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Selective Synthesis of Monoclinic Bismuth Vanadate Powders by Surfactant-Assisted Co-Precipitation Method: Study of Their Electrochemical and Photocatalytic Properties

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Monoclinic bismuth vanadate powders were selectively synthesized by surfactant-assisted co-precipitation method. The triblock copolymers $EO_{19}PO_{69}EO_{19}$ (Pluronic P-123) and $EO_{100}PO_{65}EO_{100}$ (Pluronic F-127) were utilized as morphology-directing templates. The as-synthesized samples were characterized by means of techniques such as X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), UV-vis diffuse reflectance spectroscopy (UV-vis DRS) and nitrogen adsorption-desorption isotherms (BET method). The quasi-Fermi potential of electrons of samples was determined through pH dependent photovoltage measurements. Moreover, the influence and effect of concentration of the surfactant on the morphology of the obtained materials were investigated. Experimental results indicate that self-assembling balls of m-$BiVO_4$ particles with an average size of 800 nm can be obtained at 200°C by using Pluronic P-123 in the co-precipitation process. The mechanism of formation of the as-prepared m-$BiVO_4$ samples has also been proposed. Rhodamine B photodegradation was used to evaluate the photoactivity of the samples under visible-light irradiation.

Keywords: $BiVO_4$, co-precipitation, heterogeneous photocatalysis, quasi-Fermi potential

1. INTRODUCTION

Nowadays, heterogeneous photocatalysis is considered an important tool for resolving environmental and energy problems [1-3]. To date, the semiconductor TiO_2 has undoubtedly proven to be one of the most excellent photocatalysts for the oxidative decomposition of many organic compounds. Unfortunately, due to its wide band-gap of 3.2 eV, TiO_2 can only be excited by ultraviolet or near-ultraviolet radiation, which is only about 4% of the solar light spectrum reaching the earth surface. On the other hand, the visible light covers about 43% of the solar light. In order to efficiently utilize solar energy, the development of visible-light driven photocatalysts has attracted a tremendous amount of attention. Monoclinic bismuth vanadate (m-$BiVO_4$) is a material that has recently been used as photocatalyst both, for the degradation of organic pollutants, and for the production of oxygen from water under visible-light irradiation [4-6].

To improve textural, optical, microstructural, morphological and photocatalytic properties of m-$BiVO_4$ powders, different synthetic methods have been developed by several groups including combustion synthesis method [7], ultrasonic method [8], co-precipitation method [9] and hydrothermal method [10-11]. Currently, a relatively simple way to obtain $BiVO_4$ powders with higher photocatalytic activity has been the use of the above mentioned methods assisted by morphology-directing agents, such as surfactants, polymers and organic compounds (CTAB, SDS, EDTA, EG, PEG, CMC, Pluronic P-123 and oleic acid) [12-19]. In the present study, m-$BiVO_4$ powders were synthesized by Pluronic-assisted co-precipitation method. To the best of our knowledge, this is the first report regarding this synthesis of m-$BiVO_4$ by using Pluronic surfactants as morphology-directing agents.

The triblock copolymers $EO_{19}PO_{69}EO_{19}$ (Pluronic P-123) and $EO_{100}PO_{65}EO_{100}$ (Pluronic F-127) were used as agents for the morphology control. Rhodamine B (rhB) was used as a model dye to evaluate the photocatalytic activities of different m-$BiVO_4$ samples under visible-light irradiation. Furthermore, the influence of the type of surfactant and the effect of their concentration on the morphology of the obtained materials were investigated. Moreover, the morphology evolution and the mechanism of formation have also been discussed.

2. EXPERIMENTAL

2.1 Preparation of $BiVO_4$ powders

$BiVO_4$ powders were prepared by using the polymer-assisted co-precipitation method. All chemicals used were analytical grade and were utilized as received without further purification. The morphology directing agents used were the block copolymer surfactants Pluronic P-123 (P123) and Pluronic F-127 (F127). The synthesis of $BiVO_4$ was performed starting from stoichiometric amounts of $Bi(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3. In a typical synthesis, 0.03 mol of $Bi(NO_3)_3.5H_2O$ were dissolved in 100 mL of 4 M HNO_3 solution at 70°C and 0.03 mol of NH_4VO_3 were dissolved in 100 mL of 2 M NH_4OH solution at 70°C. For those solutions, different amounts of P123 or F127 (0.1 g and 0.58 g) were dissolved in 100 mL of distilled water. Such amounts of P123 or F127 correspond to 0.5 % (P123-1 or F127-1) and 3 % (P123-3 or F127-3), weight percentages with respect to the total weight of prepared samples, respectively. The corresponding solution of P123 or F127 (50 mL) was added the Bi and V precursor solutions under continuous stirring during 1 h to obtain two transparent solutions A and B, respectively. Afterwards, solution A was added dropwise to solution B under vigorous stirring.

The pH of the mixed solution was adjusted to 9 with 2 M NH_4OH solution, and the mixture was stirred for 1 h, until a yellow suspension was obtained. This suspension was cooled at room temperature and the water was removed by freeze drying water. In order to obtain m-$BiVO_4$ the resulting dried orange powder was heated at 200°C, for 24 h (P123-1), and at 400°C for 24 h (P123-3) for the case of P123 samples and heated at 450°C for 65 h (F127-1 and F127-3) for the case of F127 samples. The heating was always done at atmospheric pressure. The thermal treatments were carried out until the weight loss of the material was negligible. In order to remove reaction by-products, the samples were washed several times with distilled water. The experimental procedure utilized in the present work has been previously investigated by our group for the controlled synthesis of m-$BiVO_4$ in presence of surfactants, such as CMC [20]. Reference bulk $BiVO_4$ was also prepared by solid-state reaction and co-precipitation methods following the procedure described previously [9].

2.2 Characterization of $BiVO_4$

X-ray powder diffraction patterns of the as-synthesized samples were measured on a D8 Advanced diffractometer (Bruker) using monochromatic Cu Kα (λ= 1.5418 Å) radiation, equipped with a Vantec high speed detector. X-ray diffraction data were collected in a 2θ range of 10-70° with increments of 0.05° and counting time of 0.5 s^{-1} per step. The morphologies of as-prepared samples were examined with scanning electron microscopy (SEM, FEI Nova Nanosem 200). Fourier transform infrared (FT-IR) spectra were obtained in the wave number range 400-4000 cm^{-1}using a Nicolet 6700 Fourier transform infrared spectrometer using the KBr pellet technique. This analysis was carried out to the samples after five water centrifugation/redispersion cycle in order to determine the presence of reaction by-products. The Brunauer-Emmett-Teller (BET) surface areas of the samples were determined by nitrogen adsorption-desorption measurements using a Bel-Japan Minisorp II surface area & pore size analyzer. The adsorption-desorption isotherms were evaluated at -196°C after the samples were degassed at 80°C for 24 h. The UV-vis diffuse reflectance absorption spectra were measured by using a Perkin Elmer Lambda 35 UV-vis spectrophotometer equipped with an integrating sphere using $BaSO_4$ as reference. The quasi-Fermi levels of electrons ($_{n}E_{F}*$) were determined by the slurry method proposed by Roy et al. [21]. For this purpose, 80 mg of photocatalyst were suspended in 80 mL of a 0.1 M KNO_3 solution containing 6 mg of methylviologen dichloride (MV^{2+}). A platinum plate electrode ($A_{electrode}$ = 1 cm^2) and a saturated calomel electrode (SCE) served as working and reference electrodes, respectively. A pH meter was utilized for monitoring the proton concentration. The suspension was magnetically stirred and flushed with N_2 during the measurement. The pH was adjusted by using a 1 M HNO_3 and solutions of NaOH (0.001 M, 0.01 M, 0.05 M, 0.1 M and 1 M). Four compact fluorescent lamps of 15 W were used as light source. Stable voltages were recordable within 30 min after changing the pH. Those values were plotted as a function of pH, and the pH_0 values obtained from the inflection points were converted to the quasi-Fermi potential electrons at pH 0 by using the equation:

$$_{n}E_{F}^{*}\ (\mathrm{pH} = 0) = E^{0}_{\mathrm{MV}^{2+/+.}} - k\,(0 - \mathrm{pH}_0) \quad \text{eq 1}$$

where E^0 is the standard reduction potential of the redox couple (-0.445 V vs NHE), and k is a constant for a certain material. A k-value of 0.054 V/pH has been previously calculated by Long et al. for powders of $BiVO_4$ [22].

2.3 Photocatalytic reactions

A cylindrical photochemical reactor made of borosilicate glass was used in this study. A Xe lamp of 6,000 K with an illuminance of 1630 lx was used as visible-light source. The IR fraction of the incident lamp was removed by water circulating in the double jacket of the photoreactor and the temperature was maintained at 25 ± 1°C. The photocatalytic activity of $BiVO_4$ was evaluated on the degradation reaction of rhB in water. In a glass beaker, 250 mL of rhB solution (5 $mg.L^{-1}$) containing 250 mg of photocatalyst were put in ultrasonic bath for 10 minutes to eliminate aggregates. In order to be sure that adsorption-desorption equilibrium of the dye on the catalyst surface was reached, the solution was kept in the dark for 1 h. After this time, the light source was turned on. During reaction, samples of 6 mL were taken at different time intervals and then separated through double centrifugation. The supernatant solution was decanted and the rhB concentration was determined through its absorption maximum band by using a UV-vis spectrophotometer (Perkin Elmer Lambda 35).

3. RESULTS AND DISCUSSIONS

3.1 Sample characterization

The phase transformation process of samples synthesized by Pluronic-assisted co-precipitation method under different conditions was investigated using XRD measurement. Fig. 1(b-c) shows the XRD patters of $BiVO_4$ powders prepared in the presence of 0.5 (P123-1) and 3 wt% (P123-3) of Pluronic P-123 at 200°C for 24 h and 400°C for 24 h, respectively. The results indicates that all the XRD patters are in good agreement with the card No. 14-0688 of the Joint Committee on Powder Diffraction Standards (JCPDS), which is assigned to monoclinic scheelite $BiVO_4$ with space group I2/a. In addition, for the samples synthesized in the presence of 0.5 (F127-1) and 3 wt% (F127-3) of Pluronic F-127 at 450°C for 65 h, all the diffraction peaks can be well-indexed to the pure monoclinic phase of $BiVO_4$, as shows Fig. 1(d-e). No peaks for any other phases or impurities were detected, indicating that these temperatures are sufficient for the formation of phase-pure monoclinic $BiVO_4$ by Pluronic-assisted co-precipitation method.

To confirm the complete elimination of Pluronic surfactants or presence of other impurities on the as-prepared samples (P123-1, P123-3, F127-1 and F127-3), FT-IR spectra of samples were recorded ranging from 400 to 4000 cm^{-1} at room temperature. The results confirm the absence of impurities on the particles. These results shown that Pluronic surfactants or reaction by-products were removed totally from the m-$BiVO_4$ samples after the thermal treatment and washing process were carried out.

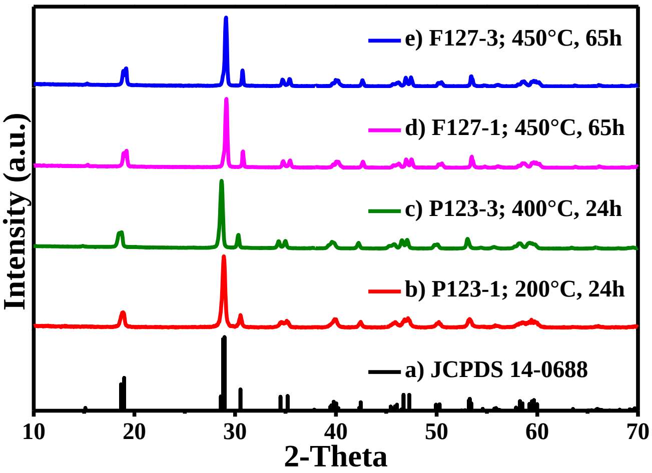

Figure 1. XRD patterns of as-prepared samples by surfactant-assisted co-precipitation method at different experimental conditions: (a) Standard XRD pattern of m-$BiVO_4$ (JCPDS No. 14-0688), (b-c) Pluronic P-123-assisted, and (d-e) Pluronic F-127-assisted.

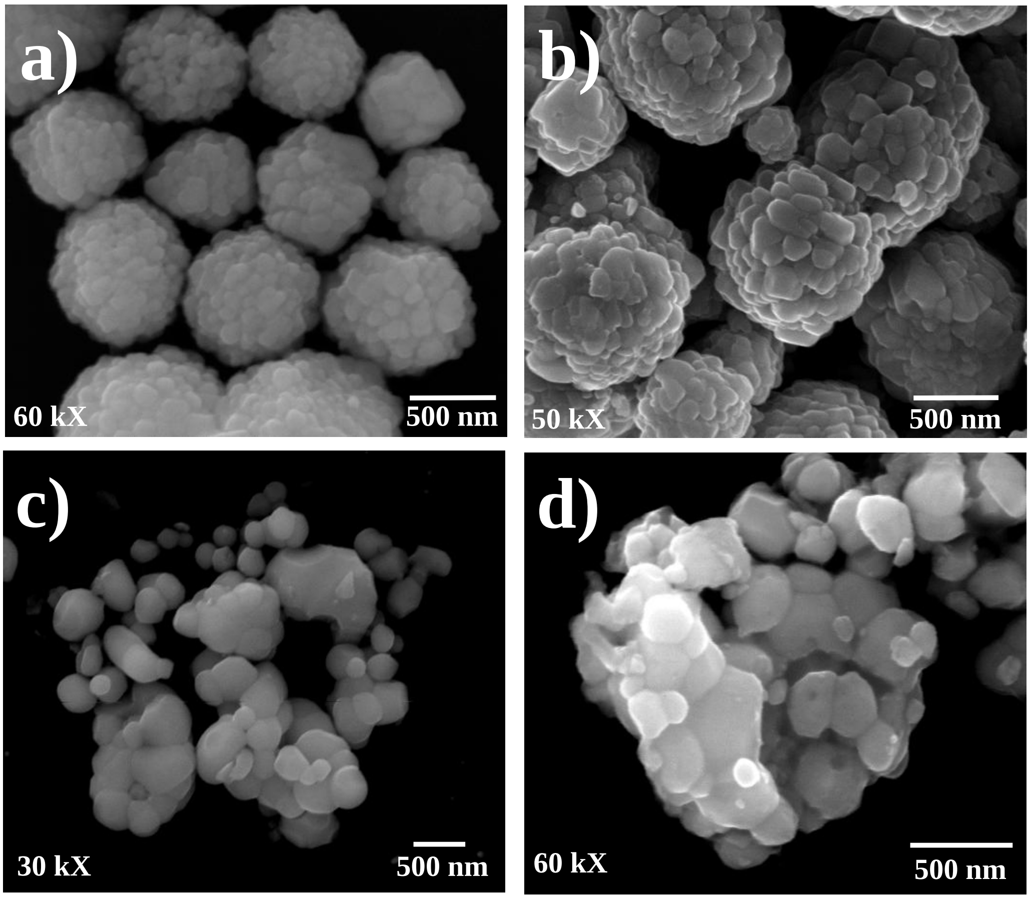

Figure 2. SEM images of m-$BiVO_4$ powders synthesized by surfactant-assisted co-precipitation method at different experimental conditions: (a-b) Pluronic P-123-assisted, and (c-d) Pluronic F-127-assisted.

The effect of the Pluronic surfactants on the morphology and microstructure of P123 and F127 samples was revealed by SEM, as shown in Fig. 2. As can be seen, the presence of Pluronic P-123 has a significant influence on the morphology control of the product. In Fig. 2(a-b) nanoparticles with average size ~100 nm that are self-assembled to form uniform spherical aggregates with a diameter of 0.8-1 μm can be seen. Fig. 2(c-d) shows that F127 samples synthesized in presence of different content of Pluronic F-127 consist of particles with irregular morphology and particle size of 100-500 nm.

The formation of spherical-shaped self-assembled structures has been previously reported for the m-$BiVO_4$ prepared by the combustion method using citric acid or urea as fuels, as well as hydrothermal method using surfactants such as sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) [13, 23-25]. In these studies the final morphology of the particles has been attributed to the presence of the structuring agents used and, in some cases, their capacity to form micelles, with which they have been able to stabilize and limit the growth of the particles.

The possible mechanisms of formation of the as-synthesized P-123 and F-127 samples with different morphologies are proposed in Fig. 3.

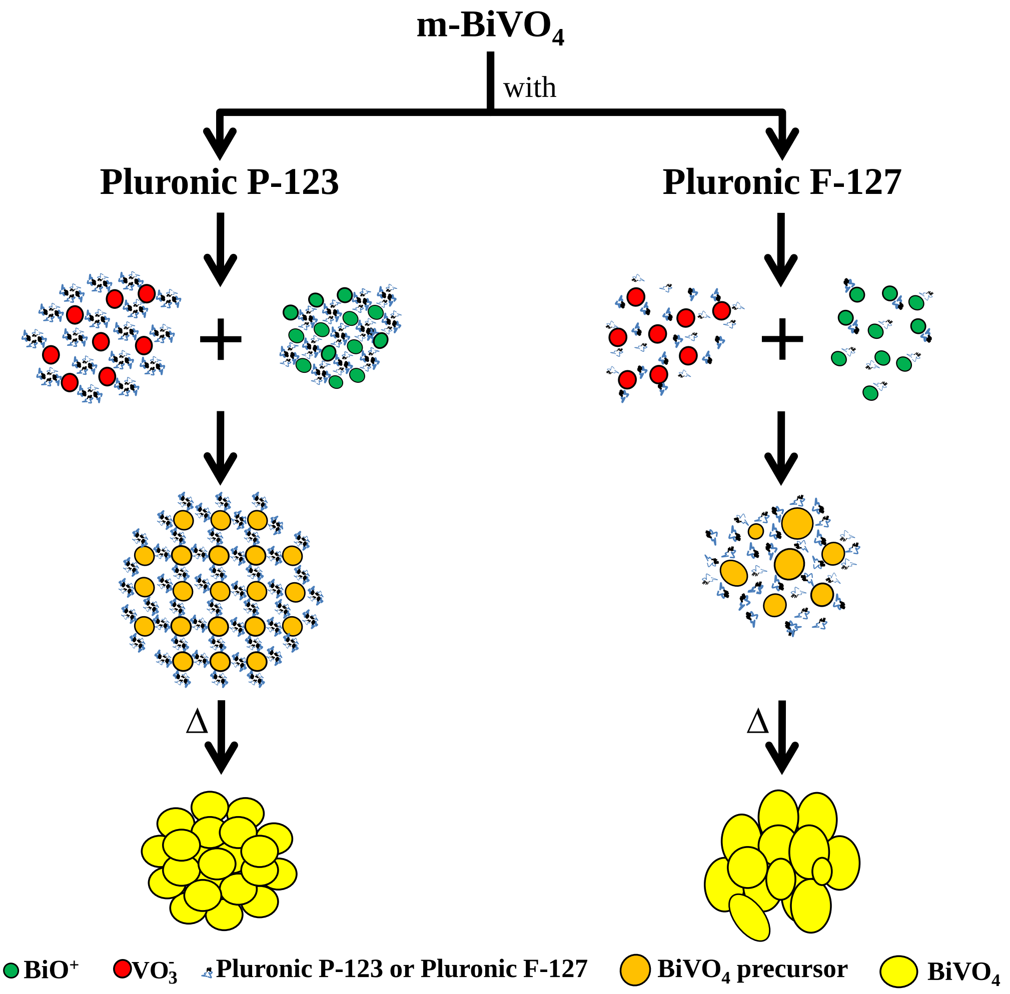

Figure 3. Schematic illustration of the mechanism of formation of the as-prepared m-$BiVO_4$ samples by Pluronic-assisted co-precipitation method.

Under the present experimental conditions, BiO^+ and VO_3^- ions are initially in solution in presence of Pluronic surfactants. However, and due to the fact that the concentrations of Pluronic P-123 (0.5 and 3 wt%) utilized in the synthesis of the P123 samples are above of its critical micelle concentration (CMC) (0.04 wt% at 25°C) [26], the surfactant molecules in the reaction are associated forming micelles. In the case of the F127 samples, the Pluronic F-127 molecules in the reaction are not associated into micelles, because the concentrations used in the synthesis are below its CMC (1 wt% at 25°C) [27].

Pluronic P-123 and Pluronic F-127 are non-ionic surfactants that consist of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(propylene oxide) (PPO) blocks arranged in A-B-A tri-block structure: PEO-PPO-PEO. In aqueous solutions at concentrations above CMC these copolymers self-assemble into micelles [28]. Therefore, after the addition of BiO^+ ions to the Pluronic surfactants solutions, electrostatic interaction of this cathion with the terminal hydroxyl groups (-OH) of the hydrophilic parts of the surfactant are established. Meanwhile, the VO_3^- anions are dispersed in the environment coexisting with surfactant molecules. Due to the negative nature of the terminal hydroxyl groups (-OH) a repulsive electrostatic interaction between vanadate ions and the hydrophilic parts of the surfactant, is established. When these two solutions are mixed, an orange precipitate of metastable $BiVO_4$ with Pluronic surfactants adsorbed on it will be immediately produced. This acts as template and protective agent in the formation of metaestable $BiVO_4$ with different morphologies by co-precipitation process. Finally, during the heat-treatment at various temperatures those metastable $BiVO_4$ precipitates would reconstruct to form yellow $BiVO_4$ powders with monoclinic structure.

The specific surface areas of all the samples were obtained by BET analysis. Table 1 shows that the samples have a surface area in the range of 0.33-1.40 $m^2\ g^{-1}$. From Table 1, it is possible to observe a 13, 10, 3 and 5 times increase of the surface area of P123-1, P123-3, F127-1 and F127-3 samples, respectively, with respect to the powder synthesized by solid state reaction (SSR).

Table 1. Band gap, quasi-Fermi potentials and BET surface area of m-$BiVO_4$ samples.

Sample	E_g (eV)	${}_nE_F^*$ (V vs NHE)	Surface Area ($m^2.g^{-1}$)
P123-1	2.42	-0.06	1.40
P123-3	2.45	0.00	1.05
F127-1	2.43	0.12	0.33
F127-3	2.42	-0.13	0.53
SSR	----	----	0.11
Cop	----	----	0.87

${}_nE_F^*$= quasi-Fermi levels of electrons determined at pH= 0

The optical properties of the m-$BiVO_4$ samples were measured using UV–vis spectroscopy. The diffuse reflectance spectra of the P123 and F127 samples showed both strong absorption in the visible and UV light regions, and this implies the possibility of photocatalytic activity of these materials under visible-light irradiation. Based on the equation $\alpha h\nu = A(h\nu - E_g)^{n/2}$ [29], the band gaps of the samples were estimated to be 2.42, 2.45, 2.43, and 2.42 eV for P123-1, P123-3, F127-1 and F127-3 samples, respectively, as shown in Table 1. These data are comparable with previous reports for the $BiVO_4$ with monoclinic structure [30-31].

The quasi-Fermi levels of electrons were obtained by measuring the photovoltage generated upon irradiation of m-$BiVO_4$ sample suspension as function of pH. Figure 4 shows the effect of pH on the photovoltage developed on irradiation of the P123 and F127 suspensions. The inflection points (pH_0) of the titration curves obtained for P123-1, P123-3, F127-1 and F127-3 samples were 7.26, 8.40, 10.57 and 5.88, respectively. Using these pH_0-values the quasi-Fermi level of electrons at pH=0 are located at −0.06 V vs NHE for P123-1, 0.00 V vs NHE for P123-3, 0.12 V vs NHE for F127-1 and -0.13 V vs NHE for F127-3, as shown in Table 1. Assuming that upon irradiation the quasi-Fermi level of electrons is equal to the conduction band edge, and taking into account the $E_{VB} = {}_{n}E_F{}^* + E_g$ relation, valence band edge potentials (E_{VB}) of 2.35, 2.45, 2.55 and 2.29 V were obtained for P123-1, P123-3, F127-1 and F127-3 samples, respectively.

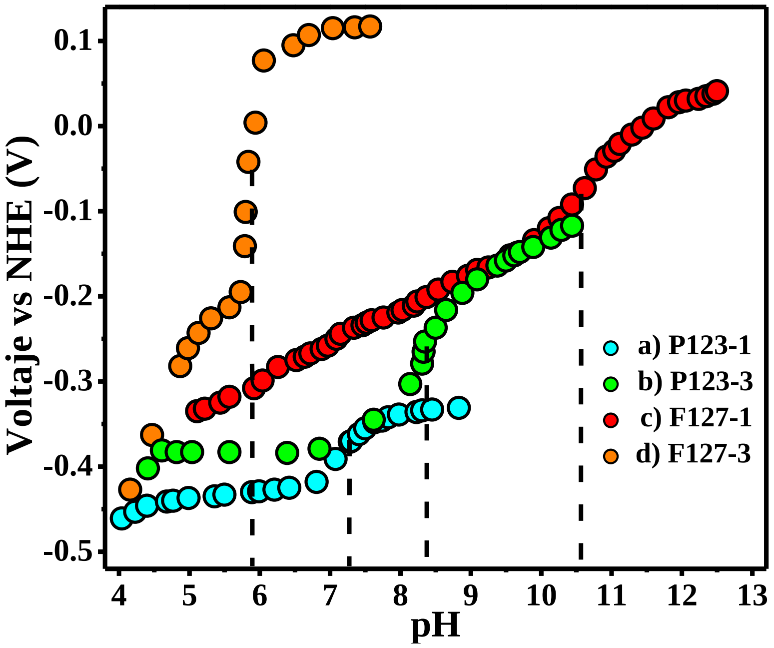

Figure 4. Variation of voltage with pH for a suspension of m-$BiVO_4$ powders in 0.1 M KNO_3 in presence of MV^{2+} under visible-light irradiation (λ ≥ 390 nm).

Figure 5 shows the relative positions of the energy bands of P123 and F127 samples at pH=0. The valance band edge of all samples is more positive than the oxidation potential of H_2O and OH^- (E° ($H_2O/OH^\bullet$) = 2.38 V vs NHE and E° ($OH^-/OH^\bullet$)= 1.55 V vs NHE). Thus, photoexcited holes may react with the adsorbed water to form hydroxyl radicals. It is well known that the $OH^\bullet$ radical is a powerful oxidizing agent capable of degrading most organic pollutants [32]. Also, can be observed that the bottom of conduction band in P123-1, P123-3 and F127-3 samples is more negative than the reduction potential of H^+ (E° ($H_2/2H^+$)= 0.00 V vs NHE). Therefore, photoexcited electrons may react with solution H^+ to produce H_2.

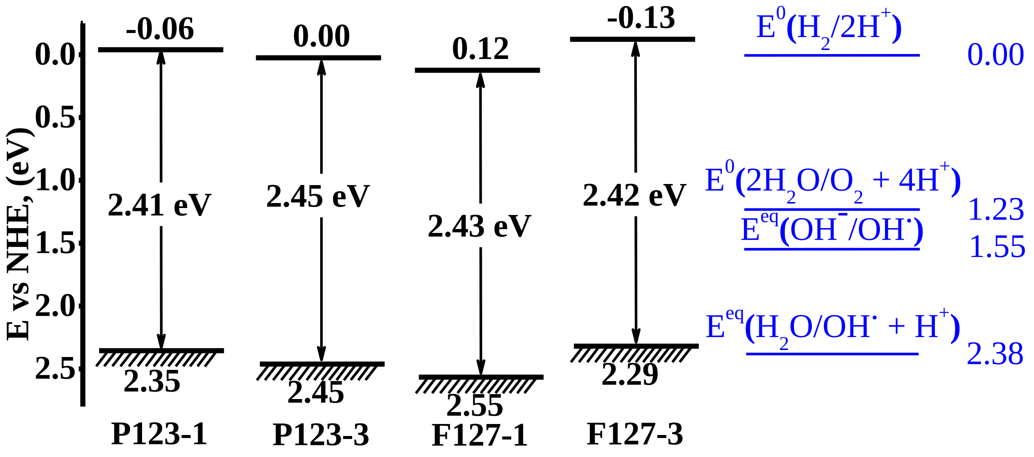

Figure 5. Electrochemical potentials (versus NHE) at pH= 0 of the band edges of m-$BiVO_4$ samples.

3.2 Photocatalytic reactions

Photocatalytic activities of the samples were evaluated by measuring the degradation of rhB in aqueous solution under visible-light irradiation. Temporal changes in the concentration of rhB were monitored by examining the variations of UV–vis absorption at 554 nm. Fig. 6 shows the results of degradation of rhB in presence of P123 and F127 samples.

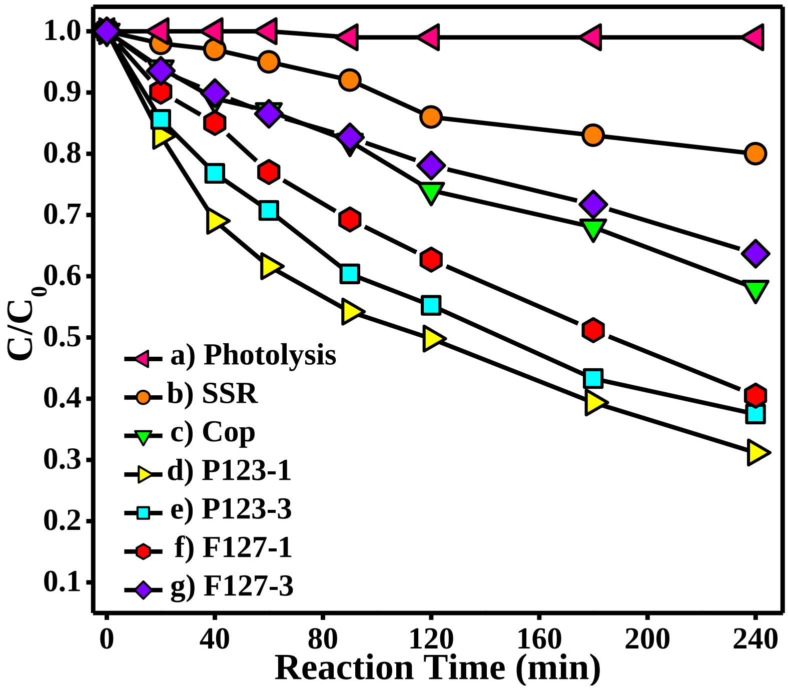

Figure 6. Change in the rhB concentration during its photocatalytic degradation in the presence of m-$BiVO_4$ samples.

Powders prepared by solid state reaction (SSR) and co-precipitation method without additives (Cop) were also tested for comparison (curves b and c). The blank experiment indicated that the photodegradation of rhB under visible-light irradiation without catalysts is insignificant (curve a). The P123-1 sample (surface area 1.40 m^2 g^{-1}) exhibited the highest visible-light photocatalytic activity toward rhB degradation (curve d). On the other hand, the activity of P123-3 was similar to F127-1 (curves e-f), while the activity of F127-3 was lowest (curve g). The decolorization radio reached after 240 min irradiation was 69, 63, 60 and 36% for P123-1, P123-3, F127-1 and F127-3, respectively. The surface area of as-prepared samples was correlated with the photocatalytic activity of rhB degradation. It is well known that properties like crystalline structure, density of OH groups, surface acidity and adsorption/desorption characteristics are crucial to the heterogeneous photodecomposition of organic compounds.

On the other hand, P123 and F127 samples, were utilized to evaluate photocatalytic water splitting into H_2 and O_2 from aqueous solutions containing sacrificial reagents. Aqueous methanol was utilized as sacrificial reagent for H_2 evolution, while for the O_2 evolution aqueous silver nitrate solution was used as sacrificial reagent. All reactions were carried out in a closed gas circulation system. The results obtained revealed that the samples had no activity toward H_2 and O_2 evolution under visible-light irradiation. These experimental results can be associates with the high recombination rate of photoexcited electrons and holes in m-$BiVO_4$ [33].

4. CONCLUSIONS

Visible-light active monoclinic bismuth vanadate photocatalysts were successfully synthesized using a facile co-precipitation process in presence of Pluronic surfactants. It was found that the critical micelle concentration of Pluronic surfactants was a crucial factor for the morphology control of the as-prepared samples. The use the Pluronic P123 as molecule template plays an important role in the formation of m-$BiVO_4$ particles self-assembled in uniform spherical aggregates. The electrochemical characterization revealed that the quasi-Fermi levels of P123-1, P123-3 and F127-1 samples were more negative than the reduction potential of H^+ at pH=0. The photocatalysis results showed that the as-prepared m-$BiVO_4$ by co-precipitation method in presence of Pluronic surfactants had a higher activity for the photodegradation of rhB than the samples prepared by solid state reaction and co-precipitation method. Also, the experimental photocatalytic results showed the null activity of materials for water splitting into H_2 or O_2 from aqueous solutions containing sacrificial reagents under visible-light irradiation.

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