

A comparative study of photocatalytically active nanocrystalline tetragonal T zircon-type and monoclinic scheelite-type bismuth vanadate ^{ch}_v

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ABSTRACT

Monoclinic scheelite-type BiVO_4 is currently considered as one of the most promising non-titania photocatalysts, whereas tetragonal zircon-type BiVO_4 is still poorly understood. Herein, a new and simple synthetic approach was applied and nanostructured single-phase zircon-type BiVO_4 was successfully prepared by a controllable ethylene-glycol colloidal route. In addition, nanostructured monoclinic scheelite-type BiVO_4 powders were also fabricated through annealing of the as-prepared samples. A comparative study of the two BiVO_4 polymorphs was conducted and it turned out that the novel synthetic approach had a significant impact on porosity and photocatalytic performance of zircon-structured BiVO_4 . All the prepared materials, as-prepared and annealed, were meso-porous, while measured values of specific surface area of some zircon-structured samples ($\sim 34 \text{ m}^2/\text{g}$) were ~ 7 times higher than those reported thus far for this phase. Interestingly, for the first time, zircon-type BiVO_4 , previously considered to be a poor photocatalyst, exhibited a better overall performance in degradation of methyl orange compared to monoclinic scheelite-type BiVO_4 . Hence, it could be expected that the here-presented synthesis and observations will both arouse interest in scarcely studied tetragonal zircon-type BiVO_4 and facilitate as well as speed up further research of its properties.

With a focus on catalysis many processes and preparative conditions have been employed to prepare ms- BiVO_4 micro- and nanoparticles of varying morphologies and sizes [1–3,8–10]. At the same time, few approaches were attempted for synthesis of the zircon-structured phase in aqueous media by the low-temperature process: a precipitation

1. Introduction

As solar energy is the most abundant energy source, harvesting energy directly from sunlight over semiconducting nanomaterials offers a very attractive approach to resolve both the potential energy crisis and problems of environmental pollution. Among non-titania (TiO_2)-based visible-light driven photocatalysts, considerable research has been devoted to bismuth vanadate (BiVO_4) [1–4]. Mainly, studies have focused on monoclinic BiVO_4 and it has proved to be an excellent material for use (under visible-light illumination) in photocatalytic water splitting and photocatalytic degradation of organic compounds (air/water pollutants) [1–7].

BiVO_4 is polymorphous and occurs naturally as three crystalline forms: orthorhombic pucherite (op- BiVO_4), tetragonal dreyerite (tz- BiVO_4 , zircon-type structure, space group I41/amd), and monoclinic clinobisvanite (ms- BiVO_4 , distorted scheelite-type structure, space group I2/b). Synthetic BiVO_4 , apart from crystallizing in dreyerite and clinobisvanite structures, also appears in tetragonal phase (ts- BiVO_4 , scheelite-type structure, space group I41/a). Pucherite is an unstable

phase and is never obtained in laboratory [1,8].

BiVO_4 -based ceramics have been intensively studied because of semiconductivity, ion conductivity, photocatalytic behavior, dielectric properties, ferroelastic-paraelastic phase transition and pigmentation. Brilliant yellow color of non-toxic ms- BiVO_4 makes it a good commercially available substitute for toxic cadmium- and lead-based yellow pigments. All crystalline phases of synthetic BiVO_4 , ts- BiVO_4 , ms- BiVO_4 and tz- BiVO_4 , are n-type semiconductors with respective band gap energies of 2.34, 2.40, and 2.90 eV [1,3]. Their thermodynamic stability varies in the order ms- BiVO_4 , ts- BiVO_4 , tz- BiVO_4 , with ms- BiVO_4 being the most stable phase. A phase transition from tz- BiVO_4 to ms- BiVO_4 takes place irreversibly upon heating to 397–497 °C; thus, tz- BiVO_4 is generally synthesized at lower temperatures. At 255 °C BiVO_4 undergoes a reversible ms- BiVO_4 -to-ts- BiVO_4 phase transition [1].

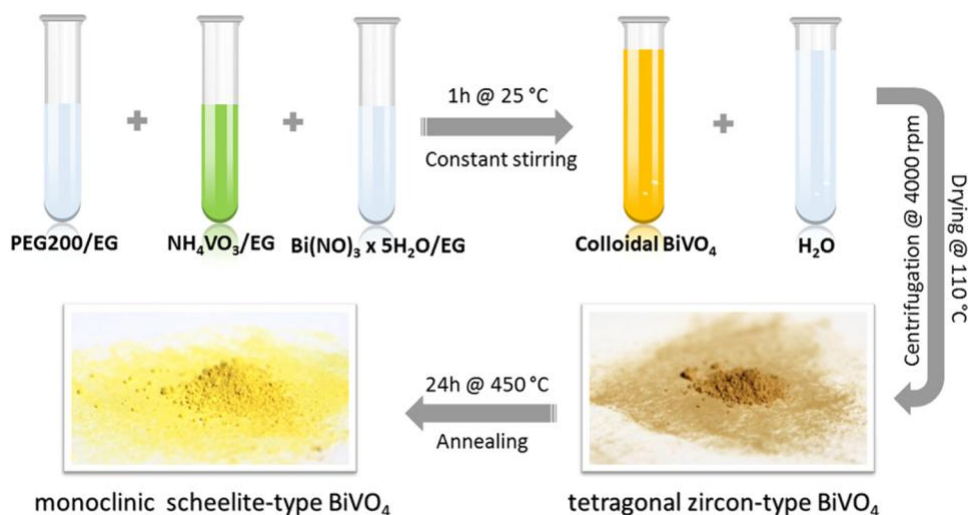


Fig. 1. A general synthetic scheme for preparing tz- BiVO_4 and ms- BiVO_4 nanoparticles.

method from a $\text{Bi}(\text{NO}_3)_3$ nitric acid solution and an aqueous NH_4VO_3 solution at room temperature [8,9,11–13], a precipitation from Bi_2O_3 and V_2O_5 in an aqueous nitric acid solution at room temperature [10], a hydrothermal method [6,14,15], and a rapid microwave-assisted aqueous process [16]. Also, rather few nanostructured zircon-type BiVO_4 were made: small ellipsoidal nanoparticles of about 20 nm [9], nano-particles with diameters in a range 10–40 nm [13], and nanoparticles with diameters of around 10–20 nm [16].

It is well-known for ms- BiVO_4 to exhibit excellent photocatalytic activity under visible light [1–7]. Compared with ms- BiVO_4 , ts- BiVO_4 is much less studied and appears to display moderate photocatalytic activity [9] although first studies declared it to be a poor photocatalyst [10,12]. On the other hand, rather few photocatalytic studies concern pure tz- BiVO_4 and it was found to be a poor (or, even inactive) photocatalyst [9,10,13–16]. Observe, however, that enhanced photocatalytic performance has been reported for a number of doped (chemically impure) BiVO_4 materials with a zircon-type structure [1–3].

Although more than 1000 research papers in the open literature have been devoted to BiVO_4 over the past decade, yet two dozen or so of them consider its zircon-type structure at any length. As suggested in [11] this could be due to its not-so-simple synthesis by conventional synthetic routes. More probably, however, its lower visible-light absorption (compared with ms- BiVO_4) may have deemed tz- BiVO_4 a less interesting material. Several reports of its poor photocatalytic performance only reinforced this view. Nevertheless, zircon-structured BiVO_4 (with a band gap of 2.9 eV) still absorbs more visible light than TiO_2 (3.2 eV for anatase)-the most widely used and most intensely studied photocatalyst. Whatever the reason, tz- BiVO_4 has not been sufficiently studied so far, and, in particular, new approaches to its preparation and better understanding of nanocrystalline tz- BiVO_4 are needed and would be of significance.

In this paper, in an attempt to address before-mentioned gaps in the literature, we aimed to develop a novel and suitable low-temperature synthesis of nanostructured single-phase tetragonal zircon-type BiVO_4 in non-aqueous medium. In order to prepare powdered nanocrystalline tz- BiVO_4 , an ethylene-glycol colloidal route at room temperature was utilized. Moreover, as a consequence of the irreversible tetragonal-to-monoclinic transition, monoclinic scheelite-type BiVO_4 could be easily obtained by thermal treatment of as-prepared powders. Further, we aimed to determine whether or not (and to what extent) the new synthetic approach to tz- BiVO_4 influenced its adsorption and/or photocatalytic performance. To do so, the selectively prepared scheelite-type BiVO_4 lent itself readily to comparison and a comparative study of two BiVO_4 polymorphs was carried out. To assess eventual influence,

photocatalytic activity for both tz- BiVO_4 and ms- BiVO_4 was evaluated by degradation of methyl orange in an aqueous solution under sun-like illumination.

2. Experimental

2.1. Preparation of tz- BiVO_4 and ms- BiVO_4 nanoparticles

Colloidal BiVO_4 samples were synthesized by ethylene glycol-mediated colloidal route at room temperature. Powders of tz- BiVO_4 were made from the previously prepared BiVO_4 colloids, while powders of ms- BiVO_4 were obtained by annealing the tz- BiVO_4 at 450 °C for 24 h. Therefore, the tetragonal and monoclinic BiVO_4 crystallites can be selectively prepared in this process simply by adjusting the calcining temperature.

All chemicals were of highest purity commercially available and were used as received without further purification. These included: $\text{Bi}(\text{NO}_3)_3 \times 5\text{H}_2\text{O}$ (Sigma-Aldrich, 97%), NH_4VO_3 (Alfa Aesar, 99.999%), ethylene glycol (Sigma-Aldrich, 97%), polyethylene glycol 200 (PEG-200, Alfa Aesar), HNO_3 (J.T. Baker, 65%) and distilled water.

In a typical synthesis of colloidal BiVO_4 , stoichiometric amounts of NH_4VO_3 , $\text{Bi}(\text{NO}_3)_3 \times 5\text{H}_2\text{O}$ and PEG-200, were separately dissolved in ethylene glycol. In this way, the 0.075 M, 0.050 M and 0.025 M ethylene glycol solutions of both precursors, NH_4VO_3 and $\text{Bi}(\text{NO}_3)_3 \times 5\text{H}_2\text{O}$, were prepared. Then, the ethylene glycol solution of PEG-200 was slowly added drop-wise into the solution of NH_4VO_3 and the resulting mixture was left under vigorous stirring for 30 min. At the same time, 200 μL of HNO_3 was added to the bismuth precursor solution. After 30 min of stirring, the bismuth precursor solution was slowly added drop-wise into the mixture of NH_4VO_3 and PEG-200 and left under vigorous stirring for 1 h. Finally, orange-yellow colloids of BiVO_4 were obtained (Fig. 1).

In order to prepare powders of BiVO_4 , the colloids made as described above were additionally treated. This treatment involved mixing of certain amounts of colloidal BiVO_4 with 5 times the amount of distilled water. A formed precipitate of BiVO_4 particles was then separated from the obtained mixture by centrifugation (15 min @ 4000 rpm), and the collected precipitate was washed several times with water and dried in an oven at 110 °C for 24 h. The resulting yellowish-brown powders of BiVO_4 were thoroughly characterized by a wide variety of methods. The samples, respectively corresponding to precursor concentrations of 0.075 M, 0.050 M, and 0.025 M, exhibited pure tz- BiVO_4 structure and they are referred to as 1, 1A and 1B.

A second series of samples was synthesized as follows. The tz- BiVO_4

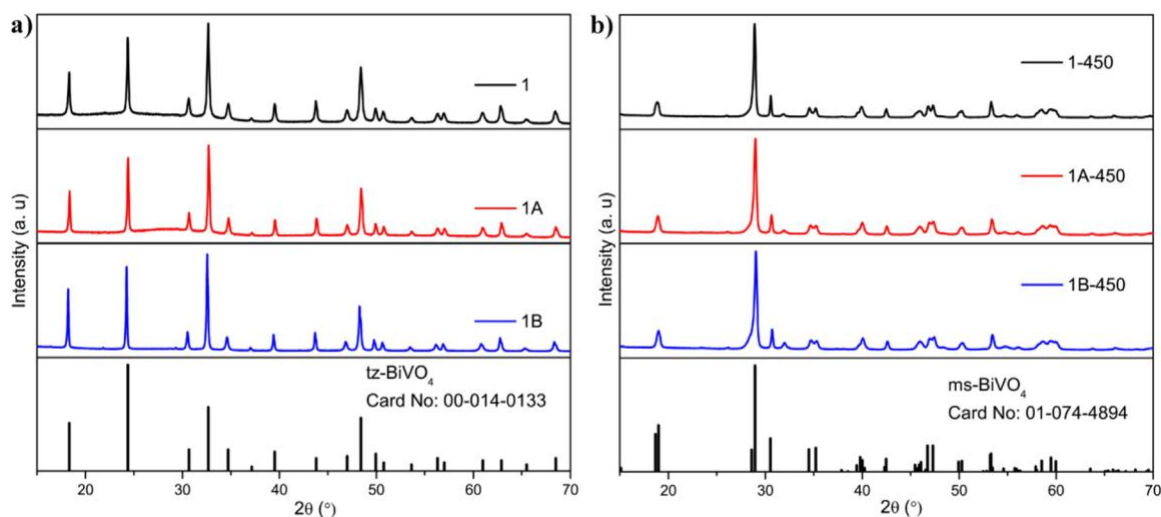


Fig. 2. XRD patterns of: a) tz-BiVO₄ and b) ms-BiVO₄ powders.

powders were annealed in air at 450 °C for 24 h and yellow-orange powders (labeled as 1-450, 1A-450, and 1B-450) were obtained. These powders were subjected to detailed characterization studies and it was shown that they exhibit the monoclinic scheelite-type structure (ms-BiVO₄).

2.2. Instrumentation

Crystalline structure of the samples was examined by powder X-ray diffraction (XRD) measurements on a Rigaku SmartLab diffractometer using Cu-K α radiation ($\lambda = 0.15405$ nm). Diffraction data were re-recorded with a step size of 0.02° and a counting time of 0.7°/min over the angular range 2θ from 10° to 100°. Transmission electron microscopy (TEM) studies were done on a Tecnai G20 (FEI) system operating at an accelerating voltage of 200 kV. The samples were placed on a perforated carbon film (S147-4, Agar scientific) and dried in air for 24 h. It was observed that at high doses of electron radiation defects were induced into the crystals until their crystalline structure dis-appeared. Hence, for HRTEM images the electron beam intensity was strongly reduced by inserting a condenser aperture and by decreasing the spot size. Diffuse reflection spectra measurements were recorded with 1 nm resolution on a Shimadzu UV-Visible UV-2600 (Shimadzu Corporation, Japan) spectrophotometer equipped with an integrated sphere (ISR-2600 Plus (for UV-2600)) in the range from 350 nm to 800 nm. FTIR spectroscopy measurements were performed on Nicolet TM 380 FT-IR spectrometer with Smart Orbit ATR accessory (Thermo Electron Corporation, Madison, U.S.A). Brunauer-Emmett-Teller (BET) surface area and porosity measurements were carried out by N₂ ad-sorption at -196 °C using Surfer (Thermo Fisher Scientific, USA). The pore size distribution was estimated by applying the Barrett-Joyner-Halenda method to desorption branch of isotherms, while mesopore surface and micropore volume were estimated using the t-plot method [17,18]. The thermal stability of the samples was investigated by simultaneous non-isothermal thermo-gravimetric analysis (TG) and differential thermal analysis (DTA) using a Setaram Setsys Evolution 1750 instrument. The measurements were performed on powder samples (cca. 10 mg each) at a heating rate of 10 °C/min, in dynamic nitrogen atmosphere with a gas flow rate of 20 ml/min, and in the temperature range of 30–900 °C.

2.3. Photocatalytic and adsorption test

Methyl orange (MO), anionic and water soluble azo dye, was used as a representative dye pollutant to evaluate photocatalytic activity of our

BiVO₄ samples. Removal of MO in aqueous solutions was carried out in an immersion-type cylindrical photochemical reactor (with an inner diameter of 10 cm and 12 cm in height). Adsorption experiments were carried out in the dark before subsequent photocatalytic experiments with light illumination. In photodegradation experiments a suspension of BiVO₄ catalyst powder and MO dye was exposed to artificial light from Osram Ultra-Vitalux 300 W lamp (radiated power 315–400 nm (UVA) = 13.6 W; radiated power 280–315 nm (UVB) = 3.0 W) placed 15 cm above the reactor. Temperature was maintained at 18 °C by continuous flow of water through the reactor during the experiments. In a typical test, MO was dissolved in 200 ml of deionized water to make a 5 mg/L solution. Catalyst concentration was 1 g/L.

During adsorption/photocatalytic experiments, MO dye solution with BiVO₄ catalyst powder was continuously magnetically stirred, and, at appropriate time intervals, fixed amounts of the suspension were collected. The MO concentration was monitored over time by tracking the change of absorbance at a wavelength of 464 nm using the UV-Vis absorption spectrophotometer. Prior to light illumination, the photo-catalyst/MO suspension was stirred in dark for 180 min to ensure ad-sorption-desorption equilibrium.

3. Results and discussion

Two series of samples were prepared and characterized: the as-prepared tz-BiVO₄ samples, respectively corresponding to precursor concentrations of 0.075 M, 0.050 M, and 0.025 M, and referred to as 1, 1A and 1B. The samples annealed at 450 °C (ms-BiVO₄) are labeled as 1-450, 1A-450, and 1B-450 (see Experimental Section).

3.1. Structural and microstructural properties of tz-BiVO₄ and ms-BiVO₄ nanoparticles

X-ray diffraction patterns of the as-prepared and annealed powders, respectively, are shown in Fig. 2, while structural details are given in Table 1. As it will be seen, the samples crystallize either in a zircon-type tetragonal or in a scheelite-type monoclinic structure. XRD patterns given in Fig. 2a clearly show the presence of a single tetragonal zircon-type phase (space group I41/amd, card No. 00-014-0133) and no peaks from any other phase or impurity. Similarly, patterns of the annealed powders (Fig. 2b) reveal the presence of a pure single monoclinic scheelite-type phase (space group: I2/b, card No. 01-074-4894).

The absence of impurities and very small shift of reflections compared to the reflection positions of bulk BiVO₄ indicate that nano-particles were successfully synthesized. In addition, relatively intense

Table 1
Structural parameters of tz-BiVO₄ and ms-BiVO₄ nanoparticles.

Sample	tz-BiVO ₄			ms-BiVO ₄		
	1	1A	1B	1-450	1A-450	1B-450
Crystallite size (nm)	9.4	4.0	4.3	21.1	16.3	16.5
a (Å)	7.31	7.30	7.30	5.19	5.18	5.18
b (Å)	7.31	7.30	7.30	5.11	5.10	5.10
c (Å)	6.49	6.47	6.47	11.70	11.70	11.69
V (Å ³)	346.80	344.79	344.79	310.29	309.09	308.83

reflection peaks suggest that the as-synthesized nanoparticles were highly crystalline, and no additional thermal treatment was required to produce tz-BiVO₄. However, in order to obtain the ms-BiVO₄ nanoparticles, the as-synthesized samples had to be annealed at 450°C. The average crystallite sizes of 4–9.4 nm for tz-BiVO₄ and 16.3–21 nm for ms-BiVO₄ were estimated from the diffraction peaks by the Halder–Wagner method (see Table 1).

Representative HRTEM images (for both low and high magnifications) of tz-BiVO₄-1A and ms-BiVO₄-1A nanoparticles are presented in

Fig. 3. These images show nanocrystals in sizes of 5–10 nm in the case of tz-BiVO₄ and larger polycrystalline particles in range of 20–60 nm for ms-BiVO₄. These estimates are somewhat consistent with the crystallite sizes evaluated from the powder XRD measurements.

3.2. Thermal properties of tz-BiVO₄ and ms-BiVO₄ nanoparticles

The TGA-DTA analysis was used to find optimal calcination temperature and to determine the phase changes between tz-BiVO₄ and ms-BiVO₄, while DSC was used to see main differences between the DSC curves for tz-BiVO₄ and ms-BiVO₄ nanoparticles. Thermal degradation properties of tz-BiVO₄-1A nanoparticles are given in Fig. 4. The results of the TGA-DTA analysis of all samples corresponded to the classical thermal behavior of BiVO₄ [19]. There is no significant weight loss in the TGA curve of BiVO₄. It could be roughly generalized that the TGA decomposition of BiVO₄ consists of four-stage weight loss at temperatures in the range of about 30–100 °C, 100–270 °C, 270–550 °C and 550–900 °C. The first stage of weight loss for the sample was 0.68%, second 2.12%, third 1.27% and fourth 0.54%. The total mass loss in the TGA of tz-BiVO₄-1A sample was about 4.6%. The DTA curves contain 4

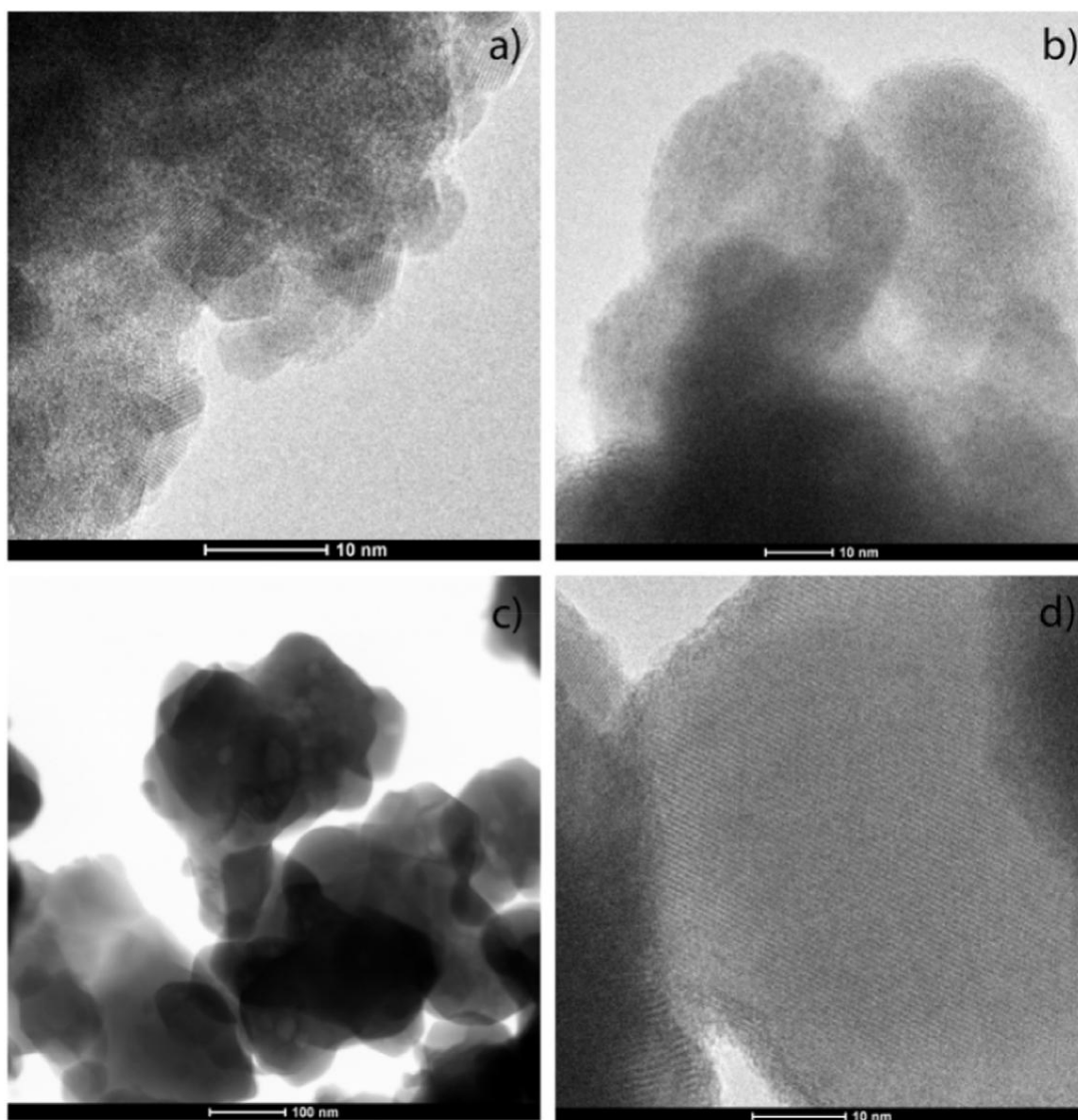


Fig. 3. TEM images of: tz-BiVO₄-1A (a, b) and ms-BiVO₄-1A (c, d) nanoparticles at different magnifications.

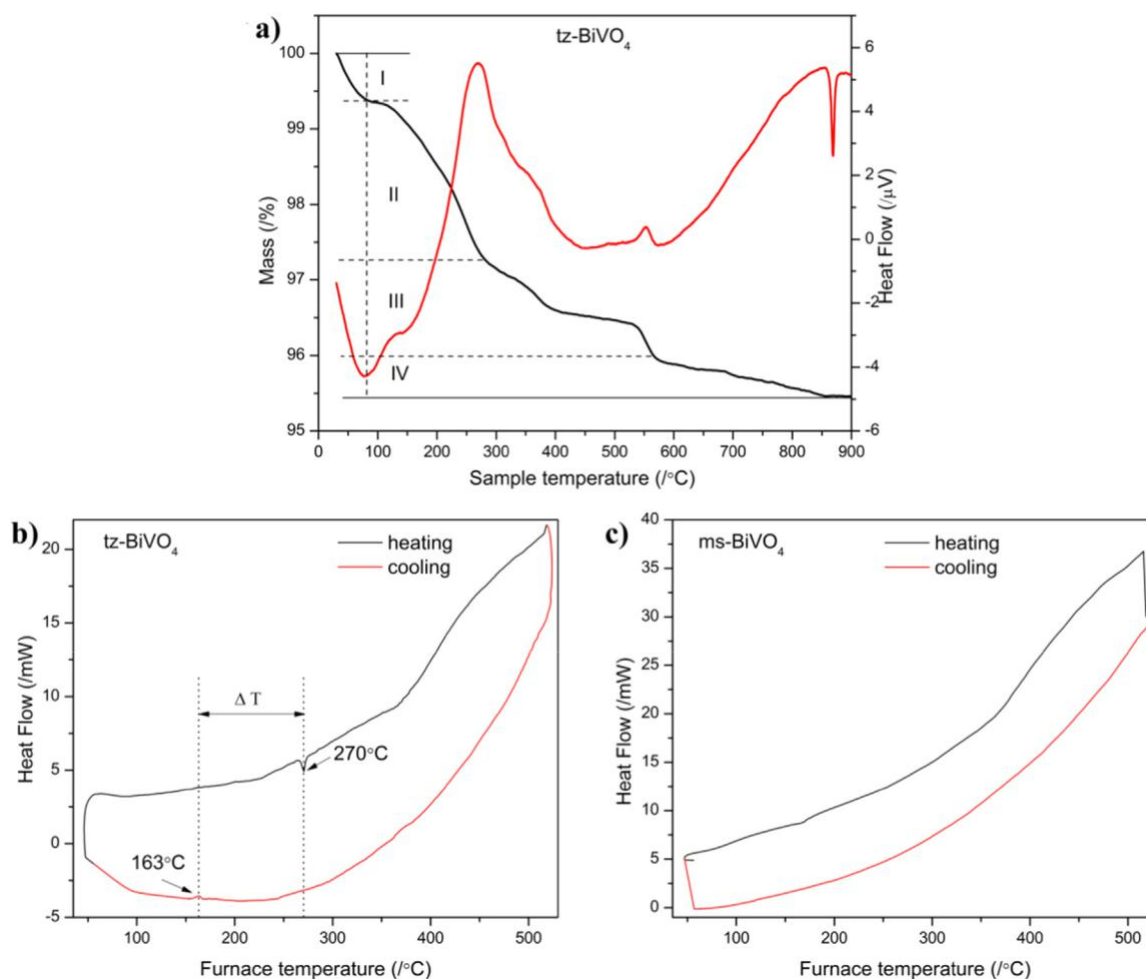


Fig. 4. a) TGA/DTA curves and DSC curves for b) tz-BiVO_4 -1A and c) ms-BiVO_4 -1A-450 nanoparticles between 20 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$ with a heating/cooling rate of 10 $^{\circ}\text{C min}^{-1}$.

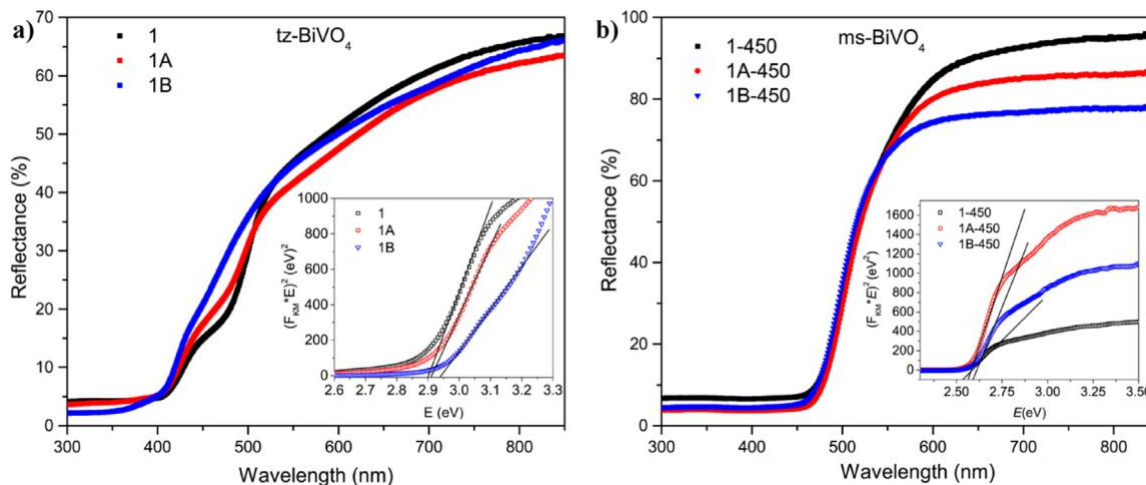


Fig. 5. UV-visible diffusive reflectance spectra of: a) tz-BiVO_4 and b) ms-BiVO_4 nanoparticles; insets show Kubelka-Munk plots and estimations of band-gap energies.

endothermic peaks observed at about 77, 150, 570 and 870 $^{\circ}\text{C}$ and two exothermic peaks at about 270 $^{\circ}\text{C}$ and 550 $^{\circ}\text{C}$.

Peak from DTA curve at 850 $^{\circ}\text{C}$ corresponds to the melting point of BiVO_4 . The phase changes of tz-BiVO_4 and ms-BiVO_4 samples were studied by differential scanning calorimetry (DSC) as shown in Fig. 4b and c.

Main difference between the DSC curves for tz-BiVO_4 and ms-BiVO_4

nanoparticles is the appearance of endothermic and exothermic peaks at different temperatures during heating-cooling processes in tz-BiVO_4 nanoparticles compared with the ms-BiVO_4 nanoparticles.

The phenomenon is so-called thermal hysteresis and it is equivalent to the difference between the temperatures of maximal endothermic peak during heating ($T_h = 270$ $^{\circ}\text{C}$) and maximal exothermic peak during cooling ($T_c = 163$ $^{\circ}\text{C}$), i.e. $T = T_h - T_c = 107$ $^{\circ}\text{C}$. Thermal

hysteresis occurs in these samples because the transitions between various structure phases occur at different temperatures for both the heating and cooling processes. This phenomenon does not occur often and could be attributed to the size of the nanoparticles. Namely, as we discussed above, tz-BiVO₄ nanoparticles have diameters in range 5–10 nm, while ms-BiVO₄ polycrystalline nanoparticles could be re-ferred to as bulk material. It is in full agreement with literature reports of ellipsoidal BiVO₄ expressing the phenomenon of thermal hysteresis compared to the bulk BiVO₄ nanoparticles [20]. In bulk ms-BiVO₄ nanoparticles this phenomenon does not appear due to irreversible monoclinic structure phase switch occurring at about 500 °C.

3.3. Optical properties of tz-BiVO₄ and ms-BiVO₄ nanoparticles

3.3.1. UV–Vis diffuse reflectance spectra

Fig. 5 shows the UV–visible diffuse reflectance spectra of the BiVO₄ powders with different structures. All the samples exhibited a strong absorption band in the near UV region and had a steep absorption edge. Spectra of ms-BiVO₄ (Fig. 5(b)) show that the absorption was extended to the visible light region. The steep absorption edge suggests that the observed absorption is not caused by transitions involving impurity levels (impurity-to-band, band-to-impurity, or impurity-to-impurity transitions). Thus, it may be attributed to band-to-band electronic transitions from the top of the valance band to the bottom of the conduction band. The band gap, E_g , was estimated from the spectra according to the following equation:

$$(F_{KM} \times hv)^{1/n} = A (hv - E_g) \quad (1)$$

where F_{KM} is the Kubelka–Munk function, with $F_{KM}(R) = (1 - R)^2 / (2R)$, where R is the observed reflectance, A is a constant and $E = hv$ is the photon energy. The values of n for direct allowed, indirect allowed and direct forbidden transitions are $n = 1/2, 2,$ and $3/2,$ respectively. BiVO₄ is a direct gap semiconductor, therefore $n = 1/2$. According to Eq. (1), a corresponding band gap value, E_g , was determined from a plot of $(F_{KM} \times E)^2$ versus incident light energy E by extrapolating the steepest portion of the graph to where it intersected the E axis. As shown in the insets of Fig. 5, the calculated band gap energies are: 2.90 eV, 2.91 eV and 2.94 eV for tz-BiVO₄-1, 1A and 1B, and 2.53 eV, 2.56 eV and 2.59 eV for ms-BiVO₄-1-450, 1A-450 and 1B-450, respectively. Note that in the case of ms-BiVO₄, E_g is somewhat larger than the value reported for the bulk material (2.40 eV), while the band gap energies of tz-BiVO₄ are in a good agreement with the data previously reported [3].

3.4. Photocatalytic/adsorptive performance of tz-BiVO₄ and ms-BiVO₄ nanoparticles

3.4.1. Adsorption isotherms (BET experiments)

Nitrogen adsorption/desorption isotherms (Fig. 6) at temperature of liquid nitrogen (-196 °C) for tz-BiVO₄ and ms-BiVO₄ were measured, and isotherm data for each powder were used to estimate specific surface area, average pore size, pore size distribution, mesopore surface area, micropore volume and mesopore volume. All samples showed a type IV isotherm curve with an H3 hysteresis loop according to IUPAC (the International Union of Pure and Applied Chemistry) classification, which is indicative of a mesoporous material [18,21]. Note that, in terms of the IUPAC nomenclature, porous materials are classified as microporous (pore diameter < 2 nm), mesoporous (2 nm < pore diameter < 50 nm), and macroporous (pore diameter > 50 nm). Adsorption/desorption isotherms on tz-BiVO₄ are presented in Fig. 6 as an illustration of N₂ adsorption measurements.

Values of the specific surface area (S_{BET}) of all the synthesized materials, calculated by means of the BET method, are listed in Table 2. Pore size distributions were estimated from the adsorption branch of the N₂ isotherms using the Barrett–Joyner–Halenda model. It was found

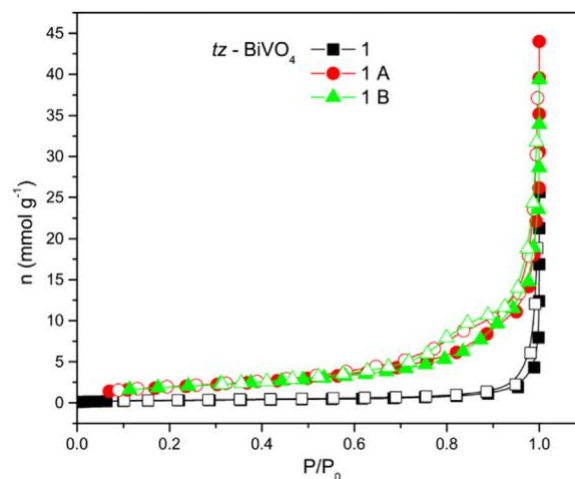


Fig. 6. Nitrogen adsorption/desorption isotherm curves (solid symbols – adsorption, open symbols – desorption) of the tz-BiVO₄ samples.

Table 2

Porous properties of synthesized tz- and ms-BiVO₄ samples.

Sample		SBET (m ² /g)	S _{meso} (m ² /g)	r _{med} (nm)
1	tz-BiVO ₄	5		9.0
1A		34		4.6
1B		32		5.0
1-450	ms-BiVO ₄	5		9.7
1A-450		10		11.2
1B-450		7		10.3

that the studied samples were mesoporous regardless of their crystalline structure (see Table 2 for values of mean pore radius, r_{med}) and in the case of tz-BiVO₄ with most pores in radii from 2 to 10 nm.

For ms-BiVO₄ (the samples 1A-450 and 1B-450) photocatalysts, thermal treatment at 450 °C caused the decreases in surface area and the increase in r_{med} , as expected. The conclusions regarding meso-porosity were further confirmed by an additional t-plot analysis showing that there was no microporosity present in any of the samples. The t-plot method provides estimates for micropore volume (V_{mic}), mesopore surface area (external surface area, S_{meso}), and micropore surface area (S_{mic} ; $S_{mic} = SBET - S_{meso}$) (see Table 2). Values of V_{mic} and S_{meso} were calculated from the intercept and slope of the straight line in the t-plot, respectively.

Most ms-BiVO₄ materials studied in the last 20 years were mainly composed of macroparticles and made by various methods with BET surface area values in the range of 1–8 m²/g. Note that 0.72 m²/g was measured for bulk ms-BiVO₄ synthesized by a solid-state method [19,20]. In this work, the nanostructured ms-BiVO₄ samples exhibited surface areas in accordance with those found in the literature for nano-sized powders: Ressnig et al. (7.4 m²/g) [22], Sun et al. (0.7–10.4 m²/g) [23], Hofmann et al. (7–16 m²/g) [24] and Luo et al. (10–17 m²/g) [25]. Zircon-type BiVO₄ has not been studied in a systematic way and only a few values of the specific area are available in the literature: 1.24 m²/g [8], 3 m²/g [9], 2.3 m²/g [26], 4.47 m²/g [27] and 5 m²/g [15]. However, for tz-BiVO₄ prepared here by a novel synthetic approach, a remarkable increase in measured surface area S_{BET} was observed: 32 m²/g and 34 m²/g, which is 45–47 times larger than that of the bulk ms-BiVO₄.

3.4.2. Photocatalytic performance

It has been generally accepted that photocatalytic performance of a semiconducting material is influenced by many factors: its structure, surface properties, energy bandgap, crystalline structure, crystallinity,

particles size and morphology, porosity, and porous texture (surface area, pore size and pore size distribution). Earlier reports indicate that the photocatalytic activity of BiVO₄ largely depends on the crystalline phases, specific surface area and the transport properties of photo-induced charge carriers. [13] Mesoporous materials, whose pore size range from 2 to 50 nm, are of interest because of their potential use in various fields including heterogeneous catalysis, energy, biotechnology, and nano-devices. Because of their high specific surface area and pore size, mesoporous materials are also promising adsorbents for removal of organic pollutants from aqueous solution.

Adsorptive and photocatalytic activity of BiVO₄ nanocrystalline powders synthesized through an ethylene glycol route at room temperature was evaluated by adsorptive removal and photocatalytic degradation of methyl orange (MO). The initial dye concentration (C₀) was 5 mg/dm³. At certain time intervals, the residual MO concentration (C) was spectrophotometrically measured at the characteristic absorption maximum of 464 nm arising from the “-N=N-” azo bonding. Plot of relative concentration of MO (i.e. C/C₀ ratio) against a treatment time t describes kinetics of the dye removal from a suspension of a BiVO₄ catalyst powder and an aqueous solution of the dye. The quantity (C₀ - C)/C₀ = 1 - C/C₀, which is usually expressed as a percentage (100 × (C₀ - C)/C₀), is called a removal (photocatalytic, or degradation) efficiency. Decolourization of MO was examined under two different experimental conditions: either there was no illumination and the BiVO₄-based photocatalyst was present, or the photocatalyst was utilized under light illumination. An artificial light source (Osram Ultra-Vitalux, 300 W) with a sun-like radiation spectrum from 280 to 1800 nm was used for illumination. Initial tests in the absence of the catalyst and under light exposure showed negligible degradation of the dye.

Adsorption experiments were carried out in the dark before photodegradation experiments. For both tz-BiVO₄ and ms-BiVO₄ powders, adsorption-desorption equilibrium of the dye on the catalyst surface was achieved within 180 min. It was found that adsorption levels were around 20% for all tz-BiVO₄ nanoparticles, whereas all ms-BiVO₄ samples exhibited negligible adsorption of MO. It is noteworthy that in either case adsorptive activity did not reflect changes in porosity. For all the samples, after adsorption equilibrium was reached, the zero time reading was chosen and then the dye solution with catalyst was exposed to UV-Vis light irradiation. Fig. 7a depicts the experimental data on the time-dependent photocatalytic removal of MO over different tz-BiVO₄ nanoparticles. As can be seen from the photocatalytic degradation curves, a contact time of 240 min was sufficient to achieve a removal efficiency of 100% in all photocatalytic activity tests. In Fig. 7b, a decrease in the absorption maximum of tz-BiVO₄-1A indicating a rapid degradation of the dye is presented.

The kinetics of degradation was approached using the Langmuir-Hinshelwood model (when the initial adsorbate concentration is low) and the pseudo-first-order kinetics. The experimental kinetic data were fitted to pseudo-first-order kinetic equation in its integrated form: $\ln(C_0/C) = k_{app} t$, where C₀ is the initial MO concentration, C is the concentration at reaction time t and k_{app} is the (apparent) rate constant [28]. For the samples 1, 1A and 1B, by the linear regression analysis (with intercept = 0), the k_{app} (min⁻¹) values (along with regression R²-squared values) were estimated to be 0.016 (0.941), 0.033 (0.994) and 0.018 (0.996) respectively. Overall, the tz-BiVO₄-1A sample showed greatest activity and observed differences in efficiency among the three samples were consistent with changes in a specific surface area. However, the difference between tz-BiVO₄-1 and tz-BiVO₄-1B was not as great as would have been expected from a change in SBET alone.

Clearly, this and other experimental findings presented here require a systematic and detailed study. These first results, however, indicate that the optimized tetragonal zircon-type-BiVO₄ exhibited a markedly good performance with respect to MO removal and it would be interesting to examine it further for use in water and wastewater treatments [29,30].

To characterize the overall performance of a photocatalyst, consideration should be given not just to its activity, but to reusability features as well. Since tz-BiVO₄-1A showed best efficiency in removing the MO from solutions of the dye, its reusability was studied. The extent of reusability was determined by reusing the catalyst for subsequent photodegradation experiments. Between the two successive photocatalytic experiments, used powder of tz-BiVO₄-1A was washed several times with water and buffer solutions and dried at 110 °C for 24 h. Afterwards, the powder was homogenized and submitted to yet another photocatalytic experiment of MO degradation. As Fig. 8 shows, there was no significant decrease of activity not even after the fifth use.

In our tests, nanosized ms-BiVO₄ (with specific surface area 5–10 m²/g) showed less catalytic degradation efficiency under UV-Vis illumination. The time-dependent dye decolorization of MO solution over all monoclinic scheelite-type materials and UV-Vis absorption spectra of MO (over ms-BiVO₄-1A) are given in Fig. 9. The removal efficiency of 30–35% was observed for all prepared catalysts. It was found that all tested ms-BiVO₄ samples exhibited a good reusability; there was no significant loss of photocatalytic activity of ms-BiVO₄-1A powder over three consecutive degradation cycles. The diminution of activity was around 3%.

Finally, FTIR analysis showed that there was no MO adsorbed on the catalyst surface (representative spectra are given in Fig. 10), which leads us to conclusion that MO was adsorbed inside mesoporous structure of the tz-BiVO₄. A very strong absorption band at 742 cm⁻¹

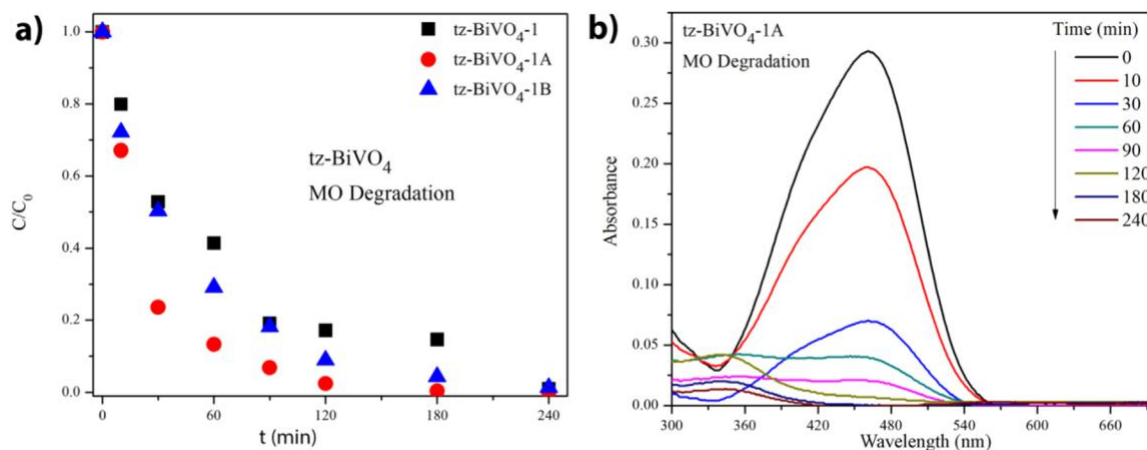


Fig. 7. a) Photocatalytic degradation curves of MO solution (5 mg/L) over different tz-BiVO₄ samples (1 g/L) under UV-Vis light irradiation. C₀ and C_t are the concentrations of MO before irradiation and after it is irradiated for t min, respectively. b) Time dependence of the UV absorption spectrum of MO dye in the aqueous suspension of tz-BiVO₄-1A.

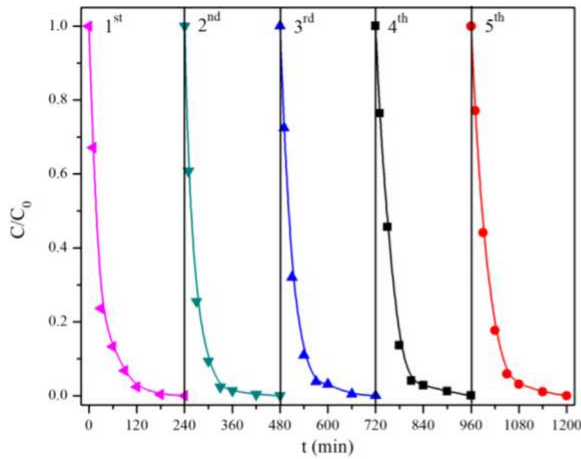


Fig. 8. Reusability of tz-BiVO₄-1A powder.

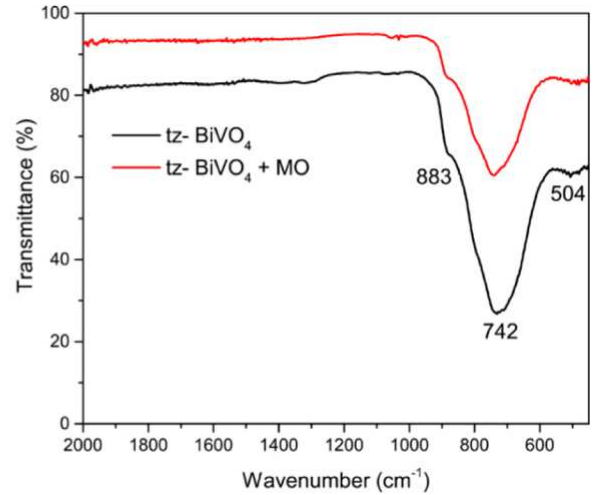


Fig. 10. FTIR spectra of tz-BiVO₄-1A powder and tz-BiVO₄-1A powder after photodegradation experiment.

with a shoulder at 883 cm⁻¹ is associated with stretching modes (asymmetric and symmetric) corresponding to the V–O bond, while an absorption band at 504 cm⁻¹ could be ascribed to bending of the va-nadate anion VO₄³⁻ [8,31].

The above results show that pure tz-BiVO₄ performed better than ms-BiVO₄ in both adsorption and photocatalytic degradation experiments. In particular, the tz-BiVO₄-1A sample displayed enhanced photocatalytic activity indicating that MO solution could be effectively decolorized under UV–Vis light. These initial results suggest that optimized zircon-type BiVO₄ may be used as a suspension-type photo-catalyst for organic pollutants in aqueous environment. However, as far as we are aware, it seems that no such experimental data have been reported before. As a matter of fact, in few available photocatalytic studies [9,10,13–16] chemically pure single-phase tz-BiVO₄ was found to be a very poor photocatalyst. Only according to one report, it exhibited better adsorption performance (for methyl blue) than ms-BiVO₄ [10], but its overall activity was significantly lower. Further, although better photocatalytic performance of tetragonal BiVO₄ compared to the monoclinic one was stated in Conclusions of [32], the sample under investigation, in fact, was tz/ms composite BiVO₄ (95% of tetragonal phase).

It should be remarked that using dyes to assess the photocatalytic efficiency is not that straightforward and could be problematic [33]. However, although the dye degradation tests are significantly influenced by various factors and may suffer from some serious drawbacks and limitations, such as difficulty to distinguish between photocatalytic

and photosensitization processes, they are inexpensive and their simplicity, easiness of use and rapidity are yet of great advantage. For these reasons, photodegradation was here utilized for first estimates of photocatalytic performance. In any case, these intriguing experimental findings were encouraging enough and clearly merit further, more elaborate investigation. It is noteworthy that tetragonal scheelite-type BiVO₄, ts-BiVO₄, the third of three commonly found polymorphs of bismuth vanadate, was recently shown to be moderately photo-catalytically active [9] although quite the opposite was suggested in the first reports [10,12].

4. Conclusions

As it can be evidenced by an exponential growth in the number of publications over the past decade, monoclinic scheelite-type BiVO₄ has attracted considerable research attention as a promising photocatalyst. However, tetragonal zircon-type BiVO₄ is still poorly understood and, here, our aims were to develop a novel low-temperature synthesis of nanostructured single-phase tz-BiVO₄ in a non-aqueous medium and to determine whether or not the new synthetic approach to tz-BiVO₄ influences its adsorption and/or photocatalytic performance (see Introduction).

To prepare nanostructured zircon-type BiVO₄ in a non-aqueous medium, a simple, non-conventional and easily scalable process was

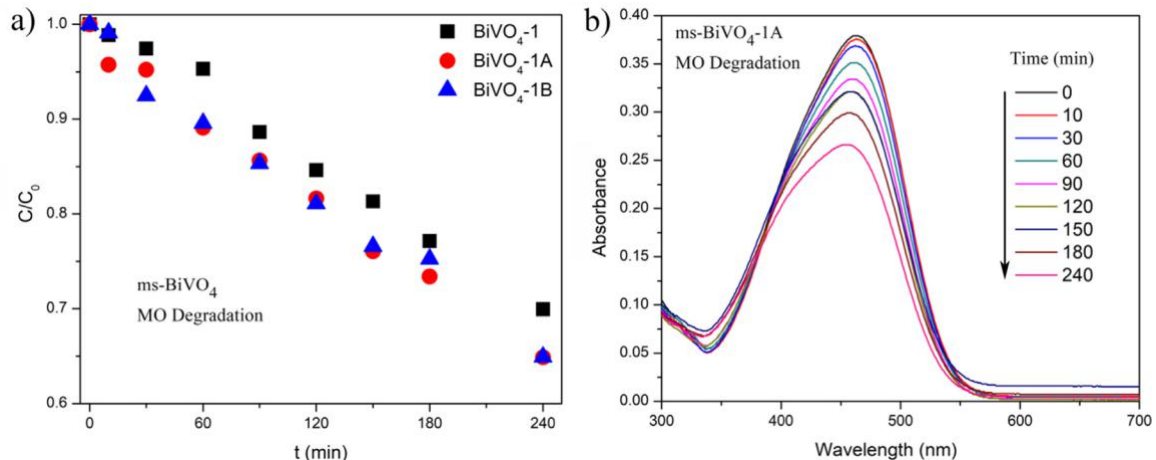


Fig. 9. a) Photocatalytic degradation curves of MO solution (5 mg/L) over different ms-BiVO₄ (1 g/L) samples under UV–Vis light irradiation. b) Time dependence of the UV absorption spectra of MO dye in the aqueous suspension of ms-BiVO₄-1A.

proposed. A controllable ethylene-glycol colloidal route at room temperature was for the first time utilized to successfully synthesize powdered tz-BiVO₄. XRD patterns of the obtained powders clearly showed presence of a pure single tetragonal zircon-type crystalline phase, while nanocrystals (5–10 nm in size) were revealed by TEM images. In addition, because of the irreversible tetragonal-to-monoclinic transition, it was possible to easily obtain powdered ms-BiVO₄ by annealing the as-prepared samples at 450 °C for 24 h. A pure single monoclinic scheelite-type phase was identified in all the annealed powders, while the average particle sizes found by TEM analysis (20–60 nm) were larger than those of the crystallites (estimated from the XRD patterns).

Crystalline phase effects on thermal and optical properties as well as on adsorption and photocatalytic activity were studied for both the as-prepared and annealed materials. To assess the extent to which the new way of preparation of tz-BiVO₄ influenced its adsorption and photocatalytic performance, for all tz-BiVO₄ and ms-BiVO₄ samples, nitrogen adsorption-desorption analysis was carried out and photocatalytic activity was evaluated by degradation of methyl orange in an aqueous solution.

It was found that the new synthetic approach to tz-BiVO₄ had a significant effect on its porosity and photocatalytic activity towards degradation of MO solution. All the prepared materials were meso-porous and for some tz-BiVO₄ powders a remarkable increase in measured surface area S_{BET} was observed: 32 m²/g and 34 m²/g, which is 45–47 times larger than that of the bulk ms-BiVO₄, or ~7 times higher than that reported thus far for this phase. Also, tz-BiVO₄ showed better overall performance than ms-BiVO₄ in adsorption/photocatalytic experiments of methyl orange degradation under sun-like illumination. To the best of our knowledge, it seems that such findings, particularly enhanced and better photocatalytic performance of tetragonal zircon-type BiVO₄, were never reported before in the open literature. It could be expected, therefore, that the present preparation method and initial experimental observations of an ongoing research will both arouse interest in scarcely studied tetragonal zircon-structured BiVO₄ and facilitate as well as speed up further research of its properties.

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