



An efficient and novel way to synthesis of highly active BiVO₄ using homogenous precipitation

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Abstract: The improvement of the photocatalyst performance with reducing both equipment and cost of its production still the most important concern for finding, 1) Required material properties, 2) Possibility of manufactured mass production from the photocatalyst. Now, we reveal, a novel way for synthesis of BiVO₄ photocatalyst by homogenous precipitation. Different surfactants were adding to assist in the orientation. XRD, SEM, Raman, and DRS were used to evaluate construction of the as-synthesized BiVO₄ photocatalysts. The performance of photocatalytic efficiency of the as-synthesized catalysts were estimated by photoelectrochemical tests and photodegradation of Methylene blue (MB) dye as wastewater module.

Keywords: BiVO₄; Photocatalyst; MB photodegradation; Homogenous precipitation

1.Introduction:

Bismuth vanadate (BiVO₄) show interesting physicochemical properties including ferroelasticity, ionic conductivity, acousto-optical photocatalytic activity [1, 2]. So, it has been recently introduced into the gas sensors devices, posistors, solid-state electrolytes, lithium batteries and non-hazardous yellow pigment for high performance lead-free paints [3]. Also, it is an excellent material in the field of visible light driven photocatalysts [4–7]. BiVO₄ exists in three polymorphs, monoclinic scheelite, tetragonal zircon, and tetragonal scheelite. The monoclinic scheelite construction being the most reactive phase with its direct band gap of ~2.4-2.5 eV at ambient temperature [8, 9]. Nevertheless, the pure monoclinic BiVO₄ was still has low activity in the visible-light range [10], due to highly recombination, diminutive lifetime of photogenerated Electron-hole pairs, low electrical conductivity, slow hole transfer kinetics for water oxidation [11]. The activity

of BiVO₄ is powerfully associated to its crystallinity and morphology [9]. Numerous techniques have been described to synthesized BiVO₄ in both bulk and thin film. For example, solid-state reaction [12], aqueous solution method [13], co-precipitation [14], solvothermal [15], molten salt method [16], Microwave irradiation [17], and Metal organic decomposition [18], have been used to prepare BiVO₄ with different shapes. In the ordinary precipitation process, the metal oxide was produced during addition ammonia directly to metal cation solution. This technique gives a slightly controlled to the shape and size of precipitated particles due to the rapid rise of solution pH and concentration of the metal oxide [19]. There is another method called homogeneous precipitation. The important feature of this technique is the a greatly uniform precipitation which carried out by a rise in the pH of the reaction mixture and this homogeneity achieved by thermal decay of

urea. This occurred when urea has been dissolved into an acidic media of a metal source and heated to about 90°C, the urea decays gradually due to ejection of ammonia and carbonate ions into the acid media. These procedures produced a regular and uniform nucleation and uniformly particles of insoluble BiVO₄ samples [20]. The homogeneous precipitation process was used previously to synthesize TiO₂ [21], Al₂O₃ [22], MgAl₂O₄ [23], Fe₃O₄ [24], and Fe(OH)₂ [25]. In this study, we report homogeneous precipitation as novel assemble of monoclinic BiVO₄.

1. Experimental part

1.1. Materials

Bismuth (III) Nitrate pentahydrate Bi(NO₃)₃·5H₂O, Ammonium metavanadate NH₄VO₃ were used as source for Bi and V, respectively, Polyvinylpyrrolidone (PVP), Ethylene glycol (Eg), cetyltrimethylammonium bromide (CETAB), Sodium Dodecyl Benzene Sulphonate (SDBS) were used as orienting agent and Urea has been employed as precipitating agent. MB has been used as wastewater module to evaluate photocatalytic activity the existed photocatalysts. All compounds in our work were analytical grade reagents and they were obtained from Sinopharm Chemical Reagent Co., Ltd.

1.1. Homogenous Precipitation of BiVO₄

Firstly, Solution A: 0.24 mol/L (Bi(NO₃)₃·5H₂O) in 100 ml of 2M nitric acid (HNO₃) and solution B: 0.24 mol/L (NH₄VO₃) in 100 ml of 2M nitric acid (HNO₃) were prepared. After completely dissolving of the precursor and mixed solution A and B together with stirring for 30 min, yellow solution was obtained. Then surfactants were used as orienting agent. After each surfactant dissolved the mixture transfer to the round flask with 0.3M of urea to complete the precipitation and neutralized the reaction mixture.

2.3. Characterization of the BiVO₄ photocatalysts.

X-ray diffraction (XRD) shapes were verified on a Bruker D8-advance x-ray diffractometer using Cu K α radiation $\lambda = 0.15478$ nm, 40kv, 30mA. All results were measured at a 2 θ range between 10° and 80. The morphologies and microstructures of as-

synthesized samples were observed with scanning electron microscopy (JSM-6390LV). The Raman pattern were measured by a microprobe Raman (Thermo scientific, DXR 532 laser) device, and the excitation wavelength was at 532 nm. The spectra of the produced samples were measured on a doubled-beam UV-vis spectrophotometer (JASCO V 750) equipped with an integrating sphere. The UV-vis spectra were performed in the diffuse reflectance mode (R) and tuned to the Kubelka-Munk function F(R) to isolated the amount of light absorption from scattering. Furthermore, the band gap of prepared samples were estimated from the curve of the modified Kubelka-Munk function (F(R)E²) against the absorbed light energy E, during to the subsequent equation [26].

$$F(R) E^2 = \left(\frac{(1-R)^2}{2R} \times h\nu \right)^2 \quad (1)$$

Spectrofluorophotometer, (RF-5301 PC, Japan, SHIMADZU, 400 W, 50/60 Hz) was used to measure the photoluminescence (PL) of the produced samples with 365nm as excitation wavelength.

2.3. Photocatalytic efficiency and photoelectrochemical performance

The investigation of photocatalytic activity was carried out by irradiation of the MB dye include BiVO₄ photocatalysts using XPA-7 type photochemical reactor (Xujiang Machine Factory, Nanjing, China) attached by a 800 W Xenon lamp with a 420 nm cut-off filter. The light intensity on each quartz tube equal 12.7 mW/cm. A water-cooling circulation system was established to preserve a constant reaction temperature. 0.04g of our photocatalysts was blended with 40 ml MB [1 g/L] solution in a quartz reactor. Before the photocatalytic degradation, the solution was incubated under stirring and far from the light at room temperature for 60 min to neglect the amount of adsorption dye. The MB absorbance after complete adsorption was recorded to be the original concentration (C₀). The degraded day calculated by withdrawn at regular samples at interval times (C_i) from the upper part of the photoreactor. 2 mL of the reaction solution were taking at interval time followed by filtration through nylon syringe filters. The remaining concentration of samples were

measured immediately after separation using a MAPADA spectrophotometer. The photocatalytic efficiency of produced samples for photodegradation of dye was calculated by equation no 2:

$$\% \text{ photocatalytic activity} = (1 - C_t) / C_0 \times 100 \quad (2)$$

The photoelectrochemical properties of as-prepared samples were estimated by an electrochemical workstation (CHI760E, Chenhua Instruments) with a typical three-electrode system. The samples coated on Fluorine-doped tin oxide (FTO) were used as working electrode, the other electrodes which used during measurement were Pt slice (2.0×2.0 cm) as counter electrode and saturated Ag/AgCl electrode were employed as reference electrode, separately. Typically, 40 mg of sample was sonicated into 1 mL of Triton X-100 mixing with 1 mL acetylacetone and 1ml Ethyl alcohol under to obtain slurry, followed by further spread onto FTO with Dimensions 1.0×1.0 cm. The prepared photoanodes were fixed at 200°C for 2 h. $0.5 \text{ M Na}_2\text{SO}_4$ and $0.1 \text{ M Na}_2\text{SO}_3$ mixture solutions were exploit as the electrolyte media. The 500 W Xenon lamp with a 420 nm cut-off filter was used for visible light source.

3.Result and dissection

3.1. Crystal structure

Figure 1, displays the XRD results of BiVO_4 surfactant free, BiVO_4 with SDBS, BiVO_4 with CETAB, BiVO_4 with Ethylene glycol and BiVO_4 growth with PVP. The XRD results of produced samples exhibit a diffraction peaks defined as monoclinic BiVO_4 (JCPDS card No. 14-0688). Excepting, SDBS- assisted BiVO_4 shows diffraction peak indexed as mixed phase from monoclinic and tetragonal phase (JCPDS card No. 14-0133), it didn't detect any unreacted material such as Bi_2O_3 or other organic compounds related to surfactant.

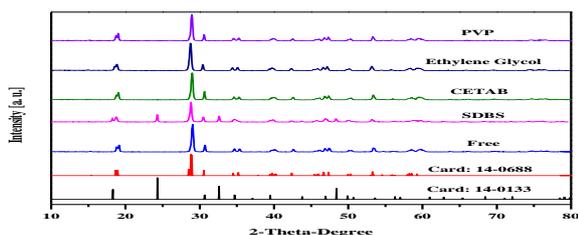


Fig 1: XRD patterns of BiVO_4 photocatalysts prepared with different

These results designated that the residual surfactant removed without calcination. Also, it can notice that the 2θ peak positions of a diffraction peaks for the produced samples are shifted in each case. For example, the location of (121) and (040) reflection in Ethylene glycol assisted BiVO_4 and PVP assisted BiVO_4 exposed an apparent change to lower angle comparing to the sample without surfactant, indicating that the using ethylene glycol and PVP as surfactant made a great influence on the crystallization faced of BiVO_4 during the homogenous precipitation technique. This impact may be due to the different molecule structures of each surfactant. Moreover, the diffraction peak at $2\theta = 19^\circ$ show more splitting with PVP assisted BiVO_4 sample which indicating the enhancement of the monoclinic crystallization phase [27]. The difference between the BiVO_4 samples at different surfactants possible to be detected by Raman technique which revealed the structural information. The Raman bands in the range between $100\text{--}1000 \text{ cm}^{-1}$ of BiVO_4 produced samples were shown in Figure 2, As we seen that the position of the band near 815 cm^{-1} an obvious shift to the lower wavenumber, from 815.87, 814.90, 812.97, and 810.08 for surfactant free, PVP, Ethylene glycol, and CTAB respectively. This attributed to different degrees of imbalance in V–O length of symmetry of VO_4 tetrahedral [28]. This result is matched with the XRD pattern shift.

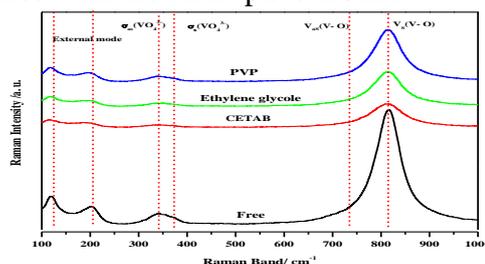


Fig 2: Raman Spectra of BiVO_4 sample fabricated using various

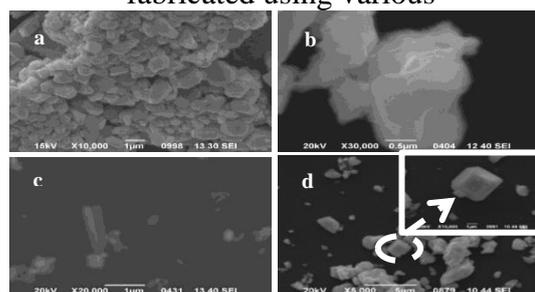


Fig 3: SEM images for morphology of BiVO_4 sample fabricated with various surfactants.

SEM images of the synthesized BiVO_4 samples with different type of surfactants are depicted in Figure. 3. It can be seen from Figure 3a that the no-surfactant-assisted BiVO_4 consisted of irregular polyhedral microcrystal. with random size distributions. After Ethylene glycol is added to the reaction mixture, the typical products consist of stacked plates Figure 3b. the presence of CTAB change the morphology to irregular rods Figure. 3c, while the presence of PVP finds a new form of crystal which appeared at Figure 3d and magnified as inset figure. this form called *Truncated Bipyramid* like shape which exhibited crystal with different exposed facets and relatively sharp edges and smooth surface.

3.2. Optical properties, Charge Separation at different surfactant

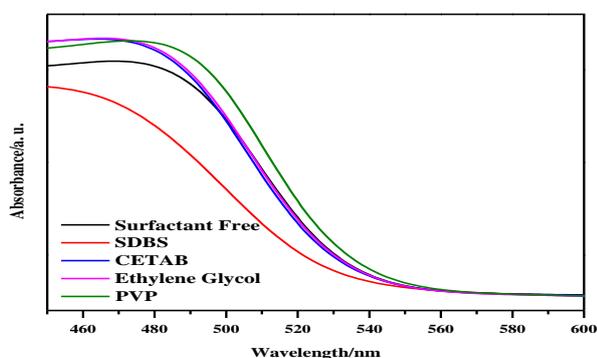


Fig 4:DRS spectra of BiVO_4 samples with different type of surfactant.

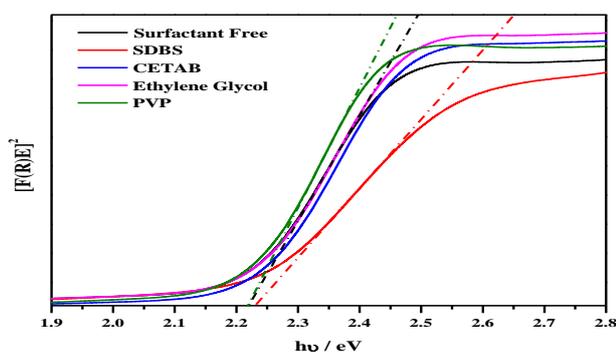


Fig 5:Plot of transferred Kubelka–Munk vs. energy of the light absorbed

The UV–vis DRS of samples with different type of surfactant displayed in Figure 4 revealed a various absorption shift of wavelength in addition to that of strong absorption in the UV-light region. It was found that BiVO_4 sample prepared with SDBS surfactant shows absorbance less than other samples due to the ratio of tetragonal phase which appeared in the XRD [29]. The band gap

(Eg) of synthesized samples have been evaluated from the curve of the modified Kubelka-Munk function $[F(R)E]^2$ against the energy of the absorbed light E [30] as defined in Figure 5, and was found that sample of PVP - assisted BiVO_4 showed the minimum band gap which indicate that this sample has the lower bandgap level, which will enhance the photoactivity distinctive in visible light. To focus on the electronic structure, electron-hole separation process and the influence of surfactant to improve the electron-hole recombination into BiVO_4 crystal, Mott Schottky (MS) and electrochemical impedance spectroscopy (EIS) curves of synthesized samples were performed. MS curves of BiVO_4 samples display positive slopes as predictable for n-type semiconductors Figure 6. The flat band potential (intercept on x axis) is positively shifted after adding the surfactants, which is attributed to the swelling of band pinning of the Fermi energy edge [31]. On the other hand, the a markedly shallower slope for BiVO_4 samples assisted by surfactants implying an increase of carrier densities indicating enhanced electronic conductivity [32].

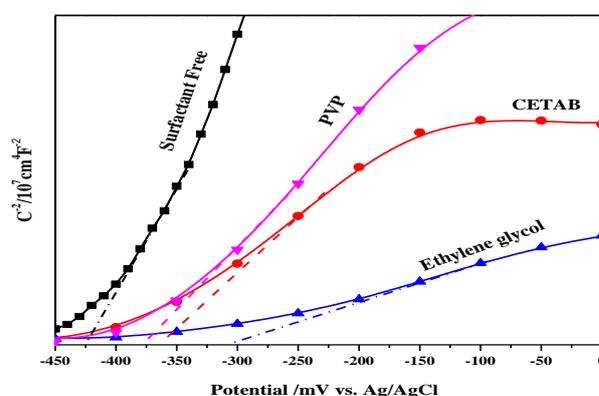


Fig 6:Variation of capacitance (C) with the applied potential in presented in the Mott-Schottky relationship for the BiVO_4 samples with different surfactant.

Moreover, Figure 7, exposed that the electrochemical impedance spectroscopy (EIS) plot giving due to the corresponding circuit model (inset in Figure 7), where R_s and R_{ct} were denoted to the series resistance and interfacial charge transfer resistance, respectively [31]. The value of R_s for all samples were neglected, due to the similarity of the series resistance effect. After adding

the surfactant, R_{ct} decreased significantly specially in PVP assisted BiVO_4 , indicating that presence of PVP greatly enhances charge transfer, these results approve that the presence of surfactant specially PVP show better electron-hole separation and electron transport property [33].

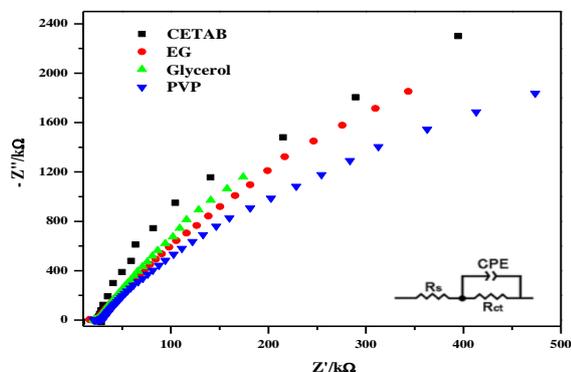


Fig 7: Electrochemical impedance spectra of the BiVO_4 samples electrolyte. The equivalent circuit (inset).

3.3. Photocatalytic activity of BiVO_4 samples at different surfactant

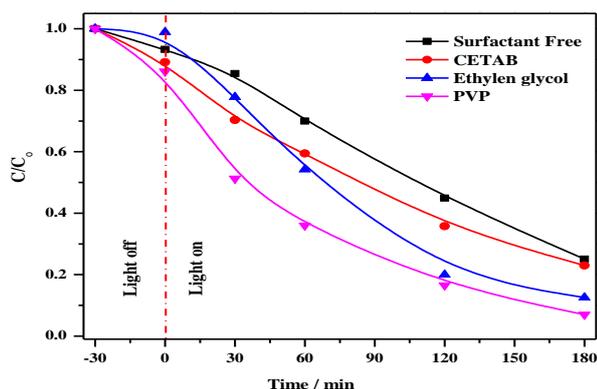


Fig 8: Photodegradation efficiencies of MB as a function of irradiation time for different photocatalysts.

The photocatalytic performances of crystalline BiVO_4 samples synthesized with different surfactant are examined in terms of the photodegradation of MB. Figure 8, revealed the reduction in concentration of MB by BiVO_4 catalysts as a function of visible irradiation time. It is clear that the photocatalytic efficiency of the BiVO_4 samples treated with various surfactant much higher than that of BiVO_4 synthesized without surfactant. Compared with the photodegradation of 70% of surfactant free- BiVO_4 , the ratio of photodegradation with PVP assisted BiVO_4 powder is up to 95% in 180 min under visible-light irradiation.

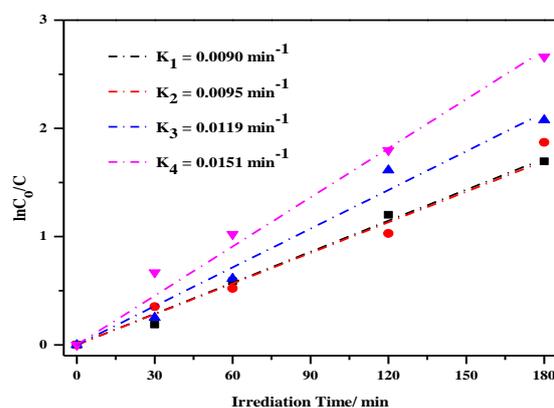


Fig 9: MB photodegradation kinetics curves by BiVO_4 samples prepared with K_1 : Surfactant Free, K_2 : CETAB, K_3 : Ethylene glycol, K_4 : PVP

Moreover, the reaction rate constant k Figure 9, confirms the photocatalytic activity results. The PVP- assisted BiVO_4 show the highest rate of reaction ($K_4=0.0151 \text{ min}^{-1}$) which highest one time and half than surfactant free BiVO_4 sample the photocatalytic activity of PVP- assisted BiVO_4 sample may be ascribed to the *Truncated Bipyramid* like shape which appeared different facets with different activity. This shape shows diminishes in the electrons and holes recombination, and enhanced the carrier density and then, enhanced efficiency of the catalytic activity. So, we should study the increasing in concentration of PVP and impact it on the catalytic activity.

4. Conclusion

In Summary, we have successfully prepared for the first-time m-s BiVO_4 photocatalyst via simple homogenous precipitation assisted by different surfactants as orienting agent. The characterization and photocatalytic experimental demonstrate that the increasing of the presence of PVP surfactant as orienting agent show the best results due to the formation of *Truncated Bipyramid* like shape which appeared different facets with different activity

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