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BiVO₄/TiO₂ core-shell heterostructure: wide range optical absorption and enhanced photoelectrochemical and photocatalytic performance

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ABSTRACT

In the present study, pristine BiVO₄, TiO₂ and BiVO₄/TiO₂ core-shell heterostructured nanoparticles are prepared by hydrothermal methods and studied for structural, morphological, optical, photoelectrochemical water splitting and photocatalytic degradation of methylene blue as an organic pollutant. Both pristine BiVO₄ and TiO₂ exhibit poor PEC and PC performance under visible light illumination. However, an enhanced PEC and PC activity in BiVO₄/TiO₂ core-shell heterostructure is observed due to high solar energy absorption and superior charge separation properties in core-shell nanoparticles. The photoelectrode prepared using BiVO₄/TiO₂ core-shell nanoparticles exhibit a photocathode behavior and produced cathodic photocurrent, however, the pristine BiVO₄ and TiO₂ photoelectrodes act as photoanode and produced anodic photocurrent. This behavior of change in current direction is also observed in the Mott-Schottky analysis where the BiVO₄/TiO₂ core-shell nanoparticles photoelectrode exhibits the positive slope showing p-type semiconducting behavior. The change in cathodic photoresponse in core-shell nanoparticles in comparison to anodic photoresponse of BiVO₄ and TiO₂ nanoparticles is explained in terms of the variations in the work function values. These results highlight the advantages of core-shell nanoparticles of suitable materials for photocatalytic and photoelectrochemical applications.

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1. Introduction

Photoelectrochemical (PEC) water splitting for hydrogen production and photocatalytic (PC) degradation of organic pollutant from wastewater has become an important research area in recent years due to their impact on energy and environmental importance [1,2]. Solar light illumination on the semiconductor materials used in both PEC and PC systems, creates the e⁻/h⁺ pairs and if the energy of photogenerated charge carriers is sufficient for the water splitting or degradation of organic pollutant, the charge carriers participate in the desired chemical reaction on the surface of the semiconductors. In PEC water splitting, the excited electron in the conduction band (CB) drives the reduction of water to H₂, whereas the hole in the valence band (VB) oxidizes water to O₂, such that the net effect is the dissociation of water into gases of its constituent elements [3]. In photocatalysis, the photogenerated charge carriers migrate to the surface and react with the organic pollutant adsorbed on the surface to decompose into the degradation products. The photodecomposition

process usually involves one or more radicals or intermediate species such as •OH, O₂⁻, H₂O₂, or O₂, which play important roles in the photocatalytic reaction mechanisms [4]. For fabricating a high efficiency and low-cost device, designing a semiconductor material with an optimized optical bandgap for maximum light absorption in full solar spectrum and proper kinetics for valence/conduction band alignment suitable for straddling H₂/O₂ redox potential are the main challenge. In addition to the above semiconductor properties, the photoactive material should satisfy chemical requirement of high surface catalytic properties and chemical stability in liquid electrolyte [5].

Titanium dioxide (TiO₂) in the form of nanoparticles is one of the most commonly used semiconductors for PEC and PC application mainly because it satisfies the requirement of valence and conduction edges which are straddled with water redox potentials and stable structural and semiconducting properties in liquid electrolyte medium [6]. Unfortunately, its relatively wider band gap of 3.2 eV in comparison to the required optimum value of 2.0 eV for maximum absorption of solar radiation makes it a poor and inefficient photocatalyst for both PEC and PC applications as most of the visible light photons just lost by transmission. The optical and semiconductor properties can be varied by making alloy, composite or by defect generation through the post-deposition surface treatments. Numer-

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ous methods have been used to improve the performance of TiO_2 such as doping, morphology tuning to shorten the required diffusion distance of minority carriers and coupling with smaller bandgap semiconductors to enhance the light absorbance [7]. In recent years, several composites have been used to improve the PEC properties. TiO_2 and other metal oxide semiconductors have been prepared and coupled with another metal oxide by the ion impregnation [8,9], photodeposition [10], hydrothermal [11,12] or other thermal [13] treatments. In search of visible light active material, BiVO_4 also serve as one of the promising material for both PEC and PC applications due to its high stability, effective sunlight utilization and high photoactivity for O_2 evolution [14]. However, due to slightly positive CB minima (CBM) of BiVO_4 as compared to the H^+ reduction potential, BiVO_4 nanoparticles has one drawback. Recently, the combination of TiO_2 with BiVO_4 to form heterojunctions has provided an effective way to improve the optical absorption, facilitate the charge separation and transfer, thus making TiO_2 more efficient for PEC and PC applications [15,16, 17]. In our previous work we reported that thin layer of TiO_2 on BiVO_4 could be used for visible-light-driven PEC hydrogen production. The BiVO_4 thin films when coupled with a thin nanocrystalline anatase TiO_2 layer exhibits higher optical absorption as compared to single TiO_2 layer and enhance the PEC performance, which was mainly attributed to the spatial transfer of visible-excited energetic electrons from BiVO_4 to TiO_2 layer after hydrogen treatment [14].

In the present study, $\text{BiVO}_4/\text{TiO}_2$ core/shell nanoparticle heterostructure are prepared by coating a thin layer of TiO_2 over the BiVO_4 nanoparticles, which helps in photo-induced charge separation upon excitation in the visible spectral region [18]. Optical, structural, PEC and PC properties of $\text{BiVO}_4/\text{TiO}_2$ core/shell nanoparticles have been compared with those of single component TiO_2 and BiVO_4 nanoparticles of similar sizes. The results of enhanced photoresponse have been explained in terms of increased overall absorption in the $\text{BiVO}_4/\text{TiO}_2$ core-shell heterostructure, increased charge separation at the interface and superior surface catalytic properties of TiO_2 .

2. Experimental section

2.1. Preparation of nanoparticles

TiO_2 nanocrystals were prepared by a wet chemical method using titanium tetra-isopropoxide, ethanol, hydrochloric acid and deionized water as reported earlier [19]. In brief, 25 mL deionized water mixed with one mL hydrochloric acid was added slowly to 10 mL of titanium tetra-isopropoxide with continuous stirring in an ice bath. A white precipitated solution was obtained, which was washed three time with deionized water and heated in air at 80°C to evaporate extra water. After evaporation of extra water, the white precipitate was dried and finally sintered at 400°C for four h. For the synthesis of BiVO_4 nanoparticles, 0.00412 mol of bismuth nitrate pentahydrate were dissolved in 50 mL of deionized water with 0.0814 mol of 70% HNO_3 solution (solution A) and 0.00412 mol of ammonium metavanadate with 3.365 g of NaOH flakes were dissolved in 50 mL of deionized water (solution B). In each solution, one g of sodium dodecyl benzene sulphonate (act as surfactant) was added and magnetically stirred for 30 min. After stirring, both the solutions were mixed and stirred again for 30 min. The mixed solution was kept in a Teflon lined vessel in an autoclave instrument at 400°C for 4 h. The prepared nanoparticles were filtered from the solution using centrifuge machine and dried at 60°C for 10 h.

After 4h grinding of BiVO_4 nanoparticles, these particles were used for making the $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles. For the synthesis of $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles, the prepared BiVO_4 particles were mixed in ethanol, hydrochloric acid and deionized

water (in a ratio used for making the TiO_2 nanoparticles). This mixture was added slowly to five mL of titanium tetra-isopropoxide with continuous stirring under ice bath to form yellows-white precipitates of TiO_2 with imbedded BiVO_4 nanoparticles as core. The yellows-white precipitate was filtered and dried at 80°C to evaporate extra water. Subsequently, prepared core-shell nanoparticles were annealed at 400°C for 4 h.

2.2. Material characterizations

The prepared nanoparticle of TiO_2 , BiVO_4 and $\text{BiVO}_4/\text{TiO}_2$ core-shell structures were characterized for structural properties by using glancing angle X-ray diffraction with the help of Philip's X'Pert PRO-PW vertical system operating in reflection mode using $\text{Cu K}\alpha$ ($\lambda = 0.15406\text{ nm}$) radiation. To see any change in optical absorption in BiVO_4 imbedded TiO_2 core-shell structures, the optical absorption behavior of all the three samples was measured on a Perkin-Elmer Lambda 35 UV visible spectrometer in the wavelength range of 200–800 nm. For optical absorption, 50 mg of prepared material were pressed into a small sample container to make a flat surface and uniform density in a 'Praying Mantis' diffuse reflectance accessory. The morphological characterization of pristine and core-shell nanoparticles was performed by using FEI Quanta 3D FEG field-emission scanning electron microscope operated at an acceleration voltage of 10.0 kV. High-resolution transmission electron microscopy (TEM) images of the synthesized samples were obtained using FEITechnai-G20 with a LaB6 filament, operating at 200 keV.

In order to utilize the BiVO_4 , TiO_2 and $\text{BiVO}_4/\text{TiO}_2$ core-shell particles as a photoelectrode in the photoelectrochemical cell, pellets of diameter 1.32 cm were prepared by pressing the nanoparticles in a uniaxial palletization machine by applying a load of approximately nine tons. The prepared pellets were annealed at 400°C in air atmosphere for one h and allowed to cool down naturally to room temperature and finally polished afterward using alumina powder. Ohmic electrical contacts were generated on one side of the pellet by employing the conducting silver paste and copper wire after rubbing the surface of the pellets gently with the gallium indium eutectic. All the pellets were converted into the photoelectrodes by using non-conducting and non-transparent epoxy resin, Hysol (Dexter, Singapore), excluding an area of about 1.0 cm^2 at the center of the side of the pellet's opposite to the contact side.

Prepared photoelectrodes of pristine BiVO_4 , pristine TiO_2 and core-shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticles were used as working electrodes, Pt as the counter electrode and Ag/AgCl as the reference electrode in a one M NaOH electrolyte ($\text{pH} = 13.6$) in a PEC cell. The photoelectrochemical cell was controlled using AutoLab PEC workstation having Nova software system (X-Pot Potentiostat). Linear sweep voltammetry (LSV) scans in dark and illumination conditions and Mott–Schottky (MS) measurements in dark were carried out in the potential range of -1.0 to $+1.0\text{ V}$ (vs. Ag/AgCl) with a scan rate of 20 mV/s . Mott–Schottky (MS) measurements were carried out at an AC frequency of 1 kHz . The electrochemical impedance spectroscopy (EIS) measurements under illumination were performed in the frequency range 10 mHz – 100 kHz with an alternating current (AC) signal amplitude of 10 mV under 0 V versus Ag/AgCl .

The photocatalytic performance of all the prepared samples were evaluated by observing their abilities to degrade the methylene blue (MB) dye in aqueous solution under simulated visible irradiation induced by using a 100 W tungsten lamp equipped with a UV cut-off filter to remove the radiation below 380 nm . For photocatalytic performance, 30 mg of prepared catalysts were dispersed in a 100 mL aqueous solution of MB ($10\text{ }\mu\text{M}$) and the obtained suspensions were magnetically stirred at 250 rpm in the dark for 40 min to ensure adsorption/desorption equilibrium between the catalyst and organic

dye. The catalyst suspension was subsequently irradiated with a 100 W tungsten lamp. A sufficient amount of (two mL) dye suspension was extracted and centrifuged after every 10 min during the course of 100 min irradiation to remove the residual catalyst particulates for analysis. Control experiments were performed either without the catalyst or in the dark to attest that the degradation reaction is solely by a photocatalytic process. The photodegradation efficiency was monitored by measuring the change in intensity of the characteristic absorbance peak of MB at 664 nm using a Shimadzu UV-2450 spectrometer with 10 mm path length quartz cells.

3. Results and discussion

Pristine TiO_2 , BiVO_4 and $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles are characterized for the determination of the crystal phase structure and phase purity by XRD as shown in Fig. 1. XRD peaks for TiO_2 samples are observed at 2θ angle of 25.5° , 37.9° , 48.2° and 55.06° which correspond to (101), (004), (200) and (105) planes of anatase phase of TiO_2 [20]. Peaks observed in BiVO_4 at 2θ angle of 28.9° , 30.5° , 34.9° , 40.0° , 42.5° , 45.9° , 47.2° , 50.3° , 53.3° , and 55.9° are observed to correspond to (112), (004), (202), (114), (105), (213), (204), (220), (116) and (301) hkl indices of monoclinic phase of BiVO_4 [21]. In $\text{BiVO}_4/\text{TiO}_2$ core shell samples, XRD peaks are observed to be corresponding to both anatase TiO_2 and monoclinic BiVO_4 phases without any other peaks indicating the absence of any other impurity phase or mixed phase. This also confirms that both TiO_2 and BiVO_4 phases are present in core-shell nanoparticle sample and their crystal structure is preserved. Surface morphology obtained from

Fig. 1. X-ray diffractogram of pristine BiVO_4 , pristine TiO_2 nanoparticles and core-shell $\text{BiVO}_4/\text{TiO}_2$ heterostructure. M and A in XRD peaks represents corresponding to Monoclinic BiVO_4 and Anatase TiO_2 phases, respectively.

scanning electron microscopy (SEM) for pristine BiVO_4 , pristine TiO_2 and core-shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticles are shown in Fig. 2. SEM images for pristine BiVO_4 clearly displays the dendritic shape nanoparticles within the size range of around 80–100 nm. SEM image for TiO_2 nanoparticles show spherical shaped or quasi-spherical shaped nanoparticles with size of about 10–15 nm. Transmission electron microscopic (TEM) images of pristine BiVO_4 , pristine TiO_2 and core-shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticle are shown in Fig. 3. TEM images show the formation of nanoparticles with an average particle size of about 80–100 nm for BiVO_4 (Fig. 3a) and 10–15 nm for TiO_2 (Fig. 3b) samples. TEM analysis of sample core-shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticles (Fig. 3c and d) clearly show an approximately 10 nm thick coating of TiO_2 over the BiVO_4 particles. Further, the core-shell composition is confirmed by energy-dispersive X-ray spectroscopy (Fig. 3e and f), which revealed clearly that BiVO_4 samples is made of Bi, V and O only however, in $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticle one-addition elements Ti is present.

Diffuse reflectance spectra (DRS) for pristine BiVO_4 , pristine TiO_2 and core shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticles are shown in Fig. 4. Pristine BiVO_4 nanoparticles exhibit an absorption edge at 530 nm, while pristine TiO_2 nanoparticles display the absorption edge at 375 nm. The shape of absorption spectra in both the cases are in good agreement with previously reported values for the anatase TiO_2 [22] and monoclinic BiVO_4 [23]. Anatase TiO_2 exhibits a prominent absorption edge in the UV region of solar spectrum, however, the BiVO_4 samples exhibits the optical absorption in visible region which stated at around 530 nm with absorption tail extending up to 660 nm. The estimated band gap from the DRS spectra consistent with the known values of bandgap values of 2.4 eV and 3.2 eV for BiVO_4 and TiO_2 , respectively. Due to nanoparticle effect, a slight increase in the absorption edge values is expected. The DRS spectrum of the core-shell $\text{BiVO}_4/\text{TiO}_2$ heterostructures validates the generation of a new energy level, as a clear redshift of the absorption edge is observed compared with that of the TiO_2 . The core-shell $\text{BiVO}_4/\text{TiO}_2$ heterostructures demonstrate a characteristic absorption spectrum and the fundamental absorption stopping edge at $\lambda \approx 510$ nm lies within the visible-light region. Because of the presence of two crystal phases, two absorption edge features are clearly observed. This clearly shows that increased absorption in the visible region due to the visible optical absorption in BiVO_4 core. Thus, both UV and visible light can be utilized by $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticle which may potentially lead to improve the photocatalytic activity of $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles.

The pristine BiVO_4 , pristine TiO_2 and core-shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticles are used as working electrode in a photoelectrochemical cell to investigate the solar water splitting activity. The photocurrent density for both the pristine and core-shell nanoparticles is calculated by subtracting the dark current from that of current measured under illumination and then divided by the electrode geometric area (0.5 cm^2) of the samples. PEC results are shown in Fig. 5. It can be noted that core shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticle sample shows

Fig. 2. SEM micrographs of a) BiVO_4 nanoparticles b) TiO_2 nanoparticles c) $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticle samples.

Fig. 3. TEM images of a) BiVO_4 nanoparticles showing dendritic structure b) TiO_2 nanoparticles showing agglomerated structure c) $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles and d) magnified image of $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles clearly showing the formation of core-shell structure. TEM-EDS analysis of (e) BiVO_4 nanoparticles and (f) $\text{BiVO}_4/\text{TiO}_2$ core-shell heterostructures.

Fig. 4. Absorbance spectra of BiVO_4 , TiO_2 and $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles. Two absorption features for core-shell nanoparticles are observed.

Fig. 5. Photocurrent vs. applied bias curves for (a) TiO_2 nanoparticle samples and in inset BiVO_4 nanoparticle (b) $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles. Interestingly, both TiO_2 and BiVO_4 nanoparticles exhibit anodic behavior and relatively low photocurrent density, however, the $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles show cathodic behavior with relatively large value of photocurrent density.

the photocurrent density in cathodic side, which correspond to p-type nature of the core-shell nanoparticles. Whereas, pristine TiO_2 nanoparticle and pristine BiVO_4 nanoparticle samples show the photoanodic behavior which corresponding to n-type characteristics for both BiVO_4 and TiO_2 nanoparticles. The change from anodic to cathodic behavior in core-shell nanoparticles is an important result and will be discussed in more details later. Maximum photocurrent density of 0.1 mA/cm^2 was obtained for $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles at -0.8 V/Ag/AgCl as compared to value of 0.006 mA/cm^2 in case of BiVO_4 and 0.04 mA/cm^2 for TiO_2 . The photocurrent density values obtained for core-shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticles is approximately 2.5 times higher than the TiO_2 nanoparticle which may be attributed to the enhanced optical absorption and efficient charge separation charge separation at the interface of the BiVO_4 and TiO_2 , probably due to of built in electric field at the BiVO_4 and TiO_2 interface.

The charge transfer process at the electrolyte and semiconducting material surface is also investigated using electrochemical impedance spectroscopy (EIS) measurements under light conditions. Fig. 6 show the Nyquist plots for pristine BiVO_4 , pristine TiO_2 and core-shell $\text{BiVO}_4/\text{TiO}_2$ nanoparticles. As shown in Fig. 6, it is evident that the radii of semicircle on the real axis of Nyquist plots of $\text{BiVO}_4/\text{TiO}_2$ core-shell heterostructured sample is much smaller than those for BiVO_4 and TiO_2 samples, which indicates that the core-shell heterostructured reduces the semiconductor-electrolyte contact resistance and improves the charge transport. Therefore, the charge transport efficiency in $\text{BiVO}_4/\text{TiO}_2$ core-shell heterostructured sample increased significantly both on the surface (i.e., surface reaction kinetics) and in the bulk, leading to an improved PEC activity [24].

To determine the intrinsic electrical properties of pristine BiVO_4 , pristine TiO_2 and core-shell $\text{BiVO}_4/\text{TiO}_2$ heterostructure, Mott-Schottky measurements were carried to calculate the flat-band potential (V_{FB}) by using the Mott-Schottky equation. Fig. 7 shows the Mott-Schottky plots ($1/C^2$ vs. applied bias) for all the three samples. The flat-band potential values of these samples were obtained from the linear fit of the data of these curves using a $1/C^2$ vs. V relationship [25]. The pristine BiVO_4 and pristine TiO_2 samples show a negative slope of a linear region of a plot indicating its n-type nature with a flat band potential values of -0.38 and -0.30 V (vs. Ag/AgCl), respectively. However, $\text{BiVO}_4/\text{TiO}_2$ sample shows the positive slope of a linear region of a plot indicating its p-type nature with a flat band potential values of 0.58 V (vs. Ag/AgCl). The positive value of flat-band potential value for the core-shell $\text{BiVO}_4/\text{TiO}_2$ heterostructure based photoelectrode indicates photocathodes behavior. This change in the electronic nature of $\text{BiVO}_4/\text{TiO}_2$ heterostructure

Fig. 6. EIS spectra of for BiVO_4 , TiO_2 and $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles.

Fig. 7. $1/C^2$ vs. V curves for BiVO_4 , TiO_2 and $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticles (sample $\text{BiVO}_4/\text{TiO}_2$ core-shell).

in comparison to BiVO_4 and TiO_2 nanoparticles is in consistent with photoelectrochemical results. The more positive values of flat-band potential show the more efficient charge transport at electrolyte-semiconductor interface and its higher photoelectrochemical activity.

Further, the photocatalytic activity of all three samples is evaluated by measuring the time-dependent degradation of methylene blue (MB) under visible-light irradiation. From Fig. 8a, we can see that the pristine BiVO_4 and pristine TiO_2 nanoparticles shows poor photocatalytic activity in the visible light illumination. The degradation rate constant k of pristine BiVO_4 and TiO_2 are calculated as 2.9×10^{-3} and $\sim 3.4 \times 10^{-3} \text{ min}^{-1}$. This small value is attributed to the large band gap energy of TiO_2 . For the $\text{BiVO}_4/\text{TiO}_2$ heterostructure, the photodegradation activity increases and the photodegradation rate constant k reaches the maximum $\sim 8.4 \times 10^{-3} \text{ min}^{-1}$. This value is approximately three times of magnitude higher than that of pristine TiO_2 under visible-light irradiation. To check the long stability of the defect generated in $\text{BiVO}_4/\text{TiO}_2$ heterostructure when stored under ambient conditions, we used $\text{BiVO}_4/\text{TiO}_2$ heterostructure to re-examine the photocatalytic and photoelectrochemical application tests. We found that $\text{BiVO}_4/\text{TiO}_2$ samples still exhibit the enhanced photocatalytic activity for phenol degradation.

The central objective of the present study is to improve the solar energy absorption capacity by making the core-shell heterostructure of two different semiconductor materials, wide band gap shell (TiO_2) and smaller band gap core (BiVO_4). The pristine BiVO_4 nanoparticles were showing lower photocurrent density due to poor carrier transport properties because of lower hole diffusion length [26]. The present strategy of using core-shell heterostructure will result in photogenerated carriers very close to $\text{BiVO}_4/\text{TiO}_2$ interface. Surface catalytic properties of the semiconductor surface in contact with liquid electrolyte is also very important. Pristine TiO_2 surface is known to have superior surface photocatalytic properties in comparison to other semiconductors, as well as high stability in liquid electrolyte [27]. Therefore, the use of TiO_2 shell in $\text{BiVO}_4/\text{TiO}_2$ core-shell nanoparticle is expected to result in stability and better surface catalytic properties. Further, for improving the charge transfer at heterojunction, a favorable band alignment is an important pre-requisite. The favorable potential difference between BiVO_4 and TiO_2 for efficient charge transfer has also been reported in thin film heterojunction [28]. The improved properties at BiVO_4 and TiO_2 interface

Fig. 8. (a) Solar-light driven photocatalytic decomposition of Methylene blue (b) rate constant calculation for BiVO₄, TiO₂ and BiVO₄/TiO₂ core-shell nanoparticles.

explained in terms of favorable Fermi level alignment in the BiVO₄/TiO₂ interface with CB of BiVO₄ higher than that of TiO₂ resulting in a type II band alignment. This will favor photoelectrons created in BiVO₄ being efficiently transferred to TiO₂ preventing recombination and efficient PEC reaction at TiO₂/electrolyte interface. Based on our photoelectrochemical results, it can be confirmed that the separation of photogenerated charge carriers in BiVO₄ nanoparticles could be enhanced by depositing a thin TiO₂ shell i.e. by making the BiVO₄/TiO₂ core-shell heterostructure. Accordingly, there is an increase in photocatalytic activity for the degradation of methylene blue dye under visible-light irradiation. In previous studies [15,29,30], it has been reported that the increased separation of photogenerated charges in BiVO₄/TiO₂ heterostructure, when TiO₂ is in contact with electrolyte as an top layer, are mainly attributed to the uncommon transfers of photoexcited high energy electrons from bottom BiVO₄ layer to top TiO₂ layer, which is schematically shown in Fig. 9. When BiVO₄/TiO₂ core-shell is illuminated by solar radiation to excite the semiconductor, the TiO₂ shell layer absorb the UV radiation with wavelength shorter than 375 nm. The remaining light with wavelength larger than 375 nm and shorter than 530 nm reaches to excite the BiVO₄ core and generate the large amount of

high-energy electrons (e⁻) in BiVO₄ above the CB with positive holes (h⁺) left in the VB [29]. Generally, these high-energy electrons are active for water reduction, because they possess a higher energy level than that standard hydrogen electrode (SHE) of water reduction, while the holes would be captured by water to oxidize. However, it should be noted that the high-energy electrons migrated easily to the bottom of the CB in a remarkably short time, as they relax and then immediately recombine with the holes at the VB, leading to weakened charge separation with a lowered photoactivity. Interestingly, when the BiVO₄ is coupled with TiO₂ in core-shell configuration, the visible-light-excited high-energy electrons of BiVO₄ would thermodynamically transfer to the CB of TiO₂, which prolongs the lifetimes of the high-energy electrons. In addition, it is well known that the CB energy level of TiO₂ is higher than that of water reduction potential, meaning that the transferred high-energy electrons can be used directly for hydrogen generation [7,31,32]. One of the most important finding in the result of the present study is the change in the nature of anodic behavior of BiVO₄ and TiO₂ photoelectrode to cathodic behavior for core-shell BiVO₄/TiO₂ heterostructure along with enhanced PEC response. The change in the work function due to nanoparticle size, core-shell nanoparticle configuration and interaction of nanoparticle with water may be responsible for the change in this electronic behavior. The above discussion supports this conjecture for the enhancement of charge separation in BiVO₄/TiO₂ core-shell heterojunction [10].

4. Conclusions

In summary, we have fabricated the pristine BiVO₄, TiO₂, and BiVO₄/TiO₂ core-shell heterostructure nanoparticle by chemical method. TEM analysis confirm the formation of core-shell nanoparticles. The present study shows that the fabricated core-shell heterostructure can not only provide a high optical absorption in visible region, but also cause the formation of a staggered BiVO₄/TiO₂ heterojunction to promote the charge separation and transfer, leading to a significantly enhanced photoelectrochemical water splitting efficiency and high rate of photocatalytic degradation of organic pollution as compared to pristine BiVO₄ and TiO₂ nanoparticles. The change in PEC response from anodic (for TiO₂ and BiVO₄ nanoparticles) to cathodic for BiVO₄/TiO₂ core-shell nanoparticles is explained on the sensitive dependence of work function values to surface conditions, nanoparticle effect, core-shell configuration and interaction of core-shell nanoparticle with water.

Author contributions

S.K. and A.P.S. conceived the idea and designed the experiments. M.M. and A.P.S. have prepared and characterized the samples. M.M., A.P.S., and S.K. analyzed the experimental data for the manuscript.

Fig. 9. The schematic diagram for BiVO₄/TiO₂ core-shell heterostructure for photoelectrochemical water splitting.

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

The authors declare no competing financial interest.

Uncited references

[17].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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