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The Polymerization Effect on Synthesis and Visible-Light Photocatalytic Properties of Low-Temperature β -BiNbO₄ Using Nb-Citrate Precursor

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Abstract

Low-temperature β -BiNbO₄ powders (denoted as Low- β) were prepared by citrate and Pechini methods using homemade water-soluble niobium precursors. The addition of ethylene glycol and the resultant polymerization effect on the synthesis and visible-light photocatalytic performance of β -BiNbO₄ powders were fully investigated. The polymerization effect is beneficial to lower the phase formation temperature and obtain smaller particle catalysts. Both methods can synthesize catalysts with excellent performance of visible-light degradation of methyl violet (MV). The Low- β BiNbO₄ powder prepared by citrate method shows better degradation rate of about 1 h to decompose 80 % of MV and also displays good photocatalytic stability. The photodegradation of MV under the visible-light irradiation followed the pseudo-first-order kinetics according to the Langmuir-Hinshelwood model, and the obtained first-order rate constant and half-time are $2.85 \times 10^{-2} \text{ min}^{-1}$ and 24.3 min, respectively. The better photocatalytic performance of BiNbO₄ powders prepared by citrate method can be attributed to its smaller band gap and better crystallinity.

Keywords: β -BiNbO₄, Polymerization, Photocatalytic performance

Background

In recent years, environmental pollution, especially organic pollutants, has attracted much attention due to its deleterious effect on human health [1]. TiO₂, one of the most popular photocatalysts, can solely absorb ultraviolet (UV) light. In order to make good use of solar light source, many visible-light active photocatalysts have been deeply investigated, such as quantum dot-based photocatalysts [2–5]. Among these photocatalysts, much attention has been paid on bismuth-based photocatalytic materials, such as BiOBr [6, 7], Bi₂O₂CO₃ [8], BiVO₄ [9], BiNbO₄ [10–12], and BiTaO₄ [13, 14], due to their excellent

photooxidation ability for organic contaminant degradation via a visible-light photocatalytic process.

BiNbO₄ has orthorhombic α and triclinic β phases. In general, the low-temperature α phase synthesized at 900 °C irreversibly transforms to the high-temperature β phase (denoted as High- β) at 1020 °C [15]. While in our former work, we first synthesized the low-temperature β phase (denoted as Low- β) at 700 °C and observed the phase transition from β to α phase [16]. The visible-light photocatalytic performance test also shows that the Low- β exhibits the best photocatalytic efficiency compared with α phase and High- β [12]. The formation of a pure triclinic phase of BiNbO₄ at a low temperature of 700 °C can be attributed to the advantage of the citrate method.

The citrate method is a simple way to obtain stable precursors and reactive and stoichiometric fine powders which has been widely used in the fabrication of various simple and complicated oxides [17]. Compared to the citrate method, the Pechini method is superior to obtain a homogeneous multicomponent gel without any phase

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segregation throughout the processing, which is beneficial to prepared stoichiometric oxides with a much lower temperature and smaller particle size. The difference between these two methods is the introduction of polyhydroxy alcohol, such as ethylene glycol, and the polymerization process between metal citrate and polyhydroxy alcohol. The polymerization results in immobilization of metal complexes in rigid organic polymer nets, thus ensuring the compositional homogeneity [18].

In this work, Low- β BiNbO₄ powders were prepared by citrate and Pechini methods using homemade water-soluble niobium precursors. The addition of ethylene glycol and the resultant polymerization effect on the synthesis and visible-light photocatalytic performance of Low- β BiNbO₄ powders were investigated, including the phase formation process, particle size, optical properties, and the photocatalytic degradation of methyl violet (MV) under visible light.

Methods

The precursor materials were bismuth nitrate (Bi(NO₃)₃·5H₂O), ammonia, ethylene glycol (EG), and a Nb-citrate (Nb-CA) aqueous solution. The synthesis of water-soluble Nb-CA has been described in detail in a previous work [19]. Low- β BiNbO₄ powders were prepared by citrate and Pechini methods. Bi(NO₃)₃·5H₂O was first dissolved in Nb-CA. Then the solution was kept stirring at 60 °C, and ammonia was added to adjust the pH value to 7–8. Finally, a stable solution was obtained. The above is the citrate method process; for the Pechini method, another step is added: after the stable and transparent solution was obtained, EG was dropped as chelating agent and stirring at 80 °C to promote the polymerization between metal CA and EG. The two kinds of solutions were finally dried at 180 °C to evaporate the solvent and calcined at various temperatures from 500 to 900 °C for 3 h with a ramp rate of 3 °C min⁻¹.

The structure of the thermally treated powders was characterized by X-ray diffraction (XRD) with Cu K α radiation. The grain sizes of the powders were examined using transmission electron microscopy (TEM). The photocatalytic activity of the BiNbO₄ powders for the decomposition of MV was evaluated under irradiation of a 150-W Xe lamp at the natural pH value; the details have been described in the previous work, and the degradation process was monitored by an ultraviolet-visible near infrared (UV-vis-NIR) spectrophotometer [12].

Results and Discussion

Figure 1 gives the XRD patterns of BiNbO₄ powders prepared by citrate and Pechini methods. In Fig. 1a, it can easily be seen that there is no apparent β -BiNbO₄ peaks at 550 °C, only an intermediate phase of Bi₅Nb₃O₁₅ is

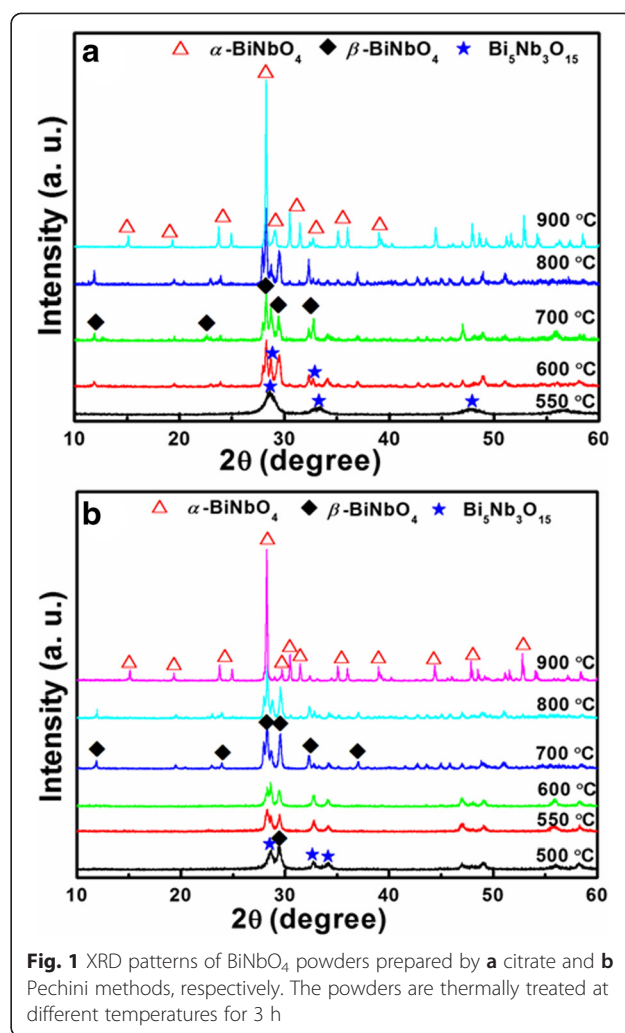


Fig. 1 XRD patterns of BiNbO₄ powders prepared by **a** citrate and **b** Pechini methods, respectively. The powders are thermally treated at different temperatures for 3 h

formed. With the temperature increase, Bi₅Nb₃O₁₅ transformed to β -BiNbO₄ gradually and pure Low- β BiNbO₄ is obtained at 700 °C. Due to the polymerization effect between CA and EG in the Pechini process, the appearance of Low- β BiNbO₄ seems much easier, as shown in Fig. 1b. Even at 500 °C, Low- β BiNbO₄ has been formed and coexisted with the Bi₅Nb₃O₁₅ phases. At 550 °C, quite different from that of the citrate method, Low- β BiNbO₄ is the major phase and pure Low- β BiNbO₄ is also obtained at 700 °C. Low- β BiNbO₄ is thermodynamically unstable and transforms to α phase at 900 °C, the same as in other literatures [15]. The differences of the phase formation process can be attributed to the polymerization effect between CA and EG. In the citrate process, the solution consists of Nb-CA and Bi-citrate (Bi-CA) metal complexes and is weakly interconnected by van der Waals or hydrogen bonding; while for the Pechini process, Nb-CA and Bi-CA were coordinated by the polymerization effect between CA and EG to form a homogeneous multicomponent gel, which is crucial for complex oxide preparation [18].

The polymerization is beneficial to obtain smaller particles, as seen in the TEM images of Low- β BiNbO₄ prepared by the two methods in Fig. 2. The particle size is between 70 and 100 nm for the Pechini method, smaller than that of the citrate method, about 150 nm, while the shape of Low- β BiNbO₄ powders seems irregular for both methods due to the uncompleted crystal evolution.

The room-temperature UV-vis absorption spectra of Low- β BiNbO₄ powders are recorded in Fig. 3. A pressed BaSO₄ powder was used as a reference, and the absorption spectra of the data were transformed from the diffuse reflection spectra according to the Kubelka-Munk (K-M) theory. Because Low- β BiNbO₄ is the indirect band gap

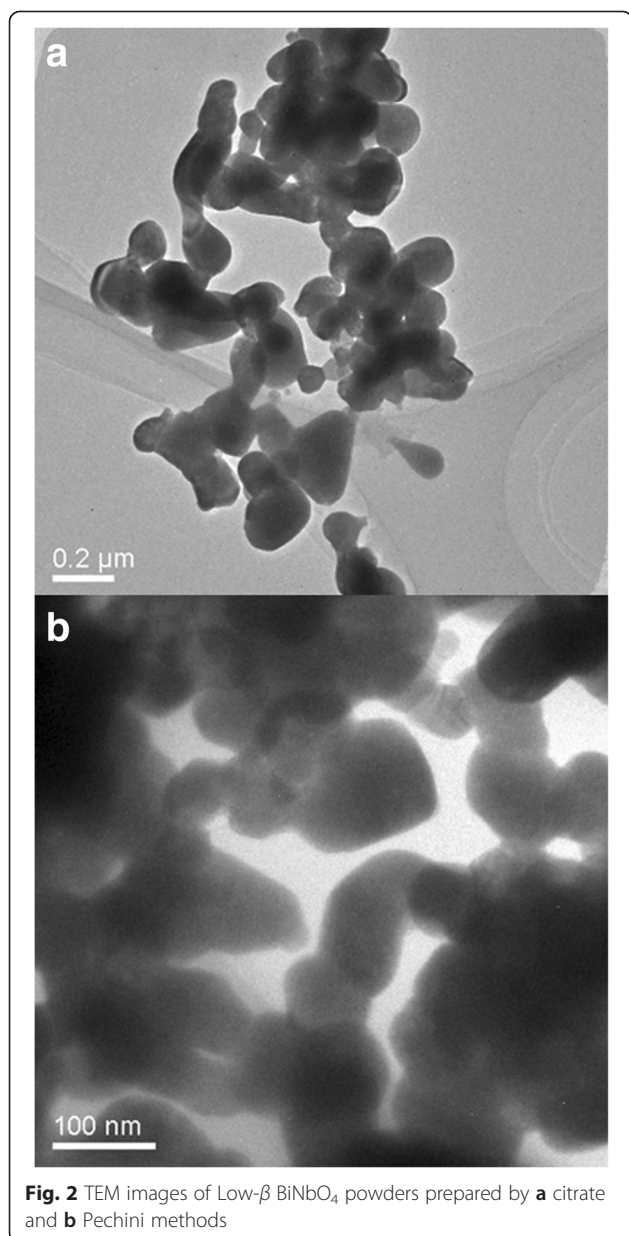


Fig. 2 TEM images of Low- β BiNbO₄ powders prepared by **a** citrate and **b** Pechini methods

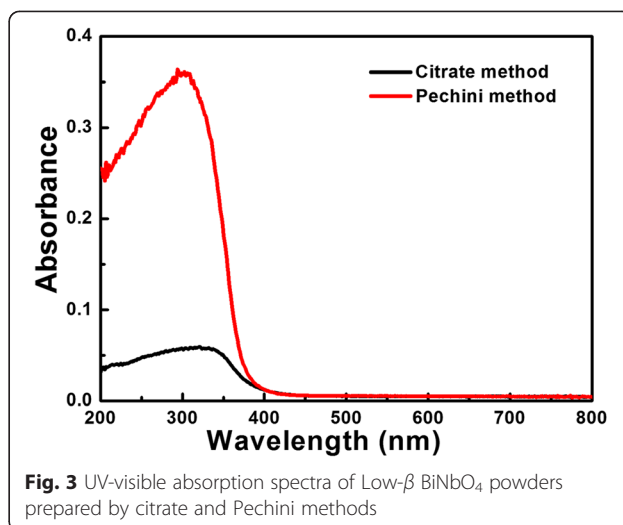


Fig. 3 UV-visible absorption spectra of Low- β BiNbO₄ powders prepared by citrate and Pechini methods

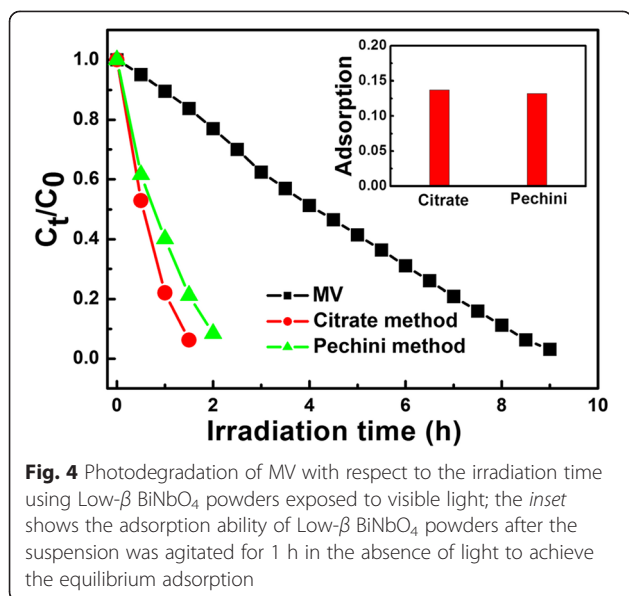
semiconductor, the relation between the absorption edge and photon energy ($h\nu$) can be written as follows:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (1)$$

where A is the absorption constant of the materials of indirect band gap semiconductor. The absorption coefficient (α) is determined from the scattering and reflectance spectra according the K-M theory. The energy band gaps (E_g) of the catalysts prepared by the citrate and Pechini methods are estimated to be 2.85 and 3.1 eV, respectively, based on Eq. (1). It seems that the former catalyst can absorb the visible light better. It is consistent with the appearance of the Low- β BiNbO₄ catalyst prepared by the citrate method, which is pale yellow, indicating that this material indeed absorbs the visible light to some extent, while the appearance of the sample prepared by the Pechini method is white. The larger band gap with Low- β BiNbO₄ powders prepared by the Pechini method can be attributed to their smaller grain size and insufficient growth of grain.

The visible-light photocatalytic activity of pure Low- β BiNbO₄ powders has been investigated under visible-light irradiation ($\lambda > 400$ nm), as shown in Fig. 4. MV is adopted as a representative organic dye to evaluate the photocatalytic performance. C_0 is the initial concentration of MV, and C_t is the equilibrium concentration of MV at visible-light irradiation time.

For BiNbO₄ particles, the mechanism of MV degradation under visible-light irradiation involves photocatalytic and photosensitization pathways, and the latter has a dominant role in the degradation [12]. Both catalysts exhibit excellent performance of visible-light degradation of MV, compared with the degradation of MV without a catalyst. The Low- β BiNbO₄ powder prepared by the citrate method shows a better degradation rate of about 1 h



to decompose 80 % of MV. The better photocatalytic performance can be attributed to its smaller band gap and better crystallinity than that of catalysts prepared by the Pechini method. Better crystallinity plays an important role in the degradation of MV, corresponding to the adsorption ability test of BiNbO₄ powders, as seen in the inset in Fig. 4. Though the catalysts prepared by the Pechini method are with a smaller particle size, the adsorption ability is equal to that of catalysts by citrate method.

In the heterogeneous photocatalytic studies, the photocatalytic degradation rate of the most organic compounds can be described by the modified Langmuir-Hinshelwood kinetics model [20, 21]. The photocatalytic degradation of MV using Low- β BiNbO₄ powders obeys the pseudo-first-order kinetics. The representation of the rates of photodegradation of MV is given by

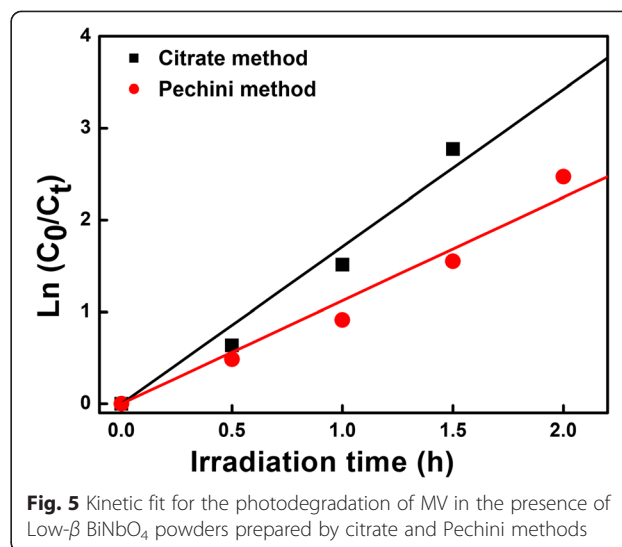
$$\ln C_t = -kt + \ln C_0 \quad (2)$$

This equation can be modified to demonstrate linearity of data, if the Eq. (2) is given by

$$\ln(C_0/C_t) = kt \quad (3)$$

where k is the constant of the pseudo-first-order rate.

A plot of $\ln(C_0/C_t)$ versus the visible irradiation time for the MV photodegradation catalyzed by Low- β BiNbO₄ powders is shown in Fig. 5. A linear relation between $\ln(C_0/C_t)$ and the irradiation time has been confirmed, which implies that the photodegradation of MV follows the first-order kinetics. The obtained first-order rate constant (k) and half-time ($t_{1/2}$) are $2.85 \times 10^{-2} \text{ min}^{-1}$ and 24.3 min and $1.87 \times 10^{-2} \text{ min}^{-1}$ and 37 min, respectively. The higher the first-order rate constant is, the more



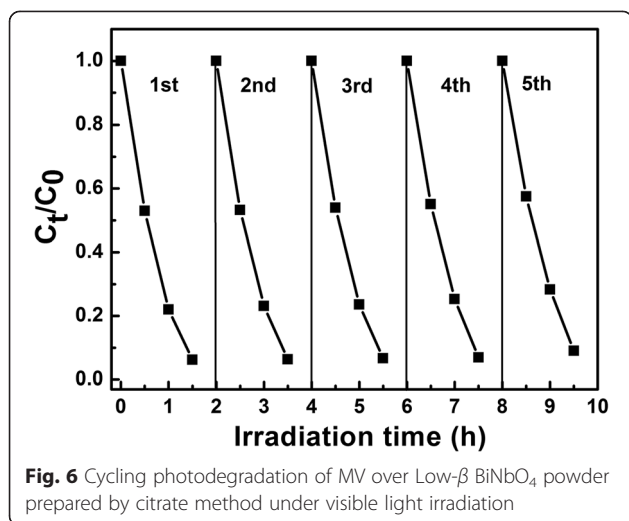
outstanding the photocatalytic performance is. So the degradation of MV using Low- β BiNbO₄ powders prepared by the citrate method shows higher k and smaller $t_{1/2}$.

The effect of operating parameters such as the amount of catalyst loading, pH value, and the additive H₂O₂ concentration on the photocatalytic performance of Low- β BiNbO₄ powders prepared by the citrate method has been investigated in our former work [12]. It shows that the optimal operation conditions are catalyst loading of 1 g L⁻¹, pH value of 8, and the additive H₂O₂ concentration of 2 mmol L⁻¹.

To evaluate the reusability and stability of the as-synthesized photocatalysts, five cycles of photodegradation of MV are conducted taking Low- β BiNbO₄ powder prepared by citrate method as typical samples. Figure 6 shows no obvious performance loss after five cycling runs of photodegradation of MV, which indicates that the Low- β BiNbO₄ photocatalyst is an efficient visible light-driven photocatalyst with good reusability for potential practical applications in wastewater treatment.

Conclusions

Low- β BiNbO₄ powders were prepared by citrate and Pechini methods using homemade water-soluble niobium precursors. The addition of ethylene glycol and the resultant polymerization effect on the synthesis and visible-light photocatalytic performance of Low- β BiNbO₄ powders were investigated. The polymerization effect is beneficial to lower the phase formation temperature and obtain smaller particle catalysts. Both methods can synthesize catalysts with excellent performance of visible-light degradation of MV. The Low- β BiNbO₄ powder prepared by the citrate method shows a better degradation rate of about 1 h to decompose 80 % of MV and also displays good photocatalytic stability. The photodegradation of MV under the visible-light irradiation followed the



pseudo-first-order kinetics according to the Langmuir-Hinshelwood model, and the obtained first-order rate constant and half-time are $2.85 \times 10^{-2} \text{ min}^{-1}$ and 24.3 min, respectively. The better photocatalytic performance of BiNbO₄ powders prepared by the citrate method can be attributed to its smaller band gap and better crystallinity.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

HZ carried the main part of the experimental work and XRD measurements and photocatalytic activity test. JK carried TEM image measurements. AW, HL, and TZ participated in the preparation of water-soluble Nb-CA precursors. AL and DW participated in the design of the study and helped to draft the manuscript. All authors read and approved the final manuscript.

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