photo-degradation of BPA (A) and PCP (B) using a 399 nm cutoff filter with (a) no catalyst; (b) Nb₂O₅; (c) K₂Nb₄O₁₁; (d) Degussa TiO₂ P25; (e) K₂Nb₄O₁₁-N.

BPA was degraded after 6 h and 80% of PCP was degraded after 2 h. This photoactivity is higher than that of Degussa TiO_2 P25, and is much higher than that of pure $K_2Nb_4O_{11}$ and Nb_2O_5 . These results confirm that nitrogen doping greatly enhances the photoactivity of $K_2Nb_4O_{11}$.

The intermediates formed during the degradation of bisphenol A were identified by LC/MS and LC/MS/MS experiments. Fig.S3 shows the total ions chromatogram (TIC) from LC/MS for the intermediates formed during bisphenol A degradation by K₂Nb₄O₁₁-N after 4 h. Five major intermediates were identified, as listed in Table 1. In the liquid chromatogram, the peak f is bisphenol A with a m/zof 227. The m/z value for each peak corresponds to the $[M-H]^$ ion that arises from deprotonation of a hydroxyl group. Since a reverse-phase LC column and a polar mobile phase were used, the products were eluted in decreasing order of polarity. Each peak was identified by interpretation of the MS/MS spectra. Similar intermediates have also been reported for the degradation of bisphenol A using Fenton's reagent, TiO₂ photocatalyst and a supported Ru polypyridyl catalyst [29–31]. The compounds in peak a and b have the same molecular weight and fragment ions, indicating that they are closely related isomers. The intermediates d and e are assigned as the hydroxylated BPA and the corresponding quinine, respectively. The formation of these intermediates is consistent with an oxidation mechanism that involves hydroxyl radicals (•OH), as proposed in our earlier report [31]. These phenolic and quinone derivatives of bisphenol A then undergo oxidative C-C bond cleavage by •OH to give benzophenone, substituted benzophenones and

Table 1	
List of major intermediates (a-e) and main fragments ((m/z) obtained by LC-MS

Peak	Retention time (min)	m/z (amu)	M. W.	MS/MS fragments (relative abundance)	Proposed structure
a	1.4	163	164	163(100) 107(64)	$H_{3}C \xrightarrow{HO} = 0$ $H_{2}C \xrightarrow{O} 0$
b	1.7	163	164	163(100) 107(64)	H ₃ C H ₂ C O
с	3.1	133	134	133(100) 117(16) 93(25)	H ₃ C H ₂ C OH
d	6.4	257	258	257(100) 242(18) 229(97) 214(50)	HO-
e	7.0	243	244	243(100) 227(60) 133(24) 7	HO-CH ₃ -OH CH ₃ OH
f	12.7	227	228	227(100) 212(63) 133(20)	HO-CH ₃ -OH CH ₃ -OH

substituted phenols (a–c). The compound in peak *a* should be more polar, hence it is assigned as the ortho-quinone derivative, while that in peak b is assigned as the para-quinone derivative. The mechanism for the generation of hydroxyl radicals will be discussed later (Section 3.7).

3.7. Proposed mechanism for photodegradation by $K_2Nb_4O_{11}-N$

Modified semiconductor materials have been receiving great attention because of their potential applications in solar-driven photocatalysis. One method for modifying the semiconductor is non-metal doping, usually with elements that can narrow the band gap and shift the optical adsorption edge of the photocatalyst to the visible region [32,33]. Nitrogen is one of the most popular dopants because of its appropriate ionic radius and the ease of doping into oxide lattices [34–36]. The mechanism of the photocatalytic activity of nitrogen doped semiconductor materials has been discussed [34–36]. Asahi et al. found that nitrogen atoms substitute the lattice oxygen sites of TiO₂ and narrow the band gap by mixing the N 2p and O 2p states [34]. However, in studying the decomposition of gaseous 2-propanol on N-doped TiO₂, Irie et al. observed that the photocatalytic quantum yields are significantly enhanced by irradiating with UV light than by visible light [35]. Therefore they suggested that the visible-light response in N-doped TiO₂ is due to the N 2p states isolated above the valence-band maximum of TiO₂, rather than to the narrowing of the band gap by mixing the N 2p and O 2p states. Recently, Lee et al. performed first-principles density-functional calculations to study the electronic properties of N-doped and C-doped TiO₂ [36], and their results is consistent with Irie's model. Our results also reveals significantly enhanced photodegradation efficiency under UV light irradiation compared to that under visible light (see Fig. 6), again in line with the above studies.

On the basis of the above analysis, a band structure for the $K_2Nb_4O_{11}$ -N is proposed, as schematically shown in Fig. S4. In the $K_2Nb_4O_{11}$ -N photocatalyst, there exists isolated N 2p states above the valence-band maximum of $K_2Nb_4O_{11}$, which give rise to the strong absorption enhancement in the visible region. Under visible light irradiation, electron and hole pairs would be generated between impurity N 2p states and the conduction band of Nb 4d (Eq. (1)).

$$K_2Nb_4O_{11}-N + visible light \rightarrow h^+ + e_{CB}^-$$
(1)

The excited electrons e_{CB}^- in the conduction band would move to the surface and combine with surface-adsorbed oxygen to produce O_2^- superoxide anion radicals. The O_2^- radicals could then



Fig. 9. Plot of C/C_0 (*C* is the concentration at time *t*, C_0 is the initial concentration) versus time for photo-degradation of BPA by K₂Nb₄O₁₁-N at different pH: (a) pH3; (b) pH6; (c) pH10.

react with H₂O to produce •OH radicals (Eq. (2)) [37,38], which is known to be a strong oxidizing species. On the other hand, the reactive holes h^+ would react with adsorbed OH⁻ on the catalyst surface to also form •OH radicals (Eqs. (3)-(4)) [37,38].

$$O_{2ads}^{\bullet-} + 2H_2O \rightarrow {}^{\bullet}OH + OH^- + H_2O_2$$
 (2)

$$H_2 O \rightarrow O H_{ads}^- + H^+$$
(3)

 $OH_{ads}^{-} + h^{+} \rightarrow \bullet OH$ (4)

The •OH radicals would react with substrates to produce H₂O and CO₂ via various intermediates.

The effects of pH on the photocatalytic degradation of BPA by K₂Nb₄O₁₁-N were also studied (Fig. 9). It was found that photocatalytic activity of K₂Nb₄O₁₁-N increases when the solution pH decreases. This may be explained by the processes shown in Eqs. (5)-(7), which occur in the presence of H⁺.

$$O_{2ads}^{\bullet-} + H^+ \to HO_{2ads}$$
(5)

 $HO_{2ads}^{\bullet} + H_2O \rightarrow {}^{\bullet}OH_{ads} + H_2O_{2ads}$ (6)

$$HO_{2ads} + e_{CB}^{-} \rightarrow \bullet OH_{ads} + OH_{ads}^{-}$$
(7)

These processes facilitate trapping of the electrons in the conduction band of K₂Nb₄O₁₁-N and produce •OH_{ads}. This trapping mechanism slows down the recombination of electron-hole pairs and allows a more efficient charge separation. Hence, the transfer of trapped electrons to dissolved oxygen in the solution would be enhanced and more holes and hydroxyl radicals will be available for the oxidation of substrate on the catalyst surface as well as in the solution phase.

4. Advantages of K₂Nb₄O₁₁-N as photocatalyst

Apart from higher photocatalytic activity, K₂Nb₄O₁₁-N is also more stable than TiO₂. Although N-doping of TiO₂ also improves its photocatalytic activity under visible light, it becomes thermally less stable [39]. Moreover, when TiO₂ is illuminated with UV light, the contact angle for water decreased to near 0, this phenomenon is called photo-induced hydrophilic (PIH) effect [40]. This means that TiO₂ nanoparticles readily undergo photo-dissolution and dispersion in water and consequently they are difficult to be separated and reused after photocatalysis. On the other hand, K₂Nb₄O₁₁-N readily settles to the bottom of the solution if left undisturbed, and it can be recovered and reused after photocatalysis by centrifugation or simple filtration. Moreover we found that in the photodegradation of PCP, K₂Nb₄O₁₁-N can be recycled at least four times without any loss of activity, i.e. the time for the degradation of 90% of 20 mg/L PCP by 10 mg of the catalysts is the same (90 min) for four consecutive runs.

5. Conclusions

In this report, K₂Nb₄O₁₁-N has been successfully prepared, fully characterized and used for the photodegradation of OG, BPA and PCP. XRD and SEM show that the crystal structures of K₂Nb₄O₁₁-N and K₂Nb₄O₁₁ are nearly identical, but the surface morphology has been changed significantly due to the nitrogen doping. XPS and PL indicate that the nitrogen doping primarily occurs at the surface of K₂Nb₄O₁₁, while UV/vis diffuse reflectance data reveal that nitrogen doping narrows the band gap of K₂Nb₄O₁₁ on the surface. The photocatalytic activity of the K2Nb4O11-N has been evaluated by photodegradation of OG, BPA and PCP under visible light irradiation (λ > 399 nm). The results show that the photocatalytic activity of K₂Nb₄O₁₁-N is significantly higher than that of pure K₂Nb₄O₁₁ and Degussa TiO₂ P25, highlighting the importance of nitrogen doping of K₂Nb₄O₁₁. Moreover, this photocatalyst is very stable (at least six months at room temperature), its preparation is simple and highly reproducible, and it is easily separated from the solution after photocatalysis and can be readily recycled without loss of activity.

Acknowledgments

The work described in this paper was supported by the University Grants Committee (UGC) of Hong Kong Special Administrative Region (AoE/P-04/04) and the State Key Laboratory in Marine Pollution (SKLMP). The equipment used in this work was also supported by a Special Equipment Grant from UGC (SEG_CityU02). Dr. Yongfu Qiu would like to thank the Natural Science Foundation of Guangdong Province (No. 10451170003004186), the Foundation for Distinguished Young Talents in Higher Education of Guangdong, China (No. LYM10125) and the National Basic Research Program of China (2010CB227306) for support of his research. We also thank Dr. Suk-Yin Lai and Mr. Fang Ying (Centre for Surface Analysis and Research, Department of Chemistry, Hong Kong Baptist University, HKSAR) for XRD and XPS measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.04.015.

References

- [1] M.A. Behnajady, N. Modirshahla, R. Hamzavi, J. Hazard. Mater. 133 (2006) 226 - 232.
- R.A. Damodar, S.J. You, H.H. Chou, J. Hazard. Mater. 172 (2009) 1321-1328.
- Z.B. Wu, F. Dong, Y. Liu, H.Q. Wang, Catal. Commun. 11 (2009) 82-86.
- [4] A. Vijayabalan, K. Selvam, R. Velmurugan, M. Swaminathan, J. Hazard. Mater. 172 (2009) 914-921.
- [5] L.W. Zhang, Y.J. Wang, H.Y. Cheng, W.Q. Yao, Y.F. Zhu, Adv. Mater. 21 (2009) 1286-1290.
- [6] H.Y. Zhu, R. Jiang, L. Xiao, Y.H. Chang, Y.J. Guan, X.D. Li, G.M. Zeng, J. Hazard. Mater. 169 (2009) 933-940.
- [7] E. Rodriguez, G. Fernandez, B. Ledesma, P. Alvarez, F.J. Beltran, Appl. Catal. B: Environ, 92 (2009) 240-249.
- X. Li, N. Kikugawa, J. Ye, Chem. Eur. J. 15 (2009) 3538.
- [9] M. Dion, M. Ganne, M. Tournoux, Mat. Res. Bull 16 (1981) 1429-1435.
- [10] J. Yoshimura, Y. Ebina, J. Kondo, K. Domen, A. Tanaka, J. Phys. Chem. 97 (1993) 1970-1973
- [11] J.H. Wu, Y.H. Cheng, J.M. Lin, Y.F. Huang, M.L. Huang, S.C. Hao, J. Phys. Chem. C 111 (2007) 3624-3628.
- [12] M. Lundberg, M. Sundberg, J. Solid State Chem. 63 (1986) 216-230.
- G.K. Zhang, X. Zou, J. Gong, F. He, H. Zhang, S. Ouyang, H. Liu, J. Mol. Catal. A: [13] Chem. 255 (2006) 109-116.
- [14] B. Muktha, G. Madras, T.N.G. Row, U. Scherf, S. Patil, J. Phys. Chem. B 111 (2007) 7994-7998
- [15] P. Mahata, G. Madras, S. Natarajan, Catal. Lett. 115 (2007) 27-32.

- [16] P. Mahata, G. Madras, S. Natarajan, J. Phys. Chem. B 110 (2006) 13759-13768.
- [17] S. Mahapatra, G. Madras, T.N. Guru Row, J. Phys. Chem. C 111 (2007) 6505-6511.
- [18] M. Sokmen, A. Ozkan, J. Photochem. Photobiol. A- Chem. 147 (2002) 77-81.
- [19] C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J.-M. Herrmann, J. Photochem. Photobiol. A- Chem. 158 (2003) 27-36.
- [20] G.K. Zhang, Y.J. Hu, X.M. Ding, J. Zhou, J.W. Xie, J. Solid Sate Chem. 181 (2008) 2133-2138.
- [21] T. Shishido, M. Oku, S. Okada, K. Kudou, J. Ye, T. Sasaki, Y. Watanabe, N. Toyota, H. Horiuchi, T. Fukuda, J. Alloys Compd. 281 (1998) 196-201.
- [22] A. Molak, E. Talik, M. Kruczek, M. Paluch, A. Ratuszna, Z. Ujma, Mater. Sci. Eng., B 128 (2006) 16-24.
- [23] S.-Y. Lai, Y. Qiu, S. Wang, J. Catal. 237 (2006) 303-313.
- [24] R. Asahi, T. Morikawa, Chem. Phys. 339 (2007) 57-63.
- [25] M.A. Butler, J. Appl. Phys. 48 (1997) 1914–1920.
- [26] T. Wu, G. Liu, J. Zhao, H. Hidaka, N. Serpone, J. Phys. Chem. B 102 (1998) 5845-5851.
- [27] A. Mills, J.S. Wang, J. Photochem. Photobiol. A 127 (1999) 123-134; M. Mrowetz, W. Balcerski, A.J. Colussi, M.R. Hoffmann, J. Phys. Chem. B 108 (2004) 17269-17273.

- [28] (a) X.L. Yan, T. Ohno, K. Nishijima, R. Abe, B. Ohtani, Chem. Phys. Lett. 429 (2006) 606-610:
 - F. Amano, A. Yamakata, K. Nogami, M. Osawa, B. Ohtani, J. Am. Chem. Soc. 130 (2008) 17650-17651
- [29] B. Gözmen, M.A. Oturan, N. Oturan, O. Erbatur, Environ. Sci. Technol. 37 (2003) 3716-3723.
- [30] S. Fukahori, H. Ichiura, T. Kitaoka, H. Tanaka, Appl. Catal. B 46 (2003) 453-462. [31] Z.M. Hu, C.F. Leung, Y.K. Tsang, H.X. Du, H.J. Liang, Y.F. Qiu, T.C. Lau, New J.
- Chem., B (2010), doi:10.1039/c0nj00583e.
- [32] T. Ohno, T. Tsubota, M. Toyofuku, R. Inaba, Catal. Lett. 98 (2004) 255-258.
- [33] J. Sun, L. Qiao, S. Sun, G. Wang, J. Hazar. Mater. 155 (2008) 312-319.
- [34] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001), 296-271. [35] H. Irie, S. Washizuka, N. Yoshino, K. Hashimoto, Chem. Commun. 11 (2003) 1298-1299.
- [36] J.Y. Lee, J. Park, J.H. Cho, Appl. Phys. Lett. 87 (2005) 011904.
- K. Nagaveni, M.S. Hegde, N. Ravishankar, G.N. Subbanna, G. Madras, Langmuir [37] 20 (2004) 2900-2907.
- [38] F. Dong, W.R. Zhao, Z.B. Wu, S. Guo, J. Hazard. Mater. 162 (2009) 763-770.
- [39] M. Batzill, E.H. Morales, U. Diebold, Phys. Rev. Lett. 96 (2006) 026103.
- [40] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Nature 388 (1997) 431-432.