



## Research paper

# A silver fluoniobate semiconductor with high photo-oxidation abilities and photocatalytic activities



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## ABSTRACT

In the past years, nano-sized Nb<sub>2</sub>O<sub>5</sub> has been widely as a potential photocatalyst due to its good chemical stability and higher conduction band edge than TiO<sub>2</sub>. However, the photocatalytic application of Nb<sub>2</sub>O<sub>5</sub> is limited by wide band gap (3.4–4 eV) because only UV light could be harvested. In this work, Nb<sub>2</sub>O<sub>5</sub>-based photocatalyst, AgNb<sub>2</sub>O<sub>5</sub>F, was developed by solid-state reaction. The phase formation and surface characteristics were investigated. AgNb<sub>2</sub>O<sub>5</sub>F has a direct allowed transition with band energy of 2.68 eV. It has a highly positive valence band. The photocatalysis degradation of MB solutions by Nb<sub>2</sub>O<sub>5</sub> is less than 10% after the light irradiation ( $\lambda > 420$  nm) in 120 min. AgNb<sub>2</sub>O<sub>5</sub>F shows a rapid degradation, which is 83% under the same conditions. AgNb<sub>2</sub>O<sub>5</sub>F presents more efficient degradation of organic dyes than Nb<sub>2</sub>O<sub>5</sub>. This semiconductor also keeps stabilities for photo-corrosions and photo-degradation reactions. The photocatalytic activities were discussed on the luminescence and decay lifetimes.

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## 1. Introduction

Over the past century, photocatalysis has been widely reported in the promising applications of environmental protecting and water splitting [1–3]. Some oxide semiconductors (e.g. TiO<sub>2</sub>, ZnO, and Nb<sub>2</sub>O<sub>5</sub> etc) have been paid great attention for the preparation and photocatalytic properties [4–6]. However, two main drawbacks delay the practical photocatalysis application for the oxide semiconductors. One is the wide band gap which limits its photo-response to only the ultraviolet wavelength region [7] and another is the high electron–hole pair recombination rate in these [8]. Thus, great efforts have been contributed to extend the optical absorption to longer wavelengths [9,10]. Certainly TiO<sub>2</sub> is the most popular candidate under the investigation as a potential photocatalyst.

Among various oxide semiconductors, Nb<sub>2</sub>O<sub>5</sub> has good acid character [11], which has been widely reported in many applications such as selective hydrogen (H<sub>2</sub>) gas sensor [12], ultra-stable Li storage [13], anode materials for lithium ion batteries [14,15]. As a candidate for photocatalyst [16–19], Nb<sub>2</sub>O<sub>5</sub> possesses wide attentions due to its good chemical stability and a higher conduction band (CB) position than TiO<sub>2</sub> [20]. Compared with

TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> presents much delayed charge recombination together with the improved lifetimes of light-induced electrons [21]. This is extremely beneficial for its photocatalysis. However, the bigger energy (3.4–4 eV) of Nb<sub>2</sub>O<sub>5</sub> strictly limits its practical application [22].

Efforts have been made to improve photocatalysis of Nb<sub>2</sub>O<sub>5</sub> by introducing metal and non-metal dopants [21]. Incorporation of F<sup>-</sup> ions has been regarded to be one of effective methods. F-doping can induce rich defects, which attract migration of light-generated charges from bulk to the surface joining in photocatalysis [23]. However, it is well-known that F<sup>-</sup> ions in an oxide cannot contribute to neither valence band (VB) nor CB due to its biggest electronegativity (=10.41 eV) [24]. On the contrary F<sup>-</sup> ions obviously widen band gap and increase band energy [25]. The harvest efficiency for the visible light is still poor.

The purposes of this work are to investigate the photochemical abilities of silver fluoniobate AgNb<sub>2</sub>O<sub>5</sub>F. The first motivation is that F<sup>-</sup> ions in lattices make covalence strength more rigid. The second consideration is based on the well-known fact: band gap of a semiconductor could be greatly narrowed by the incorporation of Ag-ions in the lattices via hybridization of Ag-4d + O-2p in valence band [26]. In fact, silver niobium photocatalysts have been intensively reported on this reason [27,28]. AgNb<sub>2</sub>O<sub>5</sub>F was synthesized by developed by solid-state reaction. The phase formation, optical absorption, band structure and photo-degradation effects on methylene blue (MB) were reported.

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## 2. Experimental

AgNb<sub>2</sub>O<sub>5</sub>F was synthesized through solid-state reaction. The raw reactants are AgF (99.99%) and Nb<sub>2</sub>O<sub>5</sub> (99.9%). In a typical example, 1.269 g AgF and 2.658 g Nb<sub>2</sub>O<sub>5</sub> were firstly mixed in an agate mortar with acetone, and then the mixtures were heated at 600 °C for 2 h using an electric furnace in air atmosphere. Secondly, the mixtures were thoroughly ground and then heated in a covered crucible at 800 °C for 2 h. Thirdly the obtained powders were finely ground, which were calcined at 900 °C for 2 h to get the final AgNb<sub>2</sub>O<sub>5</sub>F products. The single phase formation was confirmed via XRD measurements.

The optical absorption spectra were taken by UV–Vis–NIR spectrophotometer (Cary-5000). The photocatalytic tests were finished by MB degradation of MB solutions (100 mL, 10 mg L<sup>-1</sup>) with light wavelength  $\lambda > 420$  nm. The reactions were finished in a quartz reactor. For a reaction, 0.1 g powders were added in MB solutions. After equilibrium between desorption and adsorption in dark, the photocatalytic experiment was initiated. 3 mL solutions were taken from the reactor after the fixed time period, which were cen-

trifuged to filter the photocatalyst. Then optical absorption of the solutions containing MB was measured to evaluate the photocatalytic effects.

## 3. Result and discussion

The phase formation was confirmed via XRD measurements as displayed in Fig. 1. The diffraction peaks are in good agreement with the standard card (PDF#32-1017) selected from the database. The sample has a pure crystal phase formation without the any remaining Nb<sub>2</sub>O<sub>5</sub> or AgF.

Fig. 2(a) and (b) shows the SEM images of AgNb<sub>2</sub>O<sub>5</sub>F photocatalyst. It presents the well-developed grains with an average size of 1.65  $\mu$ m. TEM and HRTEM image in Fig. 2(c) confirm the single-crystalline property of the particles. The interplanar distance presented on the lattice fringe is about 0.38 nm, which is corresponding to the (3 2 0) preferable growth plane. The elements in the particles were detected via EDS measurements (Fig. 2(d)). The experimental molar ratio of Ag/Nb agrees with the stoichiometric formula.

UV–vis absorption of AgNb<sub>2</sub>O<sub>5</sub>F is displayed in Fig. 3(a), which exhibits a strong absorption below 460 nm. The steep edge indicates that the absorption is due to the intrinsic band transitions. The absorption confirms that AgNb<sub>2</sub>O<sub>5</sub>F can efficiently absorb UV–visible light. The band energy ( $E_g$ ) can be expressed by the formula  $\alpha hv \propto (hv - E_g)^k$ , where  $\alpha$  is optical absorbance,  $\nu$  is incident frequency,  $k$  is a constant deciding the transition nature.  $E_g$  value of 2.68 eV was obtained at  $k = 2$  by extrapolating the tangent to the X axis. AgNb<sub>2</sub>O<sub>5</sub>F has direct transition with band energy higher than the well-known photocatalysts such as TiO<sub>2</sub> (3.2 eV) [29], ZnO (3.37 eV) [30], Nb<sub>2</sub>O<sub>5</sub> (3.4–4 eV) [22].

Optical absorption of niobates is from electron transitions from O<sup>2-</sup> ligands to Nb<sup>5+</sup> in NbO<sub>6</sub>. The band gap absorption in Nb<sub>2</sub>O<sub>5</sub> follows this discipline. The narrowed band energy in AgNb<sub>2</sub>O<sub>5</sub>F should be ascribed to the introductions of Ag<sup>+</sup> and F<sup>-</sup> ions in the lattices. It is well-known that incorporation of F ions in an oxide cannot contribute to neither the VB nor CB due to its biggest electronegativity (=10.41 eV) [24]. On the contrary F-ions obviously widen band gap and increase band energy of an inorganic

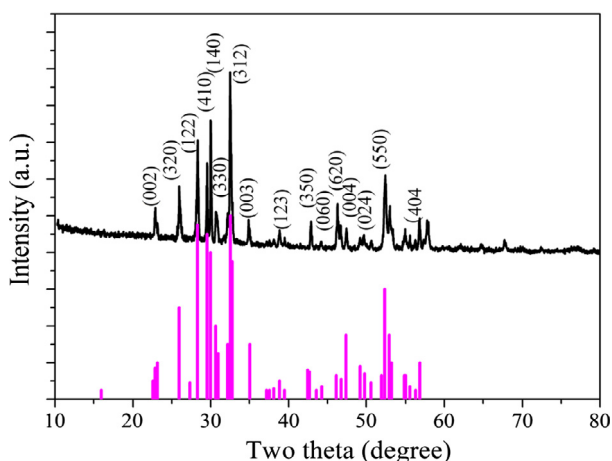


Fig. 1. XRD pattern of AgNb<sub>2</sub>O<sub>5</sub>F photocatalyst with standard card.

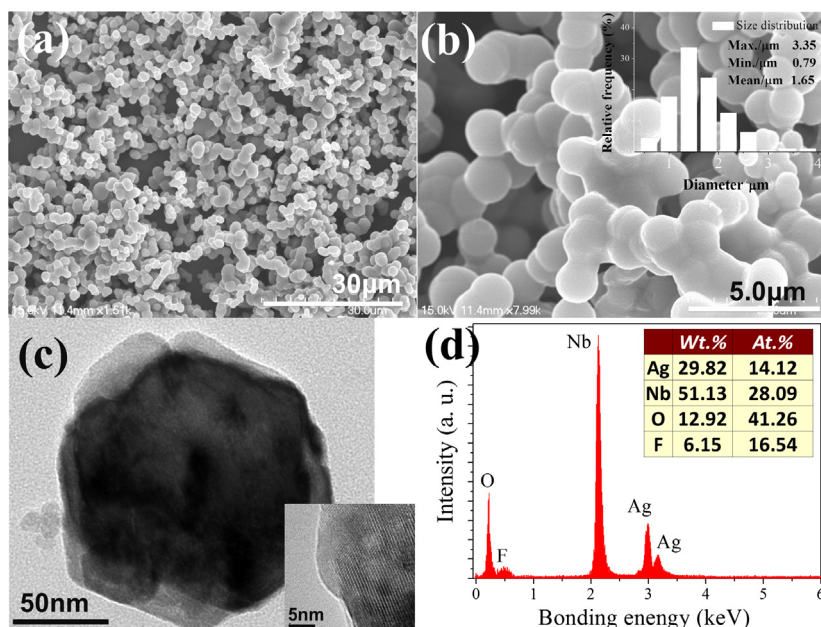


Fig. 2. SEM (a, b), TEM (c), and EDS (d) of AgNb<sub>2</sub>O<sub>5</sub>F. Inset in (b) and (c) are size distribution and HRTEM image, respectively.

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