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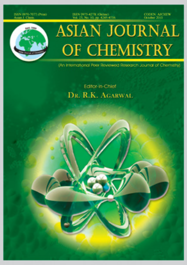

Effect of Bismuth Precursor and Temperature on Properties of Bismuth Vanadate Photocatalyst

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Bismuth vanadate ($BiVO_4$) photocatalysts were synthesized *via* solution combustion method using two different bismuth precursors (bismuth nitrate and bismuth acetate), ammonium metavanadate and citric acid as a reducing agent/fuel. The $BiVO_4$ samples formed were spherical but highly agglomerated with monoclinic scheelite structure. Photocatalytic activities of synthesized $BiVO_4$ were evaluated by photodegrading methylene blue dye under visible light irradiation. Although $BiVO_4$ synthesized prepared using bismuth nitrate and combusted at 600 ºC has the lowest surface area, it exhibited the highest photocatalytic activity due to its high monoclinic scheelite structure. It shows that the crystallinity of $BiVO_4$ is more important than surface area in photodegradation of methylene blue.

Key Words: Bismuth vanadate, Solution combustion, Photodegradation, Methylene blue.

INTRODUCTION

In recent years, water pollution has been pointed out as one of the greatest problem of modern society mainly due to intensive development of textile industry which involves high water consumption in manufacturing process and consequently leads to generating a large volume of toxic, non-biodegradable and potentially carcinogenic coloured dye effluents. Therefore, removal of these contaminants from dye effluents has become a major concern. Although various physical, biological or chemical methods have been applied on dye effluents, the use of advance oxidation process in particular photocatalysis has received a great attention in wastewater treatment technology due to its ability to utilize light to photodegrade organic contaminants to harmless products such as CO_2 and water. Lately, the idea of utilizing visible-light (which accounts almost 43 % of solar spectrum) has contributed to the development of visible-light driven photocatalyst. Bismuth vanadate ($BiVO_4$) has been reported to be as a promising visible-light driven photocatalyst. It was applied in the photooxidation of phenol and photoreduction of Cr(VI)[1] and in works on oxygen evolution from an aqueous silver nitrate solution under visible light irradiation[2]. To date, bismuth vanadate has been synthesized using various techniques such as solid-state reaction[3], hydrothermal process[4], sol gel[5] and chemical bath deposition[6] and solution combustion method[7]. In this study, bismuth vanadate was synthesized using solution combustion method because it is a facile and efficient method to produce homogeneous and fine crystalline powders[8]. The effect of bismuth precursor (nitrate and acetate) and temperature on the properties of synthesized bismuth vanadate and its photocatalytic activity will be evaluated by photodegrading methylene blue under visible light irradiation.

EXPERIMENTAL

Bismuth vanadate was synthesized by solution combustion method. Firstly, 8.0×10^{-3} mol bismuth nitrate (Acros) or bismuth acetate (Aldrich) and 1.7 g of citric acid (Fischer scientific) were dissolved in 10 mL of 3.0 M nitric acid (Fischer scientific). The pH of the resulting transparent solution was adjusted to 7.5 by using ammonia solution (Merck). Separately, 0.94 g of ammonia metavanadate (Sigma Aldrich) and 1.7 g of citric acid was dissolved in a 50 mL hot deionized water (70 ºC). Both solutions were then thoroughly mixed and heated at 65 ºC in the drying oven overnight. A transparent and uniform dark blue gel obtained was heated at 500 ºC and 600 ºC in box furnace (Carbolite, CWF 1200) for 3 h. The prepared samples are denoted as AX and NX where A and N represent acetate and nitrate precursor, respectively and X represent the combustion temperature.

Characterization: X-Ray diffraction (XRD) analysis was carried out using Shimadzu XRD-6000 diffractometer to determine the phase composition of sample. The microstructure of the samples was recorded using scanning electron microscope

(JEOL JSM-6400) and transmission electron microscope (Hitachi H-7100). Specific surface area of the samples was measured by N_2 gas adsorption at -196 ºC using quantachrome AS1win-automated gas sorption data instrument. The diffusion reflectance spectra of the prepared samples were recorded on a UV-VIS spectrophotometer (Perkin Elmer Lambda 35) for band gap determination.

Photocatalytic activity: The evaluation of phototcatalytic activity of the synthesized photocatalysts was as reported by Abdullah *et al.*[9]. In this work, 0.2 g of the catalyst was suspended in 1 L, 10 ppm methylene blue solution and was allowed to reach adsorption-desorption equilibrium in dark condition within 1 h.

RESULTS AND DISCUSSION

X-ray diffraction analysis: X-ray diffraction pattern of prepared $BiVO_4$ samples (Fig. 1) can be indexed to monoclinic $BiVO_4$ (JCPDS No. 01-075-2480. The peaks observed at 2θ = 18.5º, 35º and 46º for sample A500 and A600 are not well splitted indicating that the monoclinic structure of the acetate-based $BiVO_4$ less distorted compare to nitrate-based $BiVO_4$[10]. However, a better splitting of diffraction peak at 18.5º for sample A600 indicates that a more distorted structure can be formed at higher combustion temperature.

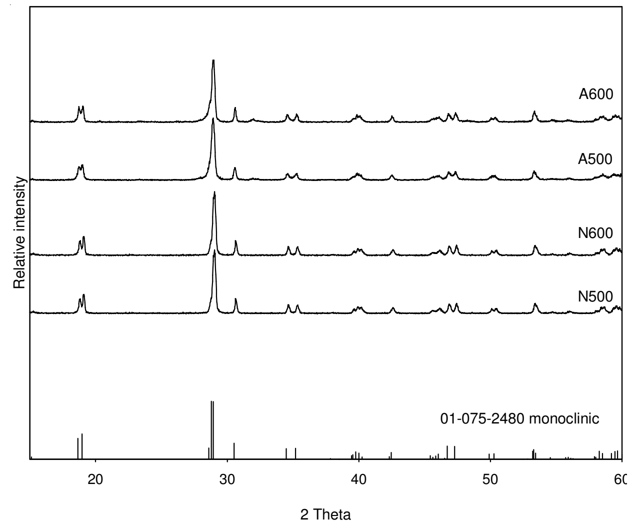

Fig. 1. XRD patterns of bismuth vanadate synthesized using different bismuth precursor combusted at 500 ºC and 600 ºC

Microstructure: SEM and TEM images of all the samples showed agglomerated spherical-shape particles (Fig. 2). Smaller and more regular particles in relatively large aggregates were observed for acetate-based $BiVO_4$ compared to that of nitrate-based $BiVO_4$ under same combustion temperature. Particle size of the samples is listed in Table-1. In solution combustion process, the citric acid metal-chelate complexes formed at pH 7.5 undergo polymerization to produce semi-rigid gelatine by encircling stable metal-chelate complexes in a growing polymer net during solvent evaporation step[11]. With increasing temperature, the long polymer chain break down to short polymer chains, which then twist and tangle together to form spherical aggregated polymer particles and subsequently form the spherical aggregated $BiVO_4$ crystallites after the polymer chains has completely oxidized[12]. The slight increase in relative high combustion temperature contributes to the growth of crystallites. The BET surface area (Table-1) also corresponds to the particle size of the prepared $BiVO_4$ with A500 exhibited the highest surface area due to its smallest particle size.

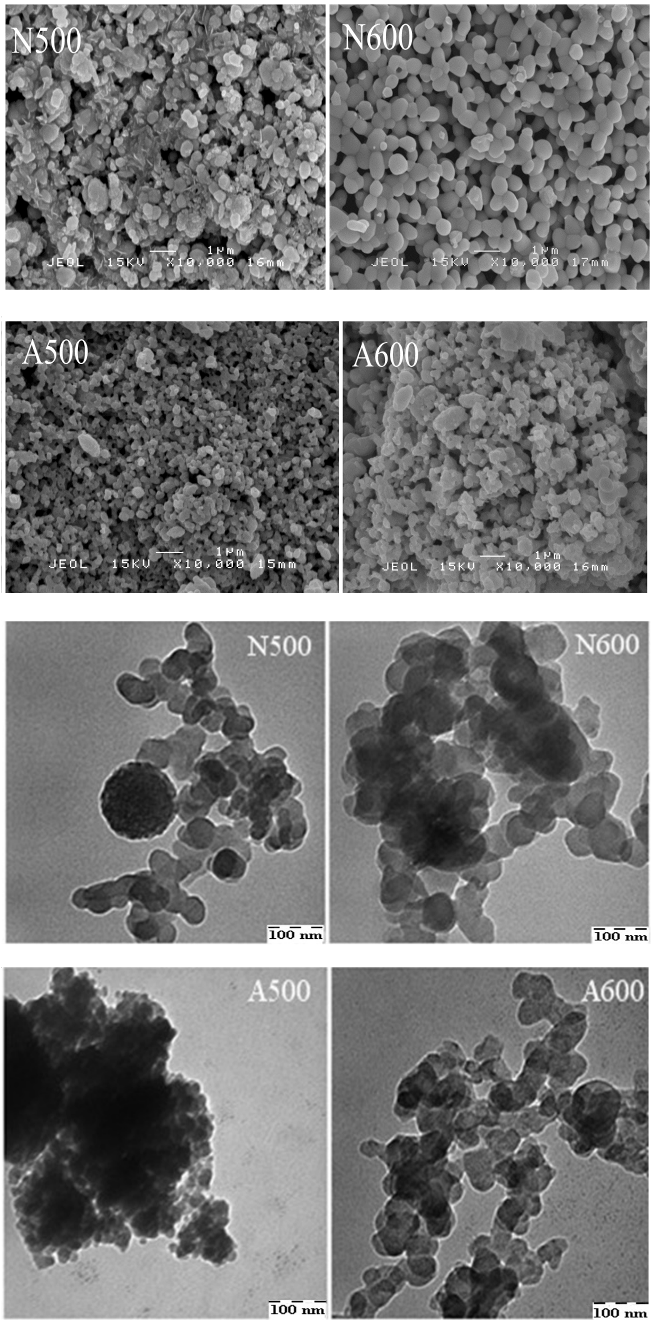

Fig. 2. SEM and TEM micrographs of prepared bismuth vanadate

TABLE-1
PHYSICAL PROPERTIES OF THE SYNTHESIZED $BiVO_4$

Sample	Particle size (nm)	BET surface area (m^2g^{-1})	Band gap energy (eV)
N500	19-57	1.76	2.40
N600	28-86	0.77	2.32
A500	10-30	3.04	2.41
A600	22-62	1.62	2.37

Optical absorption: Optical absorption property is the main factor in determining the photocatalytic activity of a semiconductor. The UV-VIS diffuse reflectance spectra (UV-VIS DRS) of the synthesized $BiVO_4$ show strong absorption in the visible light region with slight difference in the absorption band edge (Fig. 3). The optical absorption band edge follows the formula $A h\nu = c(h\nu\text{-}Eg)^n$, where A is the absorption coefficient, hν is the energy of incident photons, c is constant (c = 1), Eg is the band gap of semiconductor, n is constant and is equal to 1/2 or 2 depending on whether transition is direct or indirect. Since bismuth vanadate is a direct transition semiconductor[13], the band gap energy can be obtained from the intercept of the tangent to the $(A h\nu)^2$ *versus* hν plot (inset of Fig. 3). The difference in the band gap energy, as shown in Table-1, can be associated with the particle size of the sample.

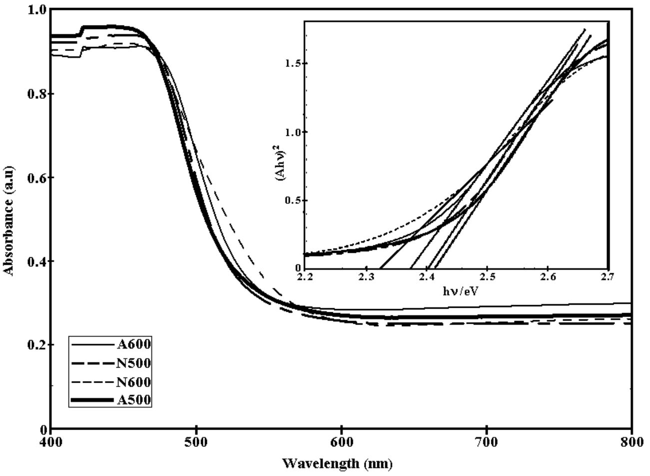

Fig. 3. UV-VIS diffuse reflectance spectra of prepared bismuth vanadate. Inset: Plot of $(A h\nu)^2$ *vs.* photon energy (hν)

Photocatalytic activity: The removal of methylene blue by different bismuth vanadate samples is shown in Fig. 4 and Table-2. In absence of bismuth vanadate, 11.5 % of the dye was photolyzed under 4 h of visible light irradiation. The removal was higher in the presence of bismuth vanadate and can be attributed to photocatalysis process. The photocatalytic degradation of methylene blue was found to follow pseudo first order kinetic (Fig. 5) and the rate constant are listed in Table-2. Although N600 has the lowest surface area, it exhibits the highest photocatalytic activity. This may be due to (i) it has the highest monoclinic scheelite structure and crystallinity, as evidenced by the well resolved XRD peak at 18.5° and 35° (ii) it absorbs slightly larger fraction of visible light (UV-VIS DRS) and (iii) it has the narrowest band gap energy. The narrow band gap suggests easier excitation of electron from valence band to conduction band in bismuth vanadate, which is necessary bring to high photocatalytic activity. By comparing the photocatalytic activities of A500 and A600, it can be deduced that the highly distorted monoclinic structure and crystallinity of bismuth vanadate play a more important role than the surface area in photodegradation of methylene blue.

Conclusion

Spherical monoclinic scheelite bismuth vanadate were successfully synthesized *via* solution combustion method using two different bismuth precursor. Although bismuth vanadate prepared using bismuth acetate possess better physical properties *i.e.* small particle size and high surface area, bismuth vanadate synthesized using bismuth nitrate exhibits better photocatalytic activity because it has higher monoclinic scheelite component and better crystallinity. Hence the crystallinity plays important role in the photodegradation of methylene blue.

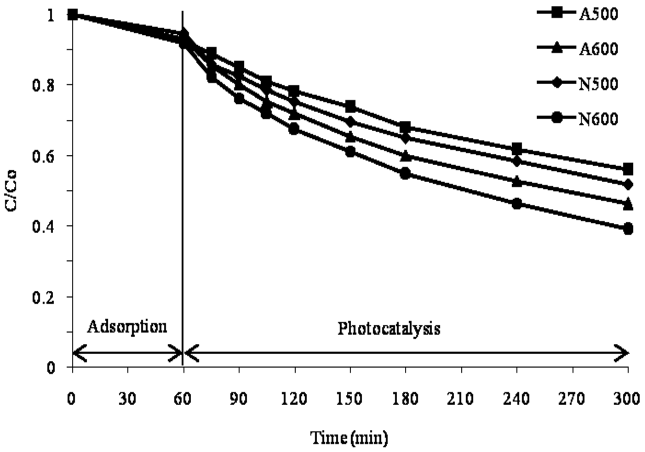

Fig. 4. Photocatalytic degradation of methylene blue under visible light irradiation over synthesized bismuth vanadate. Reaction conditions: catalyst = 0.2 g, methylene blue concentration = 10 ppm

TABLE-2
REMOVAL OF METHYLENE BLUE BY SYNTHESIZED BISMUTH VANADATE AND ITS CORRESPONDING RATE CONSTANT

Sample	Adsorption (%)	Photo-degradation (%)	Rate constant $k(10^{-3}\ min^{-1})$	R^2 value
N500	5.5	44.7	2.0	0.981
N600	8.2	57.6	3.0	0.985
A500	7.5	39.1	2.0	0.989
A600	6.9	50.5	2.0	0.980

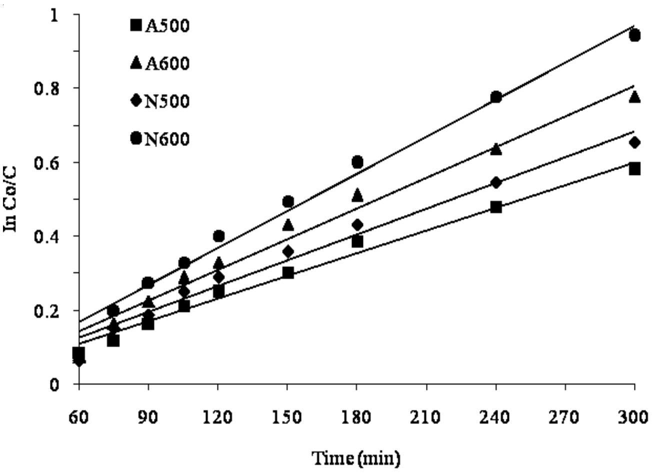

Fig. 5. Pseudo-first order kinetic graph of methylene blue degradation over the synthesized bismuth vanadate

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