Structural characterization and photocatalytic activity of NiO/AgNbO₃

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NiO/AgNbO₃ composites are prepared by wetness impregnation method. The physical and chemical properties of catalysts are characterized by XRD, XPS, SEM-EDS and DRS techniques. The photocatalytic performance of the samples is evaluated by photocatalytic oxidation of methylene blue dye under UV light irradiation. The results of XRD indicate that perovskite-type AgNbO₃ has a good crystal phase at different calcination temperatures and different NiO contents loaded. The XRD, XPS and SEM-EDS data indicate that NiO particles are presented on the surface of the pure AgNbO₃. The DRS analysis shows that the NiO formed on AgNbO₃ surface promotes the optical absorption in the visible region and makes it possible to enhance the photocatalytic activity. The result reveals that the degradation efficiency of methylene blue (MB) over NiO/AgNbO₃ is higher than that of pure AgNbO₃ under UV light and visible light irradiation, respectively. The highest photocatalytic degradation efficiency is observed when the sample calcined at 300 °C with 3 wt% Ni content under UV light irradiation with 3 h.

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1. Introduction

Semiconductor photocatalysis has attracted a great deal of attention as a useful technique of water splitting and decontamination treatment in polluted water. Recently, AgNbO₃ with a perovskite structure has been found to show photocatalytic activities for O₂ evolution from an aqueous silver nitrate solution [1,2]. However, its photocatalytic activity for decomposition of organic pollutants is not high. Therefore, it is necessary to enhance the photocatalytic activity of AgNbO₃. Metal ions or metal oxides are usually used as cocatalysts to promote the photocatalytic activity. Li et al. [3] show that the Cu doping on the surface of polyhedron-shaped AgNbO₃ photocatalysts can significantly enhance the visible light photocatalytic activity. Li et al. [4] also synthesize La-doped AgNbO₃ samples, and their photocatalytic activities are evaluated from gaseous 2-propanol decomposition under visible light irradiation. It is found that the La modified sample displays the highest photocatalytic activity, and it is more than 12-fold higher than that of AgNbO₃ [4]. Yang et al. [5] indicate that compared to the pure K₂La₃Ti₃O₁₀, V-doped K₂La₃Ti₃O₁₀ exhibits higher photocatalytic activity of hydrogen production. Liu et al. [6] prepare the ZnO/titanate nanocomposites, and the literature indicates that the nanocomposites are found to show a surprisingly high photocatalytic activity under visible light irradiation. The V₂O₅/BiVO₄ composite photocatalysts also exhibits the enhanced photocatalytic properties for degradation of methylene blue [7].

The enhancement in photocatalytic activity of semiconductor photocatalysts by loading NiO as cocatalyst has also been reported in many literatures. Partially oxidized NiO₃ cocatalysts, such as NiO₃/SrTiO₃ [8], NiO₃/K₂NbO₃O₁₇ [9], NiO₃/InNbO₃TaO₃ [10] and NiO₃/InTaO₃ [11], have been reported to be effective cocatalysts for water splitting. In these cases, the added Ni ions exist as the form of partially oxidized NiO₃. In addition, literature has reported that the photocatalytic activity of semiconductor photocatalysts can be improved by surface NiO modification. Chen et al. [12] report that the photocatalytic activity of the p–n junction NiO/TiO₂ is much higher than that of TiO₂ in reduction of Cr₂O₇²−. Hu et al. [13] indicate that monoclinic structure SrBi₂O₄ demonstrates a certain degree of photocatalytic activity and its photocatalytic activity is greatly enhanced when loaded with NiO by the impregnation method. It is attributed to the presence of NiO promoting the electron–hole separation and interfacial charge transfer. Kato and Kudo [14] also report that lanthanum doped NaTaO₃ with NiO cocatalyst shows high efficiency for water splitting. Hu and Hu [15] indicate that the activity of the Ag₅VO₄ is increased by 3.8 times after loading NiO. The result is due to the formation of a short-circuited microphotelelectrochemical cell on the surface of NiO/Ag₅VO₄. In the above cases, it is proposed that oxide nickel facilitates the photoexcited electrons transfer and hence suppresses recombinant of photogenerated electron and hole. On the basis of the above results, it is inferred that the introduction of NiO can really enhance the photocatalytic activity of semiconductor photocatalysts.

However, few reports are published on AgNbO₃ powder loaded with NiO for photocatalytic degradation of organic dyes pollu-
tants so far. In this work, NiO/AgNbO₃ composites are synthesized by wetness impregnation method. The relationship between the optical, structure features, surface properties and photocatalytic activities are elucidated. The effect of NiO on the enhanced photocatalytic activity of the pure AgNbO₃ is also investigated.

2. Experimental

2.1. Synthesis of NiO/AgNbO₃ photocatalysts

AgNbO₃ powders were prepared by conventional solid-state reactions. Starting materials AgNO₃ and Nb₂O₅ were mixed in a stoichiometric ratio. The mixtures were calcined at 880 °C for 5 h. A suitable amount of Ni(NO₃)₂·6H₂O solution was added to the synthesized AgNbO₃ to form suspension solution of Ni–AgNbO₃. The suspension was stirred by using a glass rod during evaporation of water on a water bath. The dried powders were calcined at 300 °C for 4 h. Then the NiO/AgNbO₃ photocatalyst was obtained.

2.2. Photocatalysts characterization

The crystalline phases of the prepared catalysts were analyzed by X-ray diffraction (XRD) by Bruker D8 diffractometer with CuKα radiation (λ = 1.54 Å) in the range of 2θ = 10–80°. The XPS measurement was performed on the ESCALab MKII spectrometer using Mg Kα radiation. The surface morphology and particle size of the samples were performed on a field emission scanning electron microscope (S-4800IIFESEM, Hīatchi, Japan). The elemental analysis of the photocatalysts was detected by an energy dispersive X-ray spectrometer (EDS) attached to the SEM. The diffuse reflectance spectra (DRS) were performed on a UV-2450 (Shimadzu) instrument in the range of 240 nm to 800 nm. BaSO₄ was used as the reflectance standard material.

2.3. Photocatalytic activity

The photocatalytic activities of NiO/AgNbO₃ composites were evaluated by decolorization of methylene blue (MB). Experiments were carried out in Pyrex photocatalytic reactor with two 125 W mercury lamps as UV source. 100 mg of NiO/AgNbO₃ was added to a 100 mL solution containing the MB dye (10 mg/L) solution. Prior to UV illumination, the suspension was strongly magnetically stirred for 30 min in the dark for adsorption/desorption equilibrium, and the adsorption efficiency of MB on the composites were calculated. At specific time intervals about 5 mL of the suspension were taken from the Pyrex reaction glass and analyzed after centrifugation.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of all synthesized photocatalysts are shown in Fig. 1. It is found that the positions of all diffraction peaks are assigned to AgNbO₃ with standard structure (JCPDS files: 52-0405). No diffraction peaks of Ni or NiO appears in the XRD patterns, which is attributed to the quantity of the small NiO particles that have deposited on the surface below the detection limit of XRD analysis.

As shown in Fig. 1B, the XRD patterns demonstrate that all the catalysts calcined at various temperatures are present in AgNbO₃ standard structure. It can be seen that when the calcination temperature is 200 °C, the peaks of Ni(NO₃)₂ are detected. Further increasing in the calcination temperature results in transformation from Ni(NO₃)₂ to NiO.

3.2. XPS study

Fig. 2 shows the XPS spectra of the Ag, Nb, Ni and O peak regions in the NiO/AgNbO₃ powder. Any contamination, besides carbon, is not found in XPS analysis. High resolution spectra of the Ag 3d, Nb 3d and O 1s are shown in Fig. 3A–C. It can be seen that the Ag 3d and Nb 3d spectra consist of two peaks corresponding to their angular momentum of electrons. It can be noted that the O 1s spectrum exhibits two different chemical states, which associates with the oxygen in AgNbO₃ and the oxygen in NiO, respectively. The binding energy peaks of NiO/AgNbO₃ (Fig. 3D) at 854.8 and 873.6 eV correspond to NiO 2p3/2 and 2p1/2, respectively. The result is in agreement with the reports of Allegretti et al. [17]. Therefore, it is indicated that the doped Ni should be present in the form of NiO. The oxidation state of nickel is +2.

![Fig. 1. X-ray diffraction pattern of NiO/AgNbO₃: (A) with different contents of Ni loading and (B) with different calcination temperatures.](image)

![Fig. 2. XPS spectra of NiO/AgNbO₃.](image)
3.3. Scanning electron microscopy and EDS analysis

Fig. 4 shows the FE-SEM micrographs of neat AgNbO$_3$ and NiO/AgNbO$_3$. It can be seen that the size distribution of the neat AgNbO$_3$ varies in the range of 0.5–2.5 μm (Fig. 4B). When doping with metal oxides (NiO), the size and surface roughness of the samples are changed. It is found that the surface of NiO/AgNbO$_3$ is rougher than the neat AgNbO$_3$. The EDS analysis shows that Ni element is detected on the surface of the sample. The EDS spectra of NiO/AgNbO$_3$ (NiO content: 3 wt%) are shown in Fig. 5.

3.4. DRS

Fig. 6 shows diffuse reflectance spectra of AgNbO$_3$ and NiO/AgNbO$_3$ composites. Pure AgNbO$_3$ shows absorption band from UV to 450 nm. Noticeable shifts of the absorbance shoulder from a wavelength below 400 nm to the visible light region are observed for the NiO/AgNbO$_3$ samples. Moreover, the absorbance increases with the weight percentage of Ni content. The DRS of NiO/AgNbO$_3$ (3 wt%) samples calcined at different temperatures are shown in Fig. 6B. It is also worth to note that the NiO/AgNbO$_3$
calcined below 300 °C or higher than 300 °C affects the optical absorption in the region of 450–800 nm.

By plotting \((Ahv)^2\) versus \(hv\) [18], in which \(A\) and \(hv\) is the absorption coefficient and photons’ energy, respectively. The band gap energies of pure AgNbO3 and NiO/AgNbO3 with different Ni content are calculated to be 2.86, 2.84, 2.76, 2.73, 2.60, 2.76 and 2.77 eV, respectively, as shown in Fig. 6C. This result indicates that NiO doping can narrow the band gap of catalysts, which may be beneficial for improving the photocatalytic activity of the catalysts.

3.5. Photocatalytic activities of the samples

Photocatalytic activities of the samples with different NiO content are shown in Fig. 7. It can be seen that the presence of NiO leads to obvious increase in catalytic activity. The blank test confirms that MB cannot be degraded in the dark and only be slightly degraded under UV light irradiation without photocatalysts, indicating that the photolysis and adsorption of catalysts can be ignored. The optimum Ni content is found to be 3 wt%. The higher activity of NiO/AgNbO3 can be attributed to its narrower band gap, which can enhance the light harvesting. However, more Ni contents can be detrimental to the photocatalytic degradation efficiency. It
may be explained that at higher Ni content (>3 wt%), the excess NiO covering the surface of AgNbO3 can increase the number of recombination centers, thus decrease photocatalytic activity. The order of photocatalytic activity of NiO-loaded AgNbO3 samples is as following: 3 wt% > 2 wt% > 1 wt% > 0.5 wt% > 4 wt% > 5 wt% > 0. The relationship between the photocatalytic activity of NiO/AgNbO3 composites and calcination temperature are shown in Fig. 8. It is indicated that the photocatalytic degradation efficiency decreases as the calcination temperature exceed 300 °C. With increase the calcination temperature, the Ni(NO3)2 decomposes into nickel oxides, and the crystallinity of NiO increase with increasing temperatures [19]. Long et al. [20] indicate that highly crystallized structure always favors migration of electron–hole pairs as compared to the amorphous structure, so as to high photocatalytic activity. However, at higher calcination temperatures, the NiO would agglomerate into large bulk. The large particles with low activity species would be decrease photocatalytic activities. Based on the above results, one can conclude that the 3 wt% NiO/AgNbO3 calcined at 300 °C exhibits the highest activity under UV illumination. It is also found that the present of NiO can enhance the photocatalytic activity under visible light irradiation.

Fig. 9 presents the temporal evolution of the spectral changes during the photodegradation of MB over pure AgNbO3 and NiO/AgNbO3. It can be seen that the NiO/AgNbO3 catalyst only accelerates the photocatalytic degradation rate. No obvious shift of absorbance at 664 nm is observed during the photocatalytic process as selectively shown in Fig. 9A and B. Therefore, it can be concluded that the degradation pathway of MB in our system do not change after NiO loading.

4. Conclusions

In summary, the experimental results indicate that 3 wt% NiO/AgNbO3 calcined at 300 °C exhibits the highest activity under UV illumination. At 3 wt% Ni doping content, the degradation efficiency of MB can reach 85%. The XRD, XPS and SEM-EDS data indicate that NiO particles loaded on the surface of pure AgNbO3. The DRS analysis showed that the formed NiO on the AgNbO3 surface promotes the optical absorption in the visible region and makes it possible to enhance the photocatalytic activity.

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