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### Porphyrin cobalt(II) Complex linked to TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite: Alcohol oxidation using nanohybrid materials as implement photocatalyst with mechanism approach Parvin Askari, Sajjad Mohebbi\*

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#### Abstract

A new nanohybrid catalyst by covalent linking of tetraacetate porphyrin cobalt(II) complex to  $TiO_2/BiVO_4$  nanocomposite was synthesised and its photocatalytic efficiency toward alcohol oxidation under visible light irradiation monitored by GC. This nanohybrid materials as implement photocatalyst was characterized by physicochemical techniques FE-SEM imaging, EDS, XRD, DRS, BET and FT-IR spectroscopy. Also its role as photocatalyst evaluated with mechanismetic approach in aerobic condition by changing several parameters such as solvent, substrate, oxidant, catalysts amount, reaction temperature and ratio of oxidant to substrate. The photocatalytic activity of this nanohybrid catalyst with average size 24 nm increased almost twice compared to  $TiO_2/BiVO_4$  nanocomposite from 35% to 85% conversion while the selectivity was 99%. A plausible mechanism was proposed. In fact, the cobalt porphyrin complex as a light sensitizer improves the photocatalytic activity by impregnation onto the  $TiO_2$  surface. The photocatalyst was reused for several times without significant loss of activity. So, this nanohybrid robust catalyst has excellent advantages such as facile synthesis, high activity and selectivity using  $O_2$  and other environmental friendly oxidants in mild condition toward aldehyde production.

Keywords: Photocatalyst, nanohybrid materials, aerobic oxidation, nanocomposite.

#### 1. Introduction

Semiconductor oxides are employed in the field of photocatalyst due to their specific physiochemical and optical properties.<sup>1,2</sup> In a photocatalytic process, generation of electronhole pairs  $h^+e^-$  by incident irradiation on semiconductor materials is required.<sup>3</sup> The potential of these excitons have capable of achieving the reduction and oxidation of the chemical reagents.<sup>3</sup> This bring semiconductors useful for a wide range of applications such as air purification, CO<sub>2</sub> reduction, effective degradation of organic pollutants in water or air, and hydrogen production through photocatalytic water-splitting processes.<sup>4,5</sup> Due to wide band gap of the current well known photocatalysts such as TiO<sub>2</sub>, only very narrow fraction of the solar radiation in UV light region could be used for excitation of electrons from conduction band to valence band of  $TiO_2$ .<sup>6</sup> Therefore, to utilize the visible region of the solar spectrum for photocatalytic phenomenon, tailoring the optical properties of titania is indispensable.<sup>7</sup> In this regard,  $TiO_2$  could be modified by metal doping, non-metal doping, ion implantation and surface sensitization by organic dyes.<sup>8,9</sup>

Usually, the metal oxides have shown high level of the valence band at around 3.0 V that causes a significant energy loss. But, the BiVO<sub>4</sub> as an attractive semiconductor in visible light region has relatively high conduction band edge position with band gape ( $E_g$ ) in range of 2.4–2.5 eV.<sup>10,11</sup> The reason could be related to composed of d orbitals level of the transition metal oxides comparing to 6s orbital of Bi in the VB of monoclinic BiVO<sub>4</sub>, which maintain the CB edge level decreasing to the hydrogen reduction potential as well. Through three crystalline forms of BiVO<sub>4</sub>, monoclinic BiVO<sub>4</sub> with band gap 2.4 eV shows higher photocatalytic activities than tetragonal BiVO<sub>4</sub> with band gap 3.1 eV. So, the visible-light driven efficiency of photocatalyst is influenced by its crystal form and photophysical properties.<sup>12</sup>

Hence, metalloporphyrin complexes could be considered as efficient sensitizers to harvest visible light on the surface of TiO<sub>2</sub> because of their structural analogues to chlorophyll in plant photosynthesis.<sup>13</sup> Due to an extensive delocalized  $\pi$  electron system, porphyrins have high absorption extension coefficient in the visible region.<sup>14–16</sup> Also, porphyrin with excellent photophysical properties have small singlet-triplet splitting, high quantum yield for intersystem crossing and long triplet state lifetime.<sup>13</sup>

Upon extending research in this field, meso-tetra(4-carboxyphenyl)porphyrinato cobalt(II) (CoTCPP) on TiO<sub>2</sub>/BiVO<sub>4</sub> was successfully prepared by a facile method<sup>17</sup> and was used as efficient photocatalyst under visible light irradiation toward alcohol oxidation in mild condition.

#### 2. Experimental

#### 2.1. Materials

4-formylmethylbenzoate, nitrobenzene, pyrrole, propionic acid, potassium hydroxide, hydrochloric acid, dimethylformamide, tetrahydrofuran, titanium (IV) isopropoxide, NH<sub>4</sub>VO<sub>3</sub>, Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and alcohols including benzyl alcohol, 4-cholorobenzyl alcohol, 4-

methoxybenzyl alcohol and 4-nitrobenzyl alcohol were purchased from Merck and Sigma-Aldrich suppliers and used as received without further purification. Pyrrole was distillated.

#### 2.2. Measurements

The field emission scanning electron microscopy (FESEM) images were recorded on a TSCAN, S-300000 microscope. Energy-dispersive X-ray spectroscopy (EDS, TSCAN) was used for the elemental analysis of nanomaterials. FT-IR spectra was recorded on a Bruker VERTEX 80 v model spectrometer (KBr pellets). X-ray diffraction (XRD) patterns of the samples were recorded on a Holland-Philips X-ray powder diffractometer using Cu Ka radiation ( $\lambda$ = 0.1542 nm) with scattering angles of 10° < 2 $\theta$  < 80°, operating at 40 keV, and a cathode current of 20 mA. UV-Vis diffuse reflectance spectra (DRS) of the samples were recorded at room temperature with an Avaspec-2048-TEC spectrophotometer. Ultravioletvisible spectra (UV-Vis) were measured on the Varian Cary 100 UV-Vis spectrophotometer in range of 350-800 nm. The photoluminescence (PL) spectra recorded by a Cary Eclipse fluorescence spectrophotometer (Varian, Inc.) with a xenon discharge lamp with a wavelength of 325 nm at room temperature. Nitrogen adsorption-desorption isotherms were measured with an adsorption instrument (Tristar II 3020 Micromeritics) at 77 K to determine the Brunauer-Emmett-Teller (BET) surface area and pore size distribution. Photocatalytic reactions were carried out under visible light irradiation of 7 W at 550 nm. The reaction progress was monitored by GC-MS, Agilent 7890A with both detectors FID and Mass Agilent 597530.

#### 2.3. Preparation of Cobalt(II)-meso-tetra (4-carboxyphenyl) porphyrin (Co-TCPP)

In the first, meso-tetrakis (4-carboxymethylphenyl) porphyrin (H<sub>2</sub>TCPP) was prepared using reported synthetic methodologies as follow.<sup>18</sup> To a mixture of 4-formylmethylbenzoate (20 mmol, 3.42 g), propionic acid (70 mL) and nitrobenzene (15 mL), 20 mmol distillated pyrrole (1.42 mL) was added. The mixture was refluxed under 125-130 °C condition for 3.5 h and cooled down. Lately, the purple crystals of the H<sub>2</sub>TCPP was filtrated and washed with distilled water and dried in oven at 70 °C. In the second step, the tetracarboxylic acid was obtained by the hydrolysis of 4-carboxymethylphenyl porphyrin with 10% aqueous potassium hydroxide in tetrahydrofuran/ethanol (1:1) as solvent. The meso-tetrakis (4-carboxyphenyl) porphyrin (TCPP) as a purple powder also resulted from Acidification (pH = 2) of an aqueous suspension of the porphyrin tetrapotassium salt with 1 M HCl and subsequent filtration. UV-Vis: 419 (Soret band), 516, 551, 596, 650 (Q bands). FT-IR (cm<sup>-1</sup>): 1725 (str., C=O), 3500 (str., OH) and 3300 (str., N-H). In final step, The TCPP was metallated by Co<sup>2+</sup> using

literature procedures.<sup>19</sup> 0.1 mmol of TCPP and 0.5 mmol cobalt acetate tetrahydrate was dissolved in 20 ml of DMF. The mixture was refluxed for 2 h then DMF was removed by distillation and the CoTCPP precipitated in water. Finally, the porphyrin was filtered and dried at room temperature. UV-Vis (nm): 430 (Soret band), 555, 594 (Q bands). FT-IR (cm<sup>-1</sup>): 1712 (str., C=O), 3456 (str., OH).

#### 2.4. Preparation of Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid

#### 2.4.1. Preparation of TiO<sub>2</sub>

4.9 ml of titanium (IV) isopropoxide was peptized in 58 ml of bi-distilled water. Follow, 0.419 ml of concentrated HNO<sub>3</sub> at 313 K was added. The process takes 24 h. The resulted sol was consequently basified to reach pH 7 using 2 M NaOH. The resulting white suspension was left stirring for 30 min. During hydrothermal procedure, the sol was placed in an oven dryer using Teflon-lined stainless steel autoclave at 453 K for 24 h. Finally, product was separated by centrifugation, rinsed with bi-distilled water, ethyl alcohol and dried. These processes are conducted for 12 h under a condition of 373 K for 2 h.<sup>20</sup>

#### 2.4.2. Preparation of BiVO<sub>4</sub>

5 mmol of  $NH_4VO_3$  in 2 ml of 2 M NaOH was added to a solution of 5 mmol of  $Bi(NO_3)_3.5H_2O$  in 2 ml of 4 M HNO<sub>3</sub> to form an intense orange suspension of  $BiVO_4$  precursor. The suspension was basified to pH 7 using 2 M NaOH to obtain a yellow suspension. During the hydrothermal procedure, the suspension was stirred for 30 min and placed in a convection oven using a Teflon-lined stainless steel autoclave under a condition of 453 K for 24 h. The yellow solid product was separated by centrifuge, rinsed with bi-distilled water, EtOH and expose into air for 12 h. Finally, BiVO<sub>4</sub> was dried at 373 K for 2 h.<sup>20</sup>

#### 2.4.3. Preparation of TiO<sub>2</sub>/ BiVO<sub>4</sub> nanocomposite

The TiO<sub>2</sub>/BiVO<sub>4</sub> composite was prepared by hydrothermal process with weight ratio 20% of BiVO<sub>4</sub> to 80% of TiO<sub>2</sub>. A titania sol of Ti(O<sup>i</sup>Pr)<sub>4</sub>, as mentioned earlier, was added to BiVO<sub>4</sub> precursor to reach the desired weight ratios. Afterwards, the whole mixture was basified to pH 7, stirred for 30 min and heated under a condition of 453 K for 24 h. The final solids were washed with bi-distilled water and EtOH and left in air for 12 h at room temperature consequently was dried at 373 K for 2 h.<sup>20</sup>

#### 2.4.4. Preparation of Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid

The linkage of Co-TCPP to the  $TiO_2/BiVO_4$  was done as follow: To a solution of 1 mg Co-TCPP in 15 mL methanol, 100 mg  $TiO_2/BiVO_4$  nanoparticles was added. The resulting suspension was stirred and refluxed at 40 °C for 8 h. In this way, the porphyrin was linked on the surface of  $TiO_2$  nanoparticles due to the interaction between the phenoxy of porphyrin and the hydroxyl groups on the surface of the  $TiO_2$  nanoparticles.

#### 2.5. General procedures for photocatalytic process

Photocatalytic reactions were carried out in a Pyrex glass cell while aerated by narrow nuzzle which equipped with the water circulation to keep the reaction temperature constantly. The LED lamp 7 W was applied as light source. In each catalytic reaction cycle, 10 mg of catalyst was dispersed in 1.5 ml solution of 0.1 mmol aromatic alcohol and sonicated for 30 seconds. Resulted suspension was transferred into the reaction cell under continuous stirring. The solution was placed in the dark condition for 20 min to insure equilibrium between adsorption and desorption. Then, the cell was irradiated by visible light ( $\lambda = 550$  nm) through a LED lamp for about 2 h. Reaction progress was monitored by GC by periodic sampling. After the reaction was completed, the catalyst was separated by centrifuge, and washed with acetonitrile for possible future reusing.

#### 3. Result and discussion

#### 3.1. Characterization of Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid

Co-TCPP was fixed on the surface of TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite through esterification reaction of carboxylic group of porphyrin with hydroxyl group of nanocomposite in mild condition. The obtained Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid was characterized.

The size and morphology of TiO<sub>2</sub> and BiVO<sub>4</sub> nanoparticles, TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite and Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid were determined by scanning electron microscopy (Figure 1). The SEM images of nanoparticles showed that the synthesized products were monodisperse with narrow size distributions. Also, the average size grew from 8 nm for TiO<sub>2</sub> to 24 nm for Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid. These results are in agreement with XRD. In fact, TiO<sub>2</sub> nanoparticles grow on the surface of the BiVO<sub>4</sub> and increase the size of TiO<sub>2</sub> nanoparticles. After modified TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite with metalloporphyrin, not only the size of nanoparticles was increased but also, the morphology of the nanohybrid was changed (Figure 1g-h). In this case, by high-magnification SEM images (Figure 1e)

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revelation could be seen the leaf-like porphyrin have radials growing on the surfaces of the nanocomposite.



**Fig. 1** Low- and high-magnification FESEM images of the TiO<sub>2</sub> (a, b), BiVO<sub>4</sub> (c, d), TiO<sub>2</sub>/BiVO<sub>4</sub> (e, f) and Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> (g, h).

The composition of TiO<sub>2</sub>, BiVO<sub>4</sub>, TiO<sub>2</sub>/BiVO<sub>4</sub> and porphyrin-anchored to TiO<sub>2</sub>/BiVO<sub>4</sub> nanoparticles were confirmed by energy dispersive spectroscopy (EDS) (Figure 2a-d). According to EDS analysis, the TiO<sub>2</sub> nanoparticles only consists Ti and O elements. Also, only Bi, V, and O elements was found in BiVO<sub>4</sub> nanocomposite. The molar ratios was reported on the base of EDS data sheet on the base of K $\alpha$  and M $\alpha$  in EDS, the exact weight percentage (W%) 16.52% and 65.90% was obtained for V and Bi, respectively that are equal to 1.03 mole ratio of V to Bi. Anyway, the Bi:V:O atomic molar ratio 1:1:4 was obtained, which indicated stoichiometric product BiVO<sub>4</sub>. The EDS analyses of the nanocomposite of TiO<sub>2</sub>/BiVO<sub>4</sub> (Figure 2c) were also performed to determine the Ti, Bi, V and O as major elements for TiO<sub>2</sub>/BiVO<sub>4</sub> compounds. Besides, the figure 2d shows the elements in modified nanocomposite. It was clearly confirmed the nanohybrid composition as containing Ti, O, Bi, V, N, C and Co.



Fig. 2 EDS spectrum of the TiO<sub>2</sub> (a), BiVO<sub>4</sub> (b), TiO<sub>2</sub>/BiVO<sub>4</sub> (c) and Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> (d).

The FT-IR of the samples was shown in supporting information, (Figure S1). In TiO<sub>2</sub> as prepared sample, the broad band at 3700 to 3000 cm<sup>-1</sup> and a band at 1639 cm<sup>-1</sup> were assigned to stretching of hydroxyl groups. A band between 784 and 560 cm<sup>-1</sup> was assigned to the Ti-O vibration. The symmetric and asymmetric stretching vibrations of V–O was appeared at 700-850 cm<sup>-1</sup>, and a band at 520 is due to the bending vibration of Bi–O bond in BiVO<sub>4</sub>. For the TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite, the V–O stretching vibrations shifted to 708 cm<sup>-1</sup> and 816 cm<sup>-1</sup>. Another band at 576 cm<sup>-1</sup> could be assigned to the bending vibration of Bi–O bond. Anyway, the vibration bands in the IR spectra of TiO<sub>2</sub>/BiVO<sub>4</sub> confirm existence both of Bi–O and V–O bonds with some small shifts. This indicates a successful bonding between BiVO<sub>4</sub> and TiO<sub>2</sub> in the mentioned hydrothermal process. The existence of CO-TCPP in nanohybrid was proved by comparing FT-IR, EDS and DRS of nanohybrid and nanocomposite. The FT-IR spectra of the Co-TPCC@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid clearly confirm the esterification of hydroxyl groups on the surface of nanocomposite with carboxylate group of porphyrin. Appearing new bands at 1616 cm<sup>-1</sup> and 1390 cm<sup>-1</sup>, also weakness of bands at 3421 cm<sup>-1</sup> could

be arguments toward covalence link between two moieties Co-TPCC-COOH and HO-TiO<sub>2</sub>/BiVO<sub>4</sub>. The weakness of band at 3421 cm<sup>-1</sup> is due to decreasing the number of hydroxyl groups on the surface of TiO<sub>2</sub>/BiVO<sub>4</sub> upon anchoring Co-TCPP on TiO<sub>2</sub>/BiVO<sub>4</sub>. In addition to FT-IR, strong stacking of porphyrin to surface of nanocomposite could be count as another argument to covalence bonding of carboxylate to hydroxyl groups on the surface of nanocomposite. Because, leaching of Co-TCPP was not observed after several washing of nanohybrid with the solvent. Both of washed nanohybrid and work up solvent was tested by IR, UV-Vis and EDS.

Figure 3 shows the XRD patterns of TiO<sub>2</sub>, BiVO<sub>4</sub>, TiO<sub>2</sub>/BiVO<sub>4</sub> and Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub>. Comparing the XRD patterns from the JCPD reference files, the diffraction peaks are in agreement with a Anatase and Rutile structure (JCPD=04-0477 and JCPD=77-0444 respectively). The diffraction peaks corresponded to  $(1 \ 0 \ 1), (0 \ 0 \ 4), (2 \ 0 \ 0),$  $(1\ 0\ 5)$ ,  $(2\ 0\ 4)$ ,  $(1\ 1\ 6)$  and  $(2\ 1\ 5)$  planes of crystalline TiO<sub>2</sub> by Anatase structure and  $(1\ 1\ 0)$ , (1 0 1) and (1 1 1) Rutile phase of crystalline TiO<sub>2</sub>. Figure 3b shows the XRD patterns of BiVO<sub>4</sub>. The diffraction peaks corresponded to (1 0 1), (1 1 2), (0 0 4), (2 0 0), (2 1 1), (1 0 5),  $(1 \ 2 \ 3), (2 \ 2 \ 0), (1 \ 1 \ 6), (1 \ 3 \ 2), (2 \ 2 \ 4), (3 \ 0 \ 5)$  and (2 \ 0 \ 8) planes of crystalline BiVO<sub>4</sub> by Tetragonal structure and (1 0 3), (1 1 0), (0 0 8), (1 1 6) and (2 1 3) Tetragonal phase of crystalline Bi<sub>2</sub>VO<sub>5.5</sub>. The XRD pattern of the TiO<sub>2</sub>/BiVO<sub>4</sub> composite materials (figure 3c) reveals the formation of the Anatase phase of TiO<sub>2</sub>. This trend is followed by the 20Bi-80Ti sample which the phase attributable to  $BiVO_4$  is not observed. Also, the X-ray pattern of Co- $TCPP(a)TiO_2/BiVO_4$  was corresponded to  $TiO_2/BiVO_4$  nanocomposite that means the structure of core nanocomposite remained stationary and robust (figure 3d)



Fig. 3 XRD patterns of (a) TiO<sub>2</sub>, (b) BiVO<sub>4</sub>, (c) TiO<sub>2</sub>/BiVO<sub>4</sub> and (d) Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub>.

Also, the specific surface area was measured from BET isotherms, and the pore size distribution diagram was obtained using BJH approach. Consequently, the value of BET surface area related to  $TiO_2$ ,  $TiO_2/BiVO_4$  and Co-TCPP@TiO\_2/BiVO\_4 were 17.56, 50.73 and 32.04 m<sup>2</sup>/g, respectively. So, significant difference exists between the BET surface areas of nanocomposite in compared with nanohybride. This remarkable diversity attributes to surface porosity changing and probable morphology changing of nanostructure during modification of surface of nanocomposite with Co-TCPP.

The optical properties of the as-synthesized nanoparticles were evaluated by diffuse reflectance UV-Vis spectroscopy. The band gap energy (Eg) was determined from the Tauc's plots by the equation  $\alpha hv = A (hv-E_g)^{n/2}$ , where  $\alpha$ , h, v, Eg and A are absorption coefficient near the absorption edge, Planck's constant, light frequency, band gap energy, a constant, respectively. Also n=1 is indirect band gap TiO<sub>2</sub><sup>21</sup> and n=4 is direct band gap BiVO<sub>4</sub>.<sup>22,23</sup> The band gap of TiO<sub>2</sub>, BiVO<sub>4</sub>, TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite and Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid as a key factor of photocatalytic activity<sup>24</sup> were measured 2.95, 2.24, 2.54 and 2.57 eV, respectively. The results showed the band gap of TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite and Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid photocatalyst are lower than pure TiO<sub>2</sub>, which implied

the red shift of absorption light in visible light region. In contrast with the  $TiO_2/BiVO_4$ , a qualitative red shift to higher wavelength was observed in the absorption edge of nanohybrid, whose absorption edge extended to visible wavelength of 482 nm.

The electronic absorption bands of cobalt porphyrin solution relevant the Soret band at 430 nm and Q bands at 555, 594 nm. While in solid state, DRS of nanohybrid Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> shows two peaks at 390 nm and 482 nm (figure 4b). These red shifts are due to electronic correlation between Co-TCPP to TiO<sub>2</sub> which could be assigned to the transition of  $a_{1u}(\pi)$ – $e^*_g(\pi)$  (Soret band) and  $a_{2u}(\pi)$ – $e^*_g(\pi)$  (Q band) in Co-TCPP, respectively.<sup>25</sup> The increment in Q-band absorption is strong argument for successfully linking of the porphyrin on the surface of TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite.

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**Fig. 4** Diffuse reflectance spectroscopy analysis of (a)  $TiO_2$ , (b)  $BiVO_4$ , (c)  $TiO_2/BiVO_4$  and (d) Co-TCPP@TiO\_2/BiVO\_4 and the plot of transferred Kubelka–Munk versus energy of the light absorbed by the catalyst (inset: a)  $TiO_2$ , (inset: b)  $BiVO_4$ , (inset: c)  $TiO_2/BiVO_4$  and (inset: d) Co-TCPP@TiO\_2/BiVO\_4.

The photoluminescence (PL) test of the photocatalysts could reveal the existence of surface defects, oxygen vacancies, migration, the transference, and recombination processes of the photogenerated electron and hole pairs on the samples.<sup>26,27</sup> Herein, the room-temperature PL spectra were measured in air with the excitation wavelength of 325 nm. PL emission intensity and photocatalytic performances are strongly correlated in reverse direction.<sup>28,29</sup> The lower PL intensity usually indicates the lower charge recombination of electron and hole pairs due to the high separation efficiency of photoinduced charge, thus cause the higher photocatalytic activity. Figure 5 shows PL spectra of TiO<sub>2</sub>, BiVO<sub>4</sub> and Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> should be decreased because the PL intensity was decreased. So, electron transference will be facile between two components of BiVO<sub>4</sub>/TiO<sub>2</sub> nanocomposite and follow it, the photocatalytic activity of Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> should be enhanced.



**Fig. 5** Photoluminescent spectra of the as-prepared TiO<sub>2</sub>, BiVO<sub>4</sub>, TiO<sub>2</sub>/BiVO<sub>4</sub> composite and Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid excited by photons at 325 nm.

#### 4. Study of photocatalytic activity

The photocatalytic activity and efficiency of the nanohybrid catalyst Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> was studied toward oxidation of alcohols and compared with nanocomposite TiO<sub>2</sub>/BiVO<sub>4</sub>. Photocatalytic reactions were run in a water bath and irradiated using a LED light source with wavelength 550 nm. The reaction progress was monitored by GC. The oxidation reaction condition was optimized by investigation on the influence of amount of catalyst, temperature, solvent, oxidant and reactant/oxidant mole ratio. Summary of result have inserted in tables 1 and 2.

To find optimum condition, the catalytic oxidation reaction was run in different temperature and reaction progress was monitored during 2 h in acetonitrile. At 70 °C the yield of oxidation process was reached to 80% while at 25 °C and 55 °C yield was 40% and 60%, respectively. The yield of the reaction was decreased at higher temperature than 70 °C due to deformation of porphyrin part of catalyst. Conversely, at low temperature, energy does not available enough to activate the catalyst then results in low benzyl alcohol conversion. So, the optimize temperature 70 °C was chosen for further reactions because catalyst shows higher efficiency and shorter reaction time. It is noticeable that the selectivity for aldehyde production remains at 99%. Therefore, Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> is suggested as a highly selective catalyst for the oxidation of alcohols.

Entry	Solvent	Temp. (°C)	Time (min)	Oxidant	Selectivity (%)	Yield (%)
1	CH <sub>3</sub> CN	25	120	TBHP	>99	40
2	CH <sub>3</sub> CN	55	120	TBHP	>99	60
3	CH <sub>3</sub> CN	70	120	TBHP	>99	80
4	DMF	70	120	TBHP	>99	65
5	$CH_2Cl_2$	70	120	TBHP	>99	40
6	DMF/ CH <sub>2</sub> Cl <sub>2</sub>	70	120	TBHP	>99	50
7	$H_2O$	70	120	TBHP	-	<1
8	CH <sub>3</sub> CN	25	120	$H_2O_2$	>99	20
9	CH <sub>3</sub> CN	40	120	$H_2O_2$	>99	30
10	CH <sub>3</sub> CN	50	120	$H_2O_2$	>99	40
11	CH <sub>3</sub> CN	70	120	$O_2$	-	<1
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**Table 1** The effect of various parameters on the catalytic oxidation of benzyl alcohol to benzaldehydeby Co-TCPP@TiO\_2/BiVO\_4.

Reaction condition: 10 mg catalyst, 0.1 mmol benzyl alcohol, 1.5 ml solvent, 1.5 mmol oxidant.

Entry	Catalyst	Catalyst	Ovidant	Time	Selectivity	Yield
	Catalyst	amount (mg)	Oxidant	(min)	(%)	(%)
1	Co-TCPP@TiO <sub>2</sub> /BiVO <sub>4</sub>	10	TBHP	60	>99	85
2	Co-TCPP@TiO <sub>2</sub> /BiVO <sub>4</sub>	10	$H_2O_2$	60	>99	50
3	Co-TCPP@TiO <sub>2</sub> /BiVO <sub>4</sub>	5	$O_2$	120	>99	20
4	Co-TCPP@TiO <sub>2</sub> /BiVO <sub>4</sub>	10	$O_2$	120	>99	25
5	Co-TCPP@TiO <sub>2</sub> /BiVO <sub>4</sub>	15	$O_2$	120	>99	25
6	TiO <sub>2</sub> /BiVO <sub>4</sub>	5	$O_2$	120	>99	5
7	TiO <sub>2</sub> /BiVO <sub>4</sub>	10	$O_2$	120	>99	10
8	TiO <sub>2</sub> /BiVO <sub>4</sub>	15	$O_2$	120	>99	10
9	TiO <sub>2</sub> /BiVO <sub>4</sub>	10	TBHP	60	>99	35
10	TiO <sub>2</sub> /BiVO <sub>4</sub>	10	$H_2O_2$	60	>99	25
11	No catalyst	-	$O_2$	120	-	<1
12 <sup>b</sup>	Co-TCPP@TiO <sub>2</sub> /BiVO <sub>4</sub>	10	$O_2$	120	-	<1

 Table 2 Photocatalytic oxidation of benzyl alcohol under visible light irradiation.<sup>a</sup>

<sup>a</sup>Reaction condition: benzyl alcohol (0.1 mmol), acetonitrile (1.5 ml), reaction temperature 70 °C, oxidant (1.5 mmol), in the case of  $H_2O_2$  the reaction temperature was 50 °C.  $H_2O_2$  was added in several times but all of TBHP was added once

<sup>b</sup>Result in dark.

In continue several solvents with different polarities were used in response of the oxidation of alcohols. Under the optimum reaction conditions, 10 mg catalyst and 1.5 mmol of oxidant were used in different solvents such as, acetonitrile (CH<sub>3</sub>CN), water, dimethylformamide (DMF) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). The results confirmed that the best yield was obtained in acetonitrile solvent. The CH<sub>2</sub>Cl<sub>2</sub> had the lowest conversion that should be associated with the lower boiling point of the solvent. Meanwhile, only benzaldehyde was detected as single product in all solvents. By comparing the result in table 1, acetonitrile should be selected as the best solvent. Solvent has several effect on reactions, including its role on energy transfer to avoid local overheating, mass transfer and dispersion of materials, polarization and inductive effects, activity and stability of the metal type.<sup>30</sup> However, this result could be described as faster mass transfer to/from the surface of Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> during catalytic reaction. The results revealed that the solvent significantly influenced the adsorption of reagents and the diffusion of products during the oxidation.

To optimize the substrate to oxidant ratio, different molar ratios of benzyl alcohol to aqueous TBHP at 1:1, 1:1.5 and 1:2 molar ratios were applied (Figure 6). The highest conversion percent was obtained at 1:1.5 molar ratio. Further increasing of oxidant was not affected the conversion percent. However, exceeding the TBHP caused some decreasing of conversion due to the generation of tert-butyl alcohol, which act as a competitive inhibitor in the oxidation process.<sup>31,32</sup>

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Fig. 6 Oxidation of benzyl alcohol with different molar ratios of benzyl alcohol/TBHP.

Table 3 shows the summarized results of the oxidation reaction of primary alcohols in the presence of Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> in optimized conditions. The smooth changes in the yield of the reaction should be due to the effect of the electron-donating and electron-withdrawing properties of functional groups on the benzene ring. Anyway, the selectivity was remained about 99%.

Entry	Substrate	Product	Selectivity %	yield %
1	HO		>99	80
2	HO	CI	>99	75
3	HOOCH3	OOCH3	>99	70
4	HONO2	NO2	>99	60

Table 3 Catalytic activity of Co-TCPP@TiO2/BiVO4 nanohybrid in optimized conditions.<sup>a</sup>

<sup>&</sup>lt;sup>a</sup> Reaction condition: Substrate (0.1 mmol), Amount of catalyst (10 mg), TBHP (1.5 mmol), reaction temperature 70 °C, acetonitrile (1.5 ml).

In order to understand the catalytic process, different oxidant such as molecular oxygen  $(O_2)$ , hydrogen peroxide  $(H_2O_2)$  and t-butyl hydroperoxide (TBHP), as an organic hydroperoxides were considered. Among these oxidants, the TBHP has shown higher performance than  $H_2O_2$  and  $O_2$  in both dark and under visible light irradiation. The concise of result are shown in table 2. However, in spite of inactivity of the molecular oxygen in dark condition, it acts as a moderate oxidant under visible light irradiation, which could be explained by consideration of mechanism of this reaction. This noticeable finding could be described by understanding the role of each component in photocatalytic process.

#### 4.1. Stability and reusability of catalyst

The performance of catalyst was studied by reusing the recycled catalyst toward benzyl alcohol oxidation. To do so, the used catalyst was filtered, washed with acetonitrile, and utilized for the new catalytic oxidation reaction in the same condition. The results revealed that the catalyst was being active even after eight consecutive usages without losing significant photocatalytic activity and selectivity (Fig. 7). Anyway, a little decreasing of activity should be due to missing some ultrafine particles during washing process in each step.

Also, XRD and FT-IR analysis were performed before and after reaction for study the stability of the Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> catalyst (Figure 8 and S2). Actually, no changes was observed in the FT-IR spectra and XRD patterns of the fresh and recycled catalyst, which corresponds to state stability of Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> structure in the oxidation reaction process.

Meanwhile, the UV–Vis spectra (Figure 9) of the reaction solution after filtration did not show any absorption peaks related to Co-TCPP, which confirm that the Co-TCPP leaching not happen during the oxidation reactions.



Fig. 7. Number of recycling of the catalyst.



Fig. 8 XRD patterns of the Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid, after (a) and before (b) catalytic reaction.



**Fig. 9** UV-Visible spectra of mixture reaction contain Co-TCPP@TiO<sub>2</sub>/ BiVO<sub>4</sub> nanocatalyst after the eighth recovery for test of leaching (inset: UV-vis spectra of Co-TCPP).

#### 5. Plausible mechanism

To understand the primary active species in the aerobic oxidation reaction of benzyl alcohol in the presence of Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> under visible light irradiation, a series of controlled experiments was performed under argon atmosphere or in the presence of radical scavenger compounds. In this research, benzoquinone (BQ) was used as a superoxide radical (O2<sup>-</sup>) scavenger, tert-butyl alcohol (t-BuOH) as scavenger for hydroxyl radicals, ammonium oxalate (AO) as a photogenerated holes scavenger and silver nitrate as electrons scavenger. As shown in Figure 10, converting alcohols to aldehydes in argon atmosphere is meaningless, which this test confirmed that the oxygen was the main species in the oxidation of benzyl alcohol. Increasing the BQ to the reaction does not have a significant effect on conversion of benzyl alcohol with H<sub>2</sub>O<sub>2</sub> and TBHP oxidants but significantly reduces the conversion of alcohols to aldehydes with  $O_2$  oxidant, which confirms the essential role of  $O_2$  in the oxidation of alcohols. A similar inhibitory effect was observed by AO reducing. The conversion in this case represents the essential role of holes that created by light incident during the reaction by three oxidants. On the other side, increasing t-BuOH (TBA) to the reaction does not have a significant effect on reaction except on reaction by TBHP oxidant. This confirms being ineffective of OH on the progress of the reaction. The reason to this may associate with the reaction in acetonitrile solvent and solvent production, which do not let the OH to be produced during the time of reaction.<sup>33</sup> Based on the above test results, the species

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 $O_2$  and created holes were recognized as main species in the oxidation reaction of alcohol with  $O_2$ . Moreover, it is well understood that, the OH radicals are operating as non-selective agent in the progress of reactions and in the absence of such radicals; the reaction would be selective.<sup>34</sup>



**Fig. 10** The photocatalytic oxidation of benzyl alcohol by the Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanocatalyst in present of oxygen (a) and argon (b).

According to control experiments conducted in this section, a possible mechanism in converting aromatic alcohols to aldehydes was carried out according to the following:

The mechanism of dye sensitized TiO<sub>2</sub> under visible light, involves the electron transition from the ground state of porphyrin dye [Pp] to the singlet excited state <sup>1</sup>[Pp]<sup>\*.35</sup> The relaxation of the singlet excited state, generates the triplet excited state <sup>3</sup>[Pp]<sup>\*</sup> through a process of intersystem crossing. In fact, the photogenerated electron transitions from <sup>1</sup>[Pp]<sup>\*</sup> and <sup>3</sup>[Pp]<sup>\*</sup> could occur to conduction band of TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite. On the based of DRS, UV-Vis and cyclic voltammetry (CV) results, energy level diagrams were obtained (Figure 11). In case, the CB and VB of BiVO<sub>4</sub> was placed between the CB and the VB of TiO<sub>2</sub> (Schematic S3). So, electron capture by O<sub>2</sub> from the conduction band of nanocomposite yield the superoxide radical anion (O<sub>2</sub><sup>--</sup>) which proceed oxidation of alcohols. Furthermore, Co-TCPP plays as a sensitizer, while partial oxidation Co-TCPP by oxygen should not be ignored that is unfavorable.<sup>36,37</sup>



Fig. 11 Proposed photocatalytic mechanism path by molecular oxygen O<sub>2</sub>.

However, when the system irradiate under visible light in present of  $H_2O_2$  as electron acceptor, an electron (e<sup>-</sup>) promotes from the valence band into the conduction band of nanocomposite and leaves a hole (h<sup>+</sup>) behind. So, the TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite will activate to generate electron-hole pairs.<sup>38,39</sup> In fact, the life time of positive hole increases by prohibition of charge recombination by intersystem electron crossing to the vacant valance band of excited Co-TCPP. This will conduct the oxidation of substrate through positive hole (figure 12). Thus, in this case porphyrin plays as sensitizer and relay moiety.



Fig. 12 Proposed photocatalytic mechanism by molecular oxygen H<sub>2</sub>O<sub>2</sub> oxidant.

#### Conclusion

The novel Co-TCPP@TiO<sub>2</sub>/BiVO<sub>4</sub> nanohybrid was prepared and used as efficient photocatalyst in aerobic oxidation of alcohols to the corresponding aldehydes. The conversion percent of oxidation reaction raised significantly up to 85 comparing to bare TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposite. Although, activity of this catalyst remain constantly upon visible light irradiation in presence of TBHP as oxidant, but it shows higher photocatalytic efficiency in present of molecular oxygen. It noticeable that no catalytic activity observed in absent of light. Also, the catalyst was recovered and reused easily without significant loss of activity. So, this nanohybrid photocatalyst could be considered as a great candidate in transformation of functional groups in organic materials with advantages high efficiency, facile procedure and high selectivity.

#### **Supporting information**

The FT-IR spectra of synthesis samples (figure S1-S2) and energy bands diagram (Schematic S3) are presented in the supporting information.

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#### References

- Z. Bian, T. Tachikawa, P. Zhang, M. Fujitsuka and T. Majima, J. Am. Chem. Soc., 2013, 136, 458–465.
- 2 J. Jiang, J. Yu and S. Cao, J. Colloid Interface Sci., 2016, 461, 56–63.
- 3 A. L. Linsebigler, G. Lu and J. T. Yates Jr, Chem. Rev., 1995, 95, 735–758.
- 4 M. Tahir, B. Tahir and N. A. S. Amin, *Appl. Surf. Sci.*, 2015, **356**, 1289–1299.
- 5 X. Zhang, Y. L. Chen, R.-S. Liu and D. P. Tsai, *Reports Prog. Phys.*, 2013, 76, 46401.
- 6 S. Bingham and W. A. Daoud, J. Mater. Chem., 2011, 21, 2041–2050.
- 7 S. G. Kumar and L. G. Devi, J. Phys. Chem. A, 2011, 115, 13211–13241.
- 8 A. F. Nogueira, L. F. O. Furtado, A. L. B. Formiga, M. Nakamura, K. Araki and H. E.

New Journal of Chemistry Accepted Manuscript

Toma, Inorg. Chem., 2004, 43, 396–398.

- 9 W. S. Tung and W. A. Daoud, ACS Appl. Mater. Interfaces, 2009, 1, 2453–2461.
- 10 C. Ding, W. Qin, N. Wang, G. Liu, Z. Wang, P. Yan, J. Shi and C. Li, *Phys. Chem. Chem. Phys.*, 2014, 16, 15608–15614.
- 11 F. F. Abdi, L. Han, A. H. M. Smets, M. Zeman, B. Dam and R. Van De Krol, *Nat. Commun.*, 2013, 4, 2195.
- M. Gotić, S. Musić, M. Ivanda, M. Šoufek and S. Popović, J. Mol. Struct., 2005, 744, 535–540.
- S. Afzal, W. A. Daoud and S. J. Langford, ACS Appl. Mater. Interfaces, 2013, 5, 4753–4759.
- W. M. Campbell, A. K. Burrell, D. L. Officer and K. W. Jolley, *Coord. Chem. Rev.*, 2004, 248, 1363–1379.
- 15 H. Kurreck and M. Huber, Angew. Chemie Int. Ed., 1995, 34, 849–866.
- 16 D. Wöhrle and D. Meissner, *Adv. Mater.*, 1991, **3**, 129–138.
- 17 S. Afzal, W. A. Daoud and S. J. Langford, J. Mater. Chem., 2012, 22, 4083–4088.
- J. Rochford, D. Chu, A. Hagfeldt and E. Galoppini, J. Am. Chem. Soc., 2007, 129, 4655–4665.
- M. Mojiri-Foroushani, H. Dehghani and N. Salehi-Vanani, *Electrochim. Acta*, 2013, 92, 315–322.
- 20 G. Longo, F. Fresno, S. Gross and U. L. Stangar, *Environ. Sci. Pollut. Res. Int.*, 2014, 21, 11189.
- K. Gupta, R. P. Singh, A. Pandey and A. Pandey, *Beilstein J. Nanotechnol.*, 2013, 4, 345.
- 22 C. Karunakaran, S. Kalaivani, P. Vinayagamoorthy and S. Dash, *Mater. Sci. Semicond. Process.*, 2014, **21**, 122–131.
- 23 A. Walsh, Y. Yan, M. N. Huda, M. M. Al-Jassim and S.-H. Wei, Chem. Mater., 2009,

**21**, 547–551.

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- M. Shang, W. Wang, L. Zhou, S. Sun and W. Yin, J. Hazard. Mater., 2009, 172, 338–344.
- 25 E. Safaei and S. Mohebbi, J. Mater. Chem. A, 2016, 4, 3933–3946.
- 26 M. Long, W. Cai, J. Cai, B. Zhou, X. Chai and Y. Wu, J. Phys. Chem. B, 2006, 110, 20211–20216.
- 27 F. Duan, Y. Zheng and M. Chen, Appl. Surf. Sci., 2011, 257, 1972–1978.
- 28 Q. C. Xu, D. V Wellia, Y. H. Ng, R. Amal and T. T. Y. Tan, J. Phys. Chem. C, 2011, 115, 7419–7428.
- 29 R. Georgekutty, M. K. Seery and S. C. Pillai, .
- 30 M. Bagherzadeh, M. Zare, T. Salemnoush, S. Özkar and S. Akbayrak, *Appl. Catal. A Gen.*, 2014, **475**, 55–62.
- A. Al-Ajlouni, A. A. Valente, C. D. Nunes, M. Pillinger, A. M. Santos, J. Zhao, C. C. Romão, I. S. Gonçalves and F. E. Kühn, *Eur. J. Inorg. Chem.*, 2005, 2005, 1716–1723.
- 32 A. Comas-Vives, A. Lledós and R. Poli, Chem. Eur. J., 2010, 16, 2147–2158.
- 33 B. Tian, C. Li, F. Gu and H. Jiang, *Catal. Commun.*, 2009, **10**, 925–929.
- 34 B. Weng, S. Liu, N. Zhang, Z.-R. Tang and Y.-J. Xu, J. Catal., 2014, 309, 146–155.
- 35 C. Wang, J. Li, G. Mele, G.-M. Yang, F.-X. Zhang, L. Palmisano and G. Vasapollo, *Appl. Catal. B Environ.*, 2007, 76, 218–226.
- 36 G. Mele, E. Garc\`\ia-Lòpez, L. Palmisano, G. Dyrda and R. Słota, J. Phys. Chem. C, 2007, 111, 6581–6588.
- 37 M. Grätzel, J. Photochem. Photobiol. C Photochem. Rev., 2003, 4, 145–153.
- 38 H. Huang, X. Han, X. Li, S. Wang, P. K. Chu and Y. Zhang, ACS Appl. Mater. Interfaces, 2015, 7, 482–492.
- 39 H. Huang, K. Xiao, Y. He, T. Zhang, F. Dong, X. Du and Y. Zhang, *Appl. Catal. B Environ.*, 2016, **199**, 75–86.

Novel visible light sensitized nanohybrid Co-TCPP@ $TiO_2/BiVO_4$  was used as high efficient, stable, reusable and robust photocatalyst using  $O_2$  toward aldehyde production.

