



High photocatalytic activity of porous $K_4Nb_6O_{17}$ microsphere with large surface area prepared by homogeneous precipitation using urea

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ARTICLE INFO

Article history:

Received 17 December 2010
Received in revised form 11 February 2011
Accepted 12 February 2011
Available online 23 February 2011

Keywords:

Photocatalytic activity
 $K_4Nb_6O_{17}$
Porous
Microsphere
Homogeneous precipitation

ABSTRACT

The porous $K_4Nb_6O_{17}$ microsphere with large surface area ($86.6 \text{ m}^2/\text{g}$) has been successfully synthesized for the first time by the homogeneous precipitation method using urea. The obtained product was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and nitrogen adsorption–desorption isotherm analysis. The photocatalytic experiments showed that the porous $K_4Nb_6O_{17}$ microsphere not only had a high activity for the degradation of Rhodamine B, two times higher than that of the commercial Degussa P25 TiO_2 , but also had much higher activity for generating H_2 with a rate of 3.0 mmol/h under UV light irradiation. The high activity of the $K_4Nb_6O_{17}$ microsphere was mainly attributed to its porous structure and high specific surface area.

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1. Introduction

In recent years, the photocatalytic properties by semiconductor-based catalysis for producing clean H_2 fuel from water and the degradation of organic pollutants have received considerable attention, owing to solar-to-chemical conversion with respect to energy and environmental concerns [1–3]. Among which, nanoporous metal oxides have captured the increasing interest of scientists and engineers owing to their much higher photocatalytic activity and reaction stabilities, and extensive studies have been carried out to further characterize photocatalysis phenomena and expand their potential practical application in the fields of environmental purification and energy fuels [4–6].

$K_4Nb_6O_{17}$, a well-known layered niobate, has received considerable attention due to its distinctive photochemical and semiconductor properties, such as photocatalytic activity in the field of water decomposition [7,8], and good properties as precursors for the synthesis of novel composite nanostructures by the ionic exchange intercalation and exfoliation reactions [9–11]. As a candidate effective photocatalytic material, several synthetic methodologies for $K_4Nb_6O_{17}$ have been developed, such as conventional solid-state reaction [12], flux growth [13,14], and hydrothermal synthesis [15–17], etc. In contrast to the other cumbersome techniques, homogeneous precipitation method is particularly promising in the preparation of porous complex oxides

with high-quality and high surface areas, all of which are important factors to improve the photocatalytic activity of the catalysts [18–20]. However, so far as we know, the synthesis and photocatalytic activity of porous $K_4Nb_6O_{17}$ microsphere with large surface area via a homogeneous precipitation method has been rarely reported.

Herein, we reported a novel procedure for the synthesis of porous multimetal oxide $K_4Nb_6O_{17}$ for the first time, which possessed large surface area ($86.6 \text{ m}^2/\text{g}$) and excellent photocatalytic activity for both photodegradation ability for Rhodamine B (RhB) and photocatalytic H_2 evolution from water-splitting. The crystal structure, microstructure and surface area of the obtained products were also carefully characterized. Moreover, for comparison, the photodegradation activities of commercial Degussa P25 TiO_2 as well as $K_4Nb_6O_{17}$ powders prepared by the SSR method were also studied.

2. Experimental

2.1. Preparation of samples

The porous $K_4Nb_6O_{17}$ microsphere was prepared by the homogeneous precipitation method. Nb_2O_5 , KOH and urea were used as the source materials. All reagents were used without further purification. At the first stage, a mixture of 0.4 g Nb_2O_5 and 40 mL of 3 mol/L KOH solution was pretreated at 180°C for 10 h in a sealed Teflon stainless autoclave until a clear solution was obtained, which was also reported in our previous work [21]; Then 3 g urea was added into the above clear solution (13.5 mL), the KOH concentra-

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tion was adjusted to 1 mol/L by adding deionized water, the clear solution was loaded into a 50 mL Teflon stainless autoclave. After the sealed Teflon stainless autoclave was heated at 220 °C for 24 h in an oven, the final products were collected by filtration, washed with deionized water and absolute ethanol for several times, and dried at ambient temperature. The $K_4Nb_6O_{17}$ powders were prepared according to Ref. [12].

2.2. Characterization of the catalyst

The crystal structures of the obtained materials were confirmed by a powder X-ray diffractometer (XRD, Rigaku D/max-2000) with monochromated $Cu K\alpha$ radiation (45 kV, 50 mA). Microstructural characterization was performed by field emission scanning electron microscopy (FESEM, MX2600FE) and transmission electron microscopy (TEM, FEI, Tecnai G2 S-Twin). BET specific surface area, and pore volume were calculated from nitrogen adsorption–desorption isotherms determined at 77 K using an AUTOSORB-1-MP surface analyzer (the sample was outgassed under vacuum at 150 °C). Ultraviolet–visible (UV–vis) diffuse reflection spectra were measured for the catalysts using a UV–vis spectrometer with an integrating sphere (PG, TU-1900), and they were converted from reflection to absorbance through the standard Kubelka–Munk method. $BaSO_4$ was used as the reflectance standard.

2.3. Photocatalytic experiments

The photocatalytic activities of $K_4Nb_6O_{17}$ photocatalysts were first evaluated by the decomposition of RhB under UV light irradiation. A 20 W UV lamp with a maximum emission at 273.5 nm was used as the light source. Aqueous suspensions of RhB (100 mL, 2×10^{-5} mol/L) and 50 mg of the powder were placed in a quartz vessel. Prior to irradiation, the suspensions were first ultrasonicated for 10 min, and then magnetically stirred in the dark for 30 min to ensure adsorption equilibrium. The suspensions were kept under constant air-equilibrated conditions before and during the irradiation. pH of the reaction suspension was not adjusted. At given time intervals, 3 mL aliquots were sampled, and centrifugated to remove the particles. The filtrates were analyzed by recording the variations of the absorption band maximum (553 nm) in UV–vis spectra of the dyes using a PG, TU-1901 spectrometer. For comparison, the photocatalytic activity of P25 TiO_2 and $K_4Nb_6O_{17}$ powders obtained by the SSR method were also carried out in the same reaction conditions.

The cycling experiment was carried out for testing the lifetime of the as-obtained photocatalyst. In the present work, six cycling runs were used. At the end of each run, the suspension was filtered off and washed with deionized water for several times, then RhB (100 mL, 2×10^{-5} mol/L) solution was added and tested again under the same measurement conditions.

Photocatalytic activity of water splitting was conducted in an outer irradiation quartz cell, which was connected to a gas-closed circulation system (dead volume: 650 cm³). The photocatalyst powder (0.1 g) was dispersed in distilled water (370 mL) in the cell, which consisted of 50 mL of methanol, by a magnetic stirring. The light source was a 350 W high-pressure Hg lamp. The generation amounts of H_2 were determined by using gas chromatograph (Agilent, GC-6820, TCD, Ar carrier). At the end of each run, the suspension was filtered off and washed with deionized water for several times, then 370 mL distilled water together with 50 mL of methanol solution was added and tested again under the same measurement conditions.

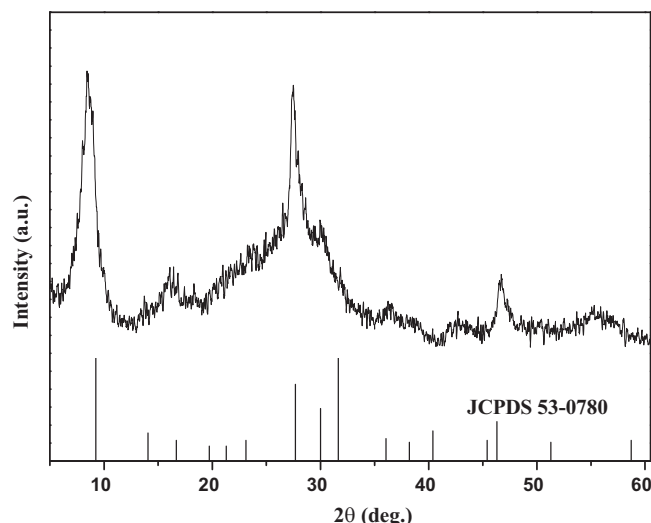


Fig. 1. XRD pattern of $K_4Nb_6O_{17}$ sample prepared by homogeneous precipitation method.

3. Results and discussion

The phase composition and crystallinity of the synthesized powder was analyzed using powder X-ray diffraction (XRD) method. Fig. 1 shows the XRD pattern of the as-prepared $K_4Nb_6O_{17}$ powder obtained by the homogeneous precipitation method using urea at 220 °C for 24 h. All diffraction peaks can be readily assigned to a pure phase $K_4Nb_6O_{17}$ (JCPDS 53-0780) and no diffraction peaks from impurity phase were observed. The weak and broad diffraction peaks for $K_4Nb_6O_{17}$ suggest that the obtained product might be composed of very small crystal grains with the size in nanoscale.

The morphology of the $K_4Nb_6O_{17}$ prepared by the homogeneous precipitation method was characterized by FESEM and TEM. Fig. 2a are the typical low-magnification SEM image of the as-synthesized product, which clearly reveals that the sample consists of uniform microspheres with an average diameter of 3–5 μm . Closer observation (Fig. 2b) demonstrates that the microspheres are composed of ultrathin nanosheets with the thickness of about 10 nm. These nanosheets are densely packed and show a porous structure. The compositions of the microspheres were also determined by EDX (Fig. 2c). The result reveals that the $K_4Nb_6O_{17}$ microspheres sample is composed of potassium, niobium and oxygen, as expected with a near stoichiometric ratio $K:Nb:O = 1:1.5:4.1$, which is consistent with the XRD result.

To reveal the detailed structure of the microsphere, TEM images were recorded. Fig. 3a shows two individual microspheres. Fig. 3b clearly demonstrates the surface structure of the microsphere, from which one can see that dozens of 2D nanosheets are intercrossed with each other and have formed into microspheres. According to the references and our experiment results, the formation mechanism of the $K_4Nb_6O_{17}$ microsphere can be ascribed to the inducing growth of CO_2 bubbles decomposed by urea as a template. It is reported that urea has been widely used in the formation of functional materials by homogeneous precipitation method [22,23]. In this paper, CO_2 bubbles of micrometer or nanometer size are slowly decomposed from urea under hydrothermal conditions, which induced the growth of the $K_4Nb_6O_{17}$ nanosheets and finally lead to the formation of the $K_4Nb_6O_{17}$ microsphere with porous structure. The similar phenomenon was also observed by Huang and coworkers [24,25]. In Huang's report, flowerlike porous carbonated hydroxyapatite (CHAp) microspheres have been successfully synthesized by using CO_2 bubbles as a template, and they also

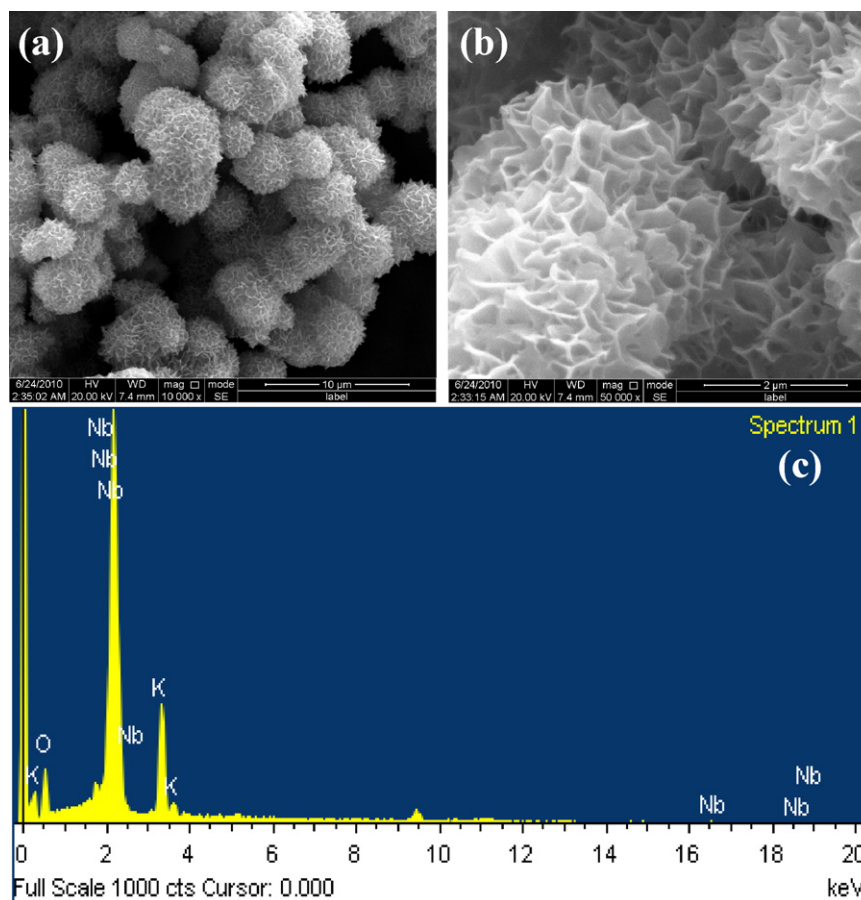


Fig. 2. FESEM images (a and b) and EDX spectrum (c) of $K_4Nb_6O_{17}$ microspheres.

attributed the formation of the CHAp microspheres to the inducing growth of CO_2 bubbles decomposed by urea as a template.

To further explore the porous structure of the as-obtained $K_4Nb_6O_{17}$ microspheres, Brunauer–Emmett–Teller (BET) gas-sorption analysis were performed. N_2 adsorption–desorption isotherms and the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution plots are shown in Fig. 4. Two well-defined steps were observed on the isotherms (Fig. 4a). The sample exhibited a typical type IV with a clear H1-type hysteresis loop in the relative pressure (p/p_0) range of 0.4–1.0, indicating the existence of mesopores. As can be seen in Fig. 4b, the pore size distributions of as-obtained $K_4Nb_6O_{17}$ microspheres showed wide distributions (2–30 nm). The surface areas and the total pore volumes of the

$K_4Nb_6O_{17}$ samples were $86.6 m^2/g$ and $0.37 cm^3/g$, respectively. The extremely high BET surface area and large total pore volume strongly support the fact that the microspheres have both mesoporous and nanoporous structure [26]. The literature has shown that porous materials with high surface-to-volume ratios can be successfully used in photocatalysis [5]. Therefore, the $K_4Nb_6O_{17}$ microsphere may exhibit high activity in photodegradation of organic pollutants and photocatalytic water splitting as shown below.

The UV–vis diffuse reflectance spectrum of $K_4Nb_6O_{17}$ product is shown in Fig. 5. It is more accurate for the determination of the band gap energy E_g of a semiconductor using the following equation: $a = A((h\nu - E_g)^{n/2})/(h\nu)$, where a , ν , E_g , and A are absorption

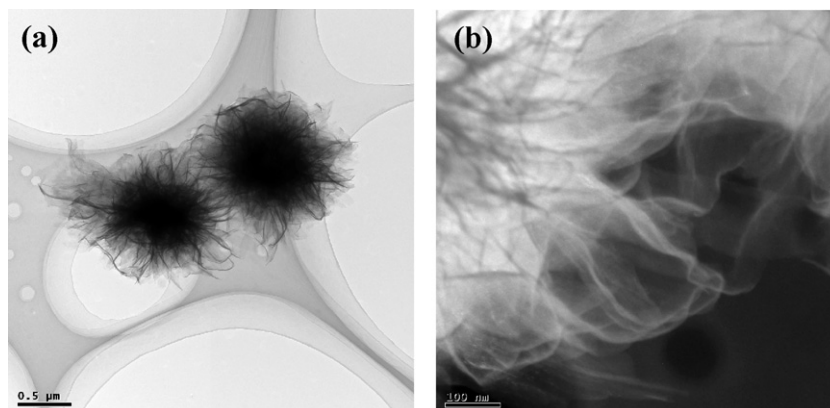


Fig. 3. TEM images of $K_4Nb_6O_{17}$ microspheres.

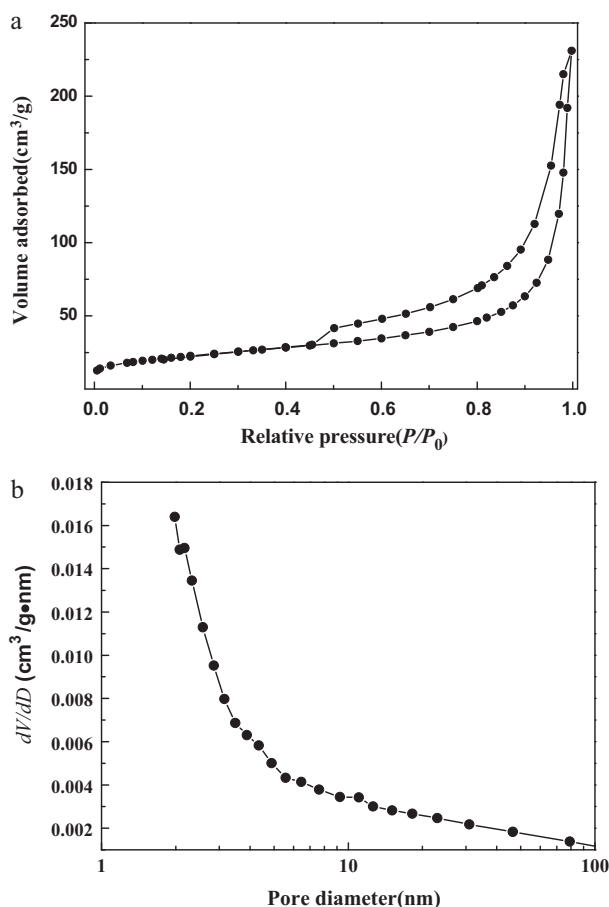


Fig. 4. (a) Nitrogen adsorption/desorption isotherms and (b) its corresponding pore diameter distribution of $K_4Nb_6O_{17}$ microspheres prepared by homogeneous precipitation method.

coefficient, light frequency, band gap, and a constant, respectively. Among them, n depends on whether the transition is direct ($n = 1$) or indirect ($n = 4$) [27]. The optical transition for $K_4Nb_6O_{17}$ is directly allowed, so the value of n for $K_4Nb_6O_{17}$ is 1. Therefore, the band gaps of $K_4Nb_6O_{17}$ is estimated to be 3.89 eV from the $(ah\nu)^2$ vs. $h\nu$ plots.

The photocatalytic activities of the as-prepared catalysts are first evaluated by photodegradation of RhB solution under UV light

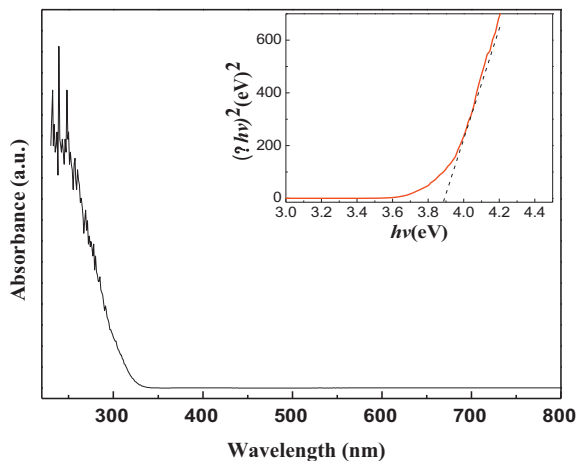


Fig. 5. UV-vis diffuse reflectance spectrum of $K_4Nb_6O_{17}$ microsphere prepared by homogeneous precipitation method with the inset curve of $(\alpha h\nu)^2$ vs. $h\nu$.

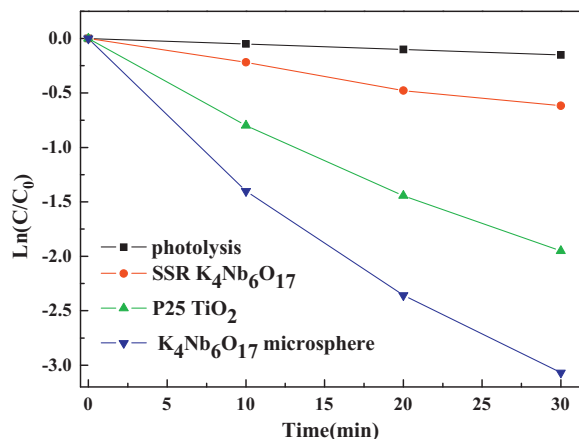


Fig. 6. Photocatalytic decomposition curves of RhB by $K_4Nb_6O_{17}$ microsphere, for comparison, the photocatalytic activity of P25 TiO_2 and $K_4Nb_6O_{17}$ powders obtained by the SSR method were also listed.

irradiation. Fig. 6 shows the decrease in RhB concentration in the $K_4Nb_6O_{17}$ microsphere suspended solution as a function of reaction time. For comparison, the photocatalytic activity of P25 TiO_2 and $K_4Nb_6O_{17}$ powders obtained by the SSR method are also given in Fig. 6. The photolysis test confirms that RhB was only slightly degraded under UV light without catalysts, indicating that the photolysis can be ignored. It can be seen that the porous $K_4Nb_6O_{17}$ microsphere showed much higher photocatalytic activity compared to the P25 TiO_2 and $K_4Nb_6O_{17}$ powder, and it can completely decompose the RhB solution in 30 min. As shown in figure, the degradation of RhB is found to follow pseudo-first-order kinetics. The apparent reaction constant for $K_4Nb_6O_{17}$ microsphere, $K_4Nb_6O_{17}$ powders and P25 TiO_2 are 0.12, 0.0012, and 0.061 min⁻¹, respectively. Obviously, the $K_4Nb_6O_{17}$ microsphere prepared by the homogeneous precipitation method exhibits the highest photocatalytic activity, nearly two times higher than that of the P25 TiO_2 .

The high activity of $K_4Nb_6O_{17}$ microsphere can also be confirmed from Fig. 7, which presents the temporal evolution of the spectral changes during the photodegradation of RhB over porous $K_4Nb_6O_{17}$ microsphere at various time intervals for the photocatalytic degradation process. It is worthy to note that the maximum absorption of RhB at 553 nm gradually decreases with the extension of the irradiation time when the mixed solution of RhB and $K_4Nb_6O_{17}$ microsphere is exposed to UV light irradiation, suggest-

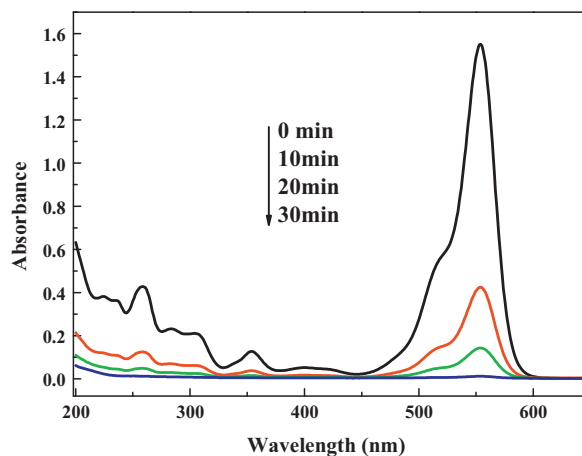


Fig. 7. The depigmentation curves of RhB solutions with the addition of $K_4Nb_6O_{17}$ microsphere under UV light irradiation.

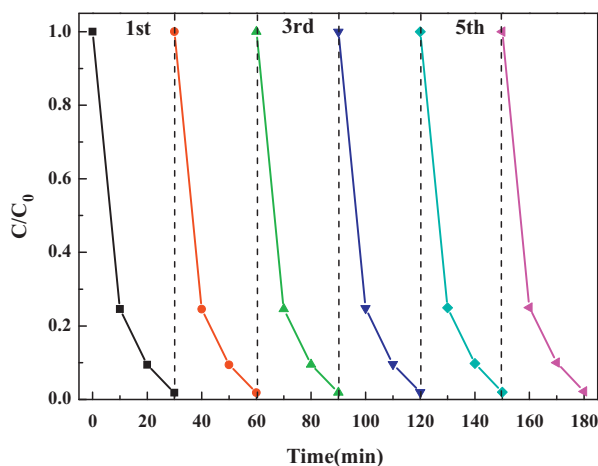


Fig. 8. Cycling runs in the photocatalytic degradation of RhB in the presence of $K_4Nb_6O_{17}$ microsphere.

ing the decomposition of the conjugated xanthene ring in RhB [28]. The RhB solution is almost decolorized when the irradiated time is up to 30 min.

In view of practical application, the photocatalyst should be chemically and optically stable after several repeated trials. The repeated experiments (Fig. 8) showed that the porous $K_4Nb_6O_{17}$ microsphere did not exhibit any significant loss of activity after six times of cycle experiment, indicating that $K_4Nb_6O_{17}$ microsphere was not photocorroded during the photocatalytic oxidation of the pollutant molecules. Furthermore, compared with P25 TiO_2 , $K_4Nb_6O_{17}$ microsphere has better sedimentation ability and can be more easily separated from the suspension by filtration after the photocatalytic reactions. The high photocatalytic activity, certain degree of photochemical stability and easy recovery by filtration from suspension suggest that the as synthesized $K_4Nb_6O_{17}$ microsphere may be a promising photocatalyst in removing the organic pollutants from wastewater.

It is known that the photocatalytic activity of a semiconductor is dominated by many factors, including the crystal structure, band gap, specific surface area, particle size, etc. The high photocatalytic activity of the porous $K_4Nb_6O_{17}$ microsphere was mainly ascribed to its porous structure and high specific surface area. The surface area of the $K_4Nb_6O_{17}$ microsphere was $86.6\text{ m}^2/\text{g}$, while for the $K_4Nb_6O_{17}$ powder obtained by the SSR method was quite low, typically less than $1\text{ m}^2/\text{g}$. Though the P25 TiO_2 has a relative large surface area ($50\text{ m}^2/\text{g}$), it is still a little small compared to our sample. Thus it can be anticipated that the porous $K_4Nb_6O_{17}$ microsphere with high surface areas exhibit improved catalytic activities, since the surface area of the photocatalyst affects the number of active sites in a photocatalytic reaction. On the other hand, the porous structure also plays an important role in improving the photocatalytic activity of the $K_4Nb_6O_{17}$ microsphere. As is well known, for photocatalysts with a nanoporous structure, the decrease of the bulk e^-/h^+ recombination, a quick surface e^-/h^+ separation, a fast interfacial charge carrier transfer and an easy charge carrier trapping are achieved [29]. Therefore, the present porous $K_4Nb_6O_{17}$ photocatalyst are capable of exhibiting a much higher activity for pollutants photodegradation.

The obtained $K_4Nb_6O_{17}$ microsphere showed not only the high activity of degradation of RhB, but also the excellent activity for photocatalytic H_2 evolution from water splitting under UV light irradiation. Fig. 9 shows the time course of H_2 evolution from an aqueous solution containing sacrificial reagents methanol over $K_4Nb_6O_{17}$ microsphere under UV light irradiation. As can be seen in Fig. 9, the $K_4Nb_6O_{17}$ microsphere shows high activity for pho-

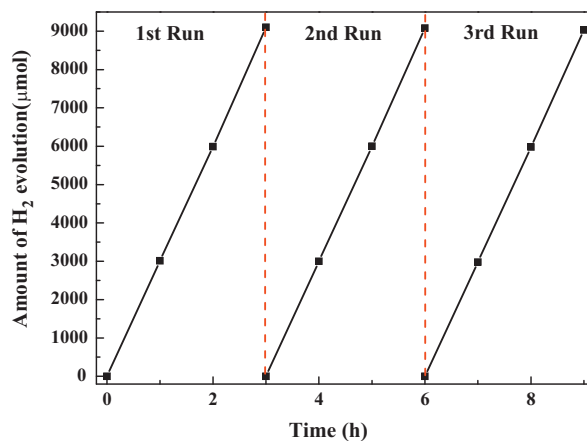


Fig. 9. The time course of H_2 evolution from an aqueous solution containing sacrificial reagents methanol over $K_4Nb_6O_{17}$ microsphere under UV light irradiation.

tocatalytic H_2 evolution, and the formation rate of H_2 evolution based on the initial 3-h values over $K_4Nb_6O_{17}$ microsphere were estimated to be 3.0 mmol/h . Furthermore, there was no appreciable decrease in gas evolution after three reaction runs, indicating that the $K_4Nb_6O_{17}$ microsphere sample was stable under UV light irradiation.

As we know, the structure of $K_4Nb_6O_{17}$ consists of stacked asymmetrical $Nb_6O_{17}^{4-}$ layers, which are composed of edge- and corner-shared NbO_6 octahedra. The stacked layers produce two distinct interlayer regions, usually designated by I and II. It has been hypothesized that water reduction occurs in interlayer I and water oxidation at interlayer II, and that an electric field gradient originating from the uneven K^+ ion distribution on both sides of the sheets may assist in electron–hole separation [7,30]. As a result, compared with the other photocatalysts reported ever, the $K_4Nb_6O_{17}$ exhibited relatively excellent photocatalytic activity for water splitting into H_2 and O_2 due to the intrinsic structure itself and it has been widely investigated by many researchers [12–15]. In the present work, the photocatalytic activity for water splitting over the porous $K_4Nb_6O_{17}$ microsphere was further improved to be 3.0 mmol/h even without loading any cocatalysts. The reason was mainly ascribed to its porous structure and high specific surface area as has been discussed above in detail. From the above analysis, it can be concluded that the preparation of porous materials may provide a new pathway to design and fabricate novel photocatalysts with excellent activities.

4. Conclusions

In summary, we have successfully prepared $K_4Nb_6O_{17}$ microsphere with porous structure via a simple homogeneous precipitation method. The photocatalytic experiments demonstrated that the porous microsphere exhibited excellent photocatalytic activity and photochemical stability for removing the organic pollutants from wastewater and photocatalytic H_2 evolution from distilled water. Our work suggested that the homogeneous precipitation method may act as a new strategy for the design of new photocatalysts with large surface areas and high activity. Furthermore, the successful synthesis of porous $K_4Nb_6O_{17}$ microsphere also makes it possible for the design of new functional nanomaterials by the ionic exchange intercalation and exfoliation reactions.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (project no. 20871036 and 21071036) and

Project-Sponsored by Program of Harbin Subject Chief Scientist (2006RFXXG001).

References

- [1] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 269–271.
- [2] Y.N. Huo, Y. Jin, Y. Zhang, *J. Mol. Catal. A: Chem.* 331 (2010) 15–20.
- [3] T. Puangpetch, T. Sreethawong, S. Yoshikawa, S. Chavadej, *J. Mol. Catal. A: Chem.* 312 (2009) 97–106.
- [4] H. Yan, J. Yang, G. Ma, G. Wu, X. Zong, J. Shi, C. Li, *J. Catal.* 266 (2009) 165–168.
- [5] J.H. Pan, H.Q. Dou, Z.G. Xiong, C. Xu, J.Z. Ma, X.S. Zhao, *J. Mater. Chem.* 20 (2010) 4512–4528.
- [6] T. Sreethawong, S. Ngamsinlapasathian, Y. Suzuki, S. Yoshikawa, *J. Mol. Catal. A: Chem.* 235 (2005) 1–11.
- [7] M.C. Sarahan, E.C. Carroll, M. Allen, D.S. Larsen, N.D. Browning, F.E. Osterloh, *J. Solid State Chem.* 181 (2008) 1678–1683.
- [8] H.Y. Lin, T.H. Lee, C.Y. Sie, *Int. J. Hydrogen Energy* 33 (2008) 4055–4063.
- [9] G.H. Du, Q. Chen, Y. Yu, S. Zhang, W.Z. Zhou, L.M. Peng, *J. Mater. Chem.* 14 (2004) 1437–1442.
- [10] G.B. Saupe, C.C. Waraksa, H.N. Kim, Y.J. Han, D.M. Kaschak, D.M. Skinner, T.E. Mallouk, *Chem. Mater.* 12 (2000) 1556–1562.
- [11] M.A. Bizeto, A.L. Shiguiharab, V.L. Constantino, *J. Mater. Chem.* 19 (2009) 2512–2525.
- [12] A. Kudo, A. Tanaka, K. Domen, K. Maruya, K. Aika, T. Onishi, *J. Catal.* 111 (1988) 67–76.
- [13] K. Teshima, K. Horita, T. Suzuki, N. Ishizawa, S. Oishi, *Chem. Mater.* 18 (2006) 3693–3697.
- [14] S.H. Lee, K. Teshima, Y. Niina, S. Suzuki, K. Yubuta, T. Shishido, M. Endo, S. Oishi, *CrystEngComm* 11 (2009) 2326–2331.
- [15] H. Hayashi, Y. Hakuta, Y. Kurata, *J. Mater. Chem.* 14 (2004) 2046–2051.
- [16] J.F. Liu, X.L. Li, Y.D. Li, *J. Cryst. Growth* 247 (2003) 419–424.
- [17] G.K. Zhang, F.S. He, X. Zou, J. Gong, H. Zhang, *J. Phys. Chem. Solids* 69 (2008) 1471–1474.
- [18] S. Yin, Y. Aita, M. Komatsu, J.S. Wang, Q. Tang, T. Sato, *J. Mater. Chem.* 15 (2005) 674–682.
- [19] V. Štengl, S. Bakardjieva, N. Murafo, V. Houšková, K. Lang, *Micropor. Mesopor. Mater.* 110 (2008) 370–378.
- [20] K.M. Parida, B. Naik, *J. Colloid Interface Sci.* 333 (2009) 269–276.
- [21] C. Zhou, G. Chen, H.J. Zhang, Q. Wang, *Mater. Lett.* 63 (2009) 1004–1006.
- [22] S.J. Kim, S.D. Park, Y.H. Jeong, *J. Am. Ceram. Soc.* 82 (1999) 927–932.
- [23] Y.K. Lin, Y.H. Su, Y.H. Huang, C.J. Hsu, Y.K. Hsu, Y.G. Lin, K.H. Huang, S.Y. Chen, K.H. Chen, L.C. Chen, *J. Mater. Chem.* 19 (2009) 9186–9194.
- [24] X.K. Chen, Q.J. He, J.Q. Li, Z.L. Huang, R. Chi, *Cryst. Growth Des.* 9 (2009) 2770–2775.
- [25] X.K. Chen, Z.L. Huang, J.Q. Li, Y. Liu, C.L. Chen, R. Chi, Y.H. Hu, *Cryst. Growth Des.* 10 (2010) 1180–1188.
- [26] J.S. Hu, L.L. Ren, Y.G. Guo, H.P. Liang, A.M. Cao, L.J. Wan, C.L. Bai, *Angew. Chem. Int. Ed.* 44 (2005) 1269–1273.
- [27] M.A. Butler, *J. Appl. Phys.* 48 (1977) 1914–1920.
- [28] J.C. Wang, P. Liu, S.M. Wang, W. Han, X.X. Wang, X.Z. Fu, *J. Mol. Catal. A: Chem.* 273 (2007) 21–25.
- [29] N. Bao, L. Shen, T. Takata, K. Domen, *Chem. Mater.* 20 (2008) 110–117.
- [30] A. Takagaki, C. Tagusagawa, S. Hayashi, M. Hara, K. Domen, *Energy Environ. Sci.* 3 (2010) 82–93.