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Interfacial charge transfer and photocatalytic activity in a reverse designed Bi₂O₃/TiO₂ core-shell

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Abstract In this study, the electronic and photocatalytic properties of core-shell heterojunctions photocatalysts with reversible configuration of TiO₂ and Bi₂O₃ layers were studied. The core-shell nanostructure, obtained by efficient control of the sol-gel polymerization and impregnation method of variable precursors of semiconductors, makes it possible to study selectively the role of the interfacial charge transfer in each configuration. The morphological, optical, and chemical composition of the core-shell nanostructures were characterized by high-resolution transmission electron microscopy, UV-visible spectroscopy and X-ray photoelectron spectroscopy. The results show the formation of homogenous TiO₂ anatase and Bi₂O₃ layers with a thickness of around 10 and 8 nm, respectively. The interfacial charge carrier dynamic was tracked using time resolved microwave conductivity and transition photocurrent density. The charge transfer, their density, and lifetime were found to rely on the layout layers in the core-shell nanostructure. In optimal core-shell design, Bi₂O₃ collects holes from TiO₂, leaving electrons free to react and increase by 5 times the photocatalytic efficiency toward H₂ generation. This study provides new insight into the importance of the design and elaboration of optimal heterojunction based on the photocatalyst system to improve the photocatalytic activity.

Keywords photocatalysis, core-shell, heterojunction, H₂, TiO₂, Bi₂O₃

1 Introduction

The decreasing of fossil resources and increasing environmental problems make it imperative to explore effective materials for clean and renewable energy conversion. Sunlight-driven photocatalytic hydrogen production from aqueous solution, as a credible solution for sustainable chemical fuel production, has attracted great research interests [1]. Metal oxides, whose stability is one of the driving force of these semiconductors, have become a very promising candidate for photocatalytic reactions [2].

TiO₂ is one of the most studied photocatalysts due to its suitable electronic and optical properties as well as good chemical stability [3]. However, despite the fact that its absorption is limited to the UV range (large band gap of 3–3.2 eV), the photoefficiency of TiO₂ for hydrogen production is very low, mainly due to the fast recombination of the photogenerated electron and hole (e⁻/h⁺). To tackle these issues, different approaches have been developed to mitigate this limitation with the aim to improve the photocatalytic hydrogen production. Coupling TiO₂ with co-catalysts has been extensively studied in the last decay and shows promising perspectives [4]. A wide range of co-catalysts, such as noble metals, low-cost metal ions/complexes, and metal-free materials have been coupled to TiO₂ to achieve efficient photocatalytic H₂ production [5–11]. The role of co-catalysts is variable regarding their localization on the active material [4]. Another interesting concept is to couple TiO₂ with semiconductors having variable potential band energy, adequately positioned (regarding to TiO₂) [9,12]. This approach shows fair benefits and weaknesses. Metal sulfide shows both a narrow band gap and suitable disposition of the band energy [13,14]. Meanwhile, the generated holes are consumed to oxidize these materials,

Received Jan. 30, 2021; accepted Apr. 29, 2021; online Sept. 10, 2021

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Special Issue—Photocatalysis: From Solar Light to Hydrogen Energy (Guest Editors: Wenfeng SHANGGUAN, Akihiko KUDO, Zhi JIANG, Yuichi YAMAGUCHI)

leading to a poor stability during the photocatalytic reaction [14]. Bismuth oxides coupled to TiO₂ offer instead a better stability and a promising photocatalytic efficiency for hydrogen generation [9,15–17]. Unlike transition metal oxides, the valence band (VB) of bismuth based semiconductors such as BiVO₄ or Bi₂O₃ are composed of both O 2p and Bi 6s orbitals, which can increase the mobility of the charge carrier [18]. The higher mobility of the charge carrier goes with fast charge carrier recombination, which requires constructing a heterojunction. Moreover, bismuth vanadate has an unfavorable low-level CB flat-band energy to energetically initiate the reduction reactions, and consequently is photocatalytically inactive for the production of hydrogen. BiVO₄/TiO₂ junction showed enhanced charge carriers separation for water splitting and a plausible photosensitization, via electron transfer from the conduction band (CB) of the BiVO₄ to the TiO₂, under visible light illumination [19].

In this context, bismuth oxide has been identified as a stable semiconductor (SC) having a low band gap energy (2.29–3.31 eV depending on the crystalline phase [20]), whose flat-band potential are adequately positioned for electron and hole collection (likewise for BiVO₄). Usually studied for water remediation either under UV or visible light [21,22], it has been recently reported that Bi₂O₃/TiO₂ junction is able to produce hydrogen from glycerol aqueous solution under UV illumination [15,23]. The mechanism proposed for the enhancement of the photocatalytic activity, often based on Type I classical electron charge separation in both SCs, is still ambiguous and needs further investigation, mainly due to the position of the respective conduction band of each SC and the arrangement of the adjacent photocatalysts. Furthermore, the charge transfer in heterojunctions remains an open question that should be investigated [24]. Indeed, the CB edge (CBE) is located just under the thermodynamic level for proton reduction to H₂ generation, thus the accumulation of electron from TiO₂ to Bi₂O₃ makes the hydrogen ions reduction thermodynamically difficult.

In this study, tunable core-shell photocatalyst nanostructures based TiO₂@Bi₂O₃ junction are elaborated to study the effect of the core-shell system on the photocatalytic efficiency of hydrogen generation. The design of photocatalytic materials in core-shell nanostructures has been proven to be an original and efficient strategy to improve the photon conversion efficiency toward hydrogen generation [4,5]. The configuration of the system has been adjusted to make selectively accessible one of the two metal oxides at the surface for the photocatalytic reaction. For this purpose, silica nanoparticles were prepared as the core material supporting both TiO₂ or Bi₂O₃ as a shell, depending on the configuration SiO₂@TiO₂@Bi₂O₃ and SiO₂@Bi₂O₃@TiO₂. The novelty of this study compared to the reported studies [15,22,23] lies in the role played by the design of core-shell system and the available metal oxide at the surface. The highest photocatalytic H₂ generation was

observed for SiO₂@Bi₂O₃@TiO₂ heterojunction (5.6 μmol/(g·min)), which was 7 and 13 times higher compared to SiO₂@TiO₂@Bi₂O₃ (0.8 μmol/(g·min)) and SiO₂@TiO₂ (0.4 μmol/(g·min)). The conduction and valence band edge position suggested a Type I for the interfacial charge transfer for SiO₂@TiO₂@Bi₂O₃, while there is a possibility of pseudo Type-II band alignment at the SiO₂@Bi₂O₃@TiO₂ core/shell interface. It is suggested that the enhancement of the photocatalytic activity is attributed to the hole accumulation in Bi₂O₃, which increases the charge separation in TiO₂, as evidenced by the time resolved microwave conductivity, the transition photocurrent density, and the photocatalytic hydrogen evolution.

2 Experiment

2.1 Chemicals

All the chemicals were of analytical grade and used directly without any further purification. They are tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄, 98%, Sigma-Aldrich), ethanol (C₂H₅OH, ACS reagent, ≥99.8%), ammonium hydroxide (NH₄OH, 28%), (3-aminopropyl) trimethoxysilane (APTMS, H₂N(CH₂)₃Si(OCH₃)₃, 97%, Sigma-Aldrich), titanium (IV) isopropoxide (Ti(OiPr)₄, TTIP, 97%, Sigma-Aldrich), bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O, ≥98%, Sigma-Aldrich), methanol (CH₃OH, ACS reagent, ≥99.8%). Deionized water (H₂O, Millipore system, 18.2 MΩ·cm) was used to prepare the aqueous solutions.

2.2 Synthesis of reverse configuration of the core-shell nanostructure

2.2.1 SiO₂ nanoparticles

SiO₂ nanoparticles were prepared following the procedures in Refs. [4,5]. Briefly, 17.1 mL of ethanol, 4.3 mL of NH₃ aqueous solution and 12.8 mL of H₂O were mixed in a 250 mL glass bottle by stirring (500 rad/min). The bottle was sealed with a cap and the mixture was heated under stirring to 40°C. Then, 4.2 mL of TEOS was rapidly injected into the solution. The mixture was left to react under stirring for 1 h to form a colloidal suspension of monodisperse SiO₂ nanoparticles. After that, the SiO₂ nanoparticles were separated by centrifugation (5000 rad/min, 20 min), and washed three times with ethanol and deionized water. Finally, the powder was dried at 70°C for 24 h.

2.2.2 Synthesis of SiO₂@TiO₂ and SiO₂@Bi₂O₃ composites

The synthetic procedures of reverse configuration of the core-shell nanostructures were presented in Fig. 1. The

as-prepared SiO_2 nanoparticles (200 mg) were added to 10 mL of ethanol under stirring, followed by sonication for 30 min for complete dispersion to avoid the aggregation of the nanoparticles. While the colloidal solution was stirred, 0.1 mL of APTMS was added to the dispersed solution dropwise and kept under stirring (500 rad/min) for 6 h at room temperature. The APTMS functionalized SiO_2 nanoparticles were collected from the colloidal solution through centrifugation and washed three times with ethanol absolute.

The $\text{SiO}_2@\text{TiO}_2$ was prepared as follows. APTMS functionalized SiO_2 nanoparticles (200 mg) were added to a mixture of 20 mL of ethanol and 0.5 mL of H_2O . To disperse the functionalized SiO_2 nanoparticles completely, sonication was performed for 30 min and the pH was adjusted at 12.4 using the NH_3 aqueous solution. After stirring for 20 min, a mixture of 50 mL of ethanol and 1.5 mL of $\text{Ti}(\text{OiPr})_4$ were added dropwise to the dispersed solution and left for 2 h under stirring (1000 rad/min) at room temperature. The coated colloidal $\text{SiO}_2@\text{TiO}_2$ nanoparticles were separated by centrifugation, washed with ethanol several times, and dried at 60°C overnight.

Similarly, Bi_2O_3 coated SiO_2 nanoparticles were synthesized from the APTMS functionalized SiO_2 nanoparticles, following the above procedure. Then, 0.5 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added into the colloidal solution. After sonication for 30 min, the mixture was stirred (500 rad/min) for 12 h. The product was separated by centrifugation (10000 rad/min), and washed several times with distilled water to remove the excess of the precursor. The SiO_2 nanoparticles impregnated with Bi^{3+} were suspended in 10 mL of ethanol, sonicated for 10 min and then, the suspension was added dropwise to 40 mL ethanol (The pH was adjusted at 8.5). The solution was stirred during 2 h at ambient temperature, then at 70°C for 30 min. The as-prepared precipitate was separated through centrifugation, washed with ethanol and water several times,

and dried at 60°C overnight. The obtained core-shell nanoparticles were calcined at 500°C during 2 h.

2.2.3 Synthesis of $\text{SiO}_2@\text{TiO}_2@\text{Bi}_2\text{O}_3$ and $\text{SiO}_2@\text{Bi}_2\text{O}_3@\text{TiO}_2$ heterojunctions

For the synthesis of $\text{SiO}_2@\text{TiO}_2@\text{Bi}_2\text{O}_3$ and $\text{SiO}_2@\text{Bi}_2\text{O}_3@\text{TiO}_2$ composites, the as-prepared $\text{SiO}_2@\text{TiO}_2$ and $\text{SiO}_2@\text{Bi}_2\text{O}_3$ composites were further functionalized with the APTMS. By repeating the above synthetic procedures, the $\text{SiO}_2@\text{TiO}_2$ composite was coated with Bi_2O_3 while the $\text{SiO}_2@\text{Bi}_2\text{O}_3$ composite was capped with the TiO_2 layer. The core-shell heterojunctions were dried at 60°C overnight and calcined at 500°C for 2 h at a rate of $2^\circ\text{C}/\text{min}$ under air.

2.3 Characterization

The optical properties were measured using diffuse reflectance spectroscopy (DRS) on a UV-vis-NIR spectrophotometer (Cary 5000 Series, Agilent Technologies) using a BaSO_4 plate as reference.

The morphology of the as-prepared composites was studied by a transmission electron microscopy (TEM). The samples were dispersed in 2-propanol under sonication and deposited on a holey carbon-coated copper grid (Quantifoil Micro Tools GmbH, Großlobichau, Germany). The typical TEM images were collected by a JEOL JEM 2100 Plus CXII equipped with LaB6 filament microscope, operating at 100 kV, and the images were collected with a 4008×2672 pixels CCD camera (Gatan Orius SC1000). The X-ray photoelectron spectroscopies (XPS) of different core-shell heterojunctions were obtained on an ESCALAB 250 spectrophotometer with $\text{Al-K}\alpha$ radiation. The binding energies were calibrated using C 1s at 284.8 eV. Bragg-Brentano X-ray diffraction (XRD) measurements were performed on an Aeris Malvern Panalytical diffractometer

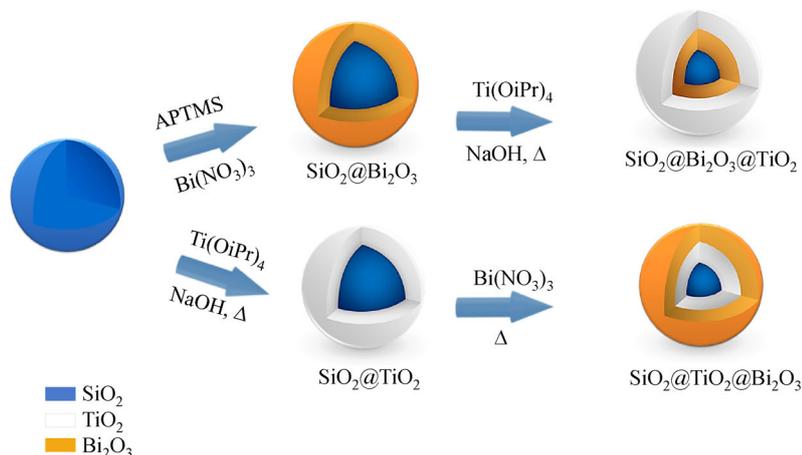


Fig. 1 Schematic representation of the synthesis of core-shell heterojunctions.

using Ni filtered Cu K_{α1} radiation (1.540598 Å) from 10° to 70° with a step size of 0.022° and a counting time of 29.070 s per step. The K_{α2} radiation (1.544426 Å) was mathematically stripped.

The dynamics of photogenerated charge carriers in the composite under UV light ($\lambda = 360$ nm) irradiation was studied by time-resolved microwave conductivity (TRMC) method. The TRMC technique used a pulsed laser source with an optical parametric oscillator (OPO; EKSPLA, NT342B), tunable in the range of 200–2000 nm. The full width at half-maximum of one pulse was 8 ns, the repetition frequency of the pulses was 10 Hz, and microwaves were generated with a Gunn diode (30 GHz). The principle of this technique was described in detail in Refs. [11,25]. In brief, the TRMC measurement of the microwave power reflected by a semiconductor sample are monitored when it is irradiated by a nanosecond pulsed laser. The signal obtained by the diode detector is correlated to voltage for input to the oscilloscope following Eq. (1).

$$\frac{\Delta P(t)}{P} = A\Delta\sigma(t) = A\mu_i\Delta n_i(t), \quad (1)$$

where ΔP is the microwave power absorbed by the sample, A is independent of time but depends on the microwave frequency and the conductivity of the sample, $\Delta\sigma(t)$ is the conductance, $\Delta n_i(t)$ is the number of excess charge carriers i at time t , and μ_i is the mobility of the charge carriers. The TRMC signal reflects the number of mobile charge carriers created right after the laser pulse excitation, the charge carriers lifetime (decay processes) during the excitation, and the decay of the signal due to the decrease of excess electrons controlled by recombination, trapping or surface reaction.

Photoelectrochemical measurements were performed in a three-electrode cell in 0.1 mol/L Na₂SO₄ solution under simulated sunlight illumination (AM 1.5 G, 100 mW/cm²). An electrochemical workstation Orignalyx (France) was used to record the current. A counter electrode of platinum disk and an Ag/AgCl electrode (3 mol/L KCl) were used as the reference ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \text{ pH}$). The electrolyte was degassed for 15 min by flushing N₂ prior to each measurement. The working electrodes were prepared by spreading the target solution (1 mg/mL) on a fluorine-doped tin oxide (FTO) glass substrate with an active area of about 1 cm², and then the film was dried at room temperature.

2.4 Photocatalytic hydrogen production

The photocatalytic production of H₂ was assessed during a standard test, a mixture solution of methanol and water ($v_m/v_w = 25/75$) with a total volume of 20 mL was added into a quartz reactor, and 20 mg of composite photocatalyst

was added under vigorous stirring. Then, the reactor was sealed and degassed with nitrogen (N₂) for 30 min to remove dissolved oxygen. Methanol is used as a hole scavenger and sacrificial electron donor. The photocatalyst was dispersed in the solution at a concentration of 1 mg/mL. A Xenon lamp (300 W) was used as light sources and the amount of H₂ produced as a function of irradiation time was monitored by a gas chromatography (GC, Agilent 7280A system) with a thermal conductivity detector (oven temperature, 70°C; detector temperature, 200°C; carrier gas, N₂).

3 Results

3.1 Morphological properties and surface chemical analysis

The morphology of the SiO₂@TiO₂ core-shell nanostructures was observed by TEM and the typical images are presented in Fig. 2. The TEM images, through contrast difference between the core and the shell, evidence the success of the coating procedure used based on the polycondensation of the TTIP precursor under the basic condition. APTMS functionalized silica core provides a nucleation site for homogenous growth of the TiO₂ at the surface of the SiO₂. Thus, the polycondensation of TiO₂ leads to the formation of a thin layer, covering the silica surface, whose size is estimated to range from 60 to 90 nm (Fig. 2(a)). The thickness of the shell is estimated to be in the range of 5–8 nm (Fig. 2(b)).

The images of the core-shell nanoparticles, demonstrated in Figs. 2(c) and 2(d), indicate that the spherical shape is maintained after both Bi₂O₃ and TiO₂ are coated. The coating procedure makes it possible to adsorb Bi³⁺ ions at the surface of silica nanoparticles under the basic condition. Bismuth ions are not stable and react with hydroxyl groups to form Bi₂O₃ [26]. The surface of the nanoparticles, after the TiO₂ layer growth, appears with a higher roughness and the contrast between metal oxides is less obvious compared to SiO₂@TiO₂ nanoparticles, probably because of the increase of the thickness of the shell of the two metal oxides. The fast Fourier transform pattern of selected area revealed (211) face of TiO₂ anatase with an interplanar spacing of 1.71 nm (inset Fig. 2(c)). The HR-TEM results depicted in Fig. 2(d) indicate that the lattice fringes with d-spacing of 0.351 nm are consistent with the (101) TiO₂ anatase crystallographic plane. Further TEM analysis of SiO₂@TiO₂@Bi₂O₃ show the success of the core-shell nanostructure and the well deposited Bi₂O₃ at the surface (Figs. 2(e) and 2(f)).

The crystalline structures of the as-prepared samples were identified by XRD and the results are displayed in Fig. 3. It is clearly observed that SiO₂@TiO₂ samples exhibit an anatase phase with (101) preferential orientation. The XRD patterns of SiO₂@BiO₂ indicates the

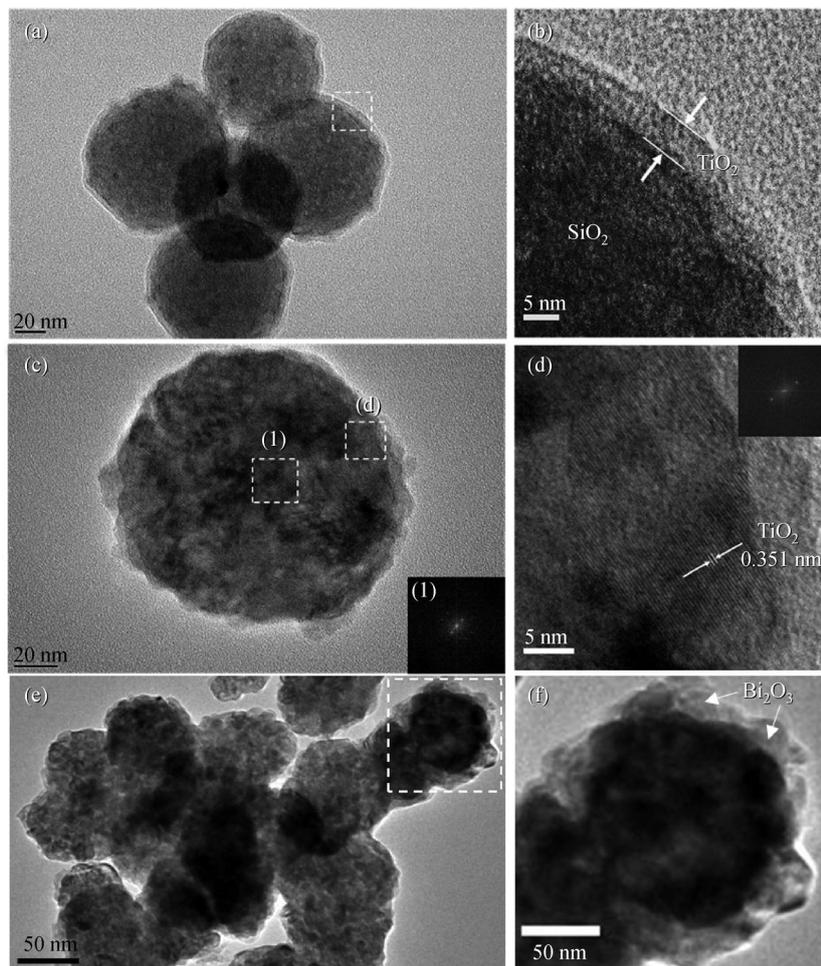


Fig. 2 TEM images.

(a) $\text{SiO}_2@\text{TiO}_2$; (b) enlargement of selected region in (a); (c) $\text{SiO}_2@\text{Bi}_2\text{O}_3@\text{TiO}_2$ core-shell nanospheres; (d) high magnification of the selected region in (c); (e) $\text{SiO}_2@\text{TiO}_2@\text{Bi}_2\text{O}_3$ core-shell nanospheres; (f) high magnification of the selected region in (e) showing Bi_2O_3 shell.

existence of crystalline Bi_2O_3 . Core-shell nanostructure for reverse configuration, $\text{SiO}_2@\text{TiO}_2@\text{Bi}_2\text{O}_3$ and $\text{SiO}_2@\text{Bi}_2\text{O}_3@\text{TiO}_2$, present both crystalline structure of TiO_2 anatase and Bi_2O_3 as evidenced in Fig. 3.

Surface analysis of $\text{SiO}_2@\text{TiO}_2$ and $\text{SiO}_2@\text{TiO}_2@\text{Bi}_2\text{O}_3$ has been carried out using XPS to determine the chemical composition of the outer surface composition of the photocatalyst (Bi_2O_3 or TiO_2), as displayed in Fig. 4. General survey of the surface of $\text{SiO}_2@\text{TiO}_2$ core-shell is depicted in Fig. 4(a). The results indicate that the surface is mainly composed of four elements, i.e., C, O, Si, and Ti, in which the concentration of each element is 18%, 9.5%, 60.5% and 11.5%, respectively. The presence of Si elements is due to the thinness of the shell (measured to be in the range of 5–8 nm). XPS analyses the surface up to approximately 8 nm, which means that the silica core is also detected. Furthermore, during the calcination step, a diffusion of Si could occur from the core to the shell [27]. The Si 2p region shows a peak centered at that correspond

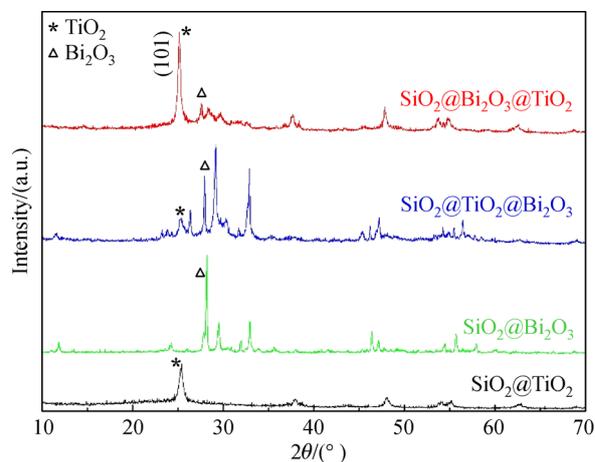


Fig. 3 X-ray diffractograms of different core-shell nanostructures.

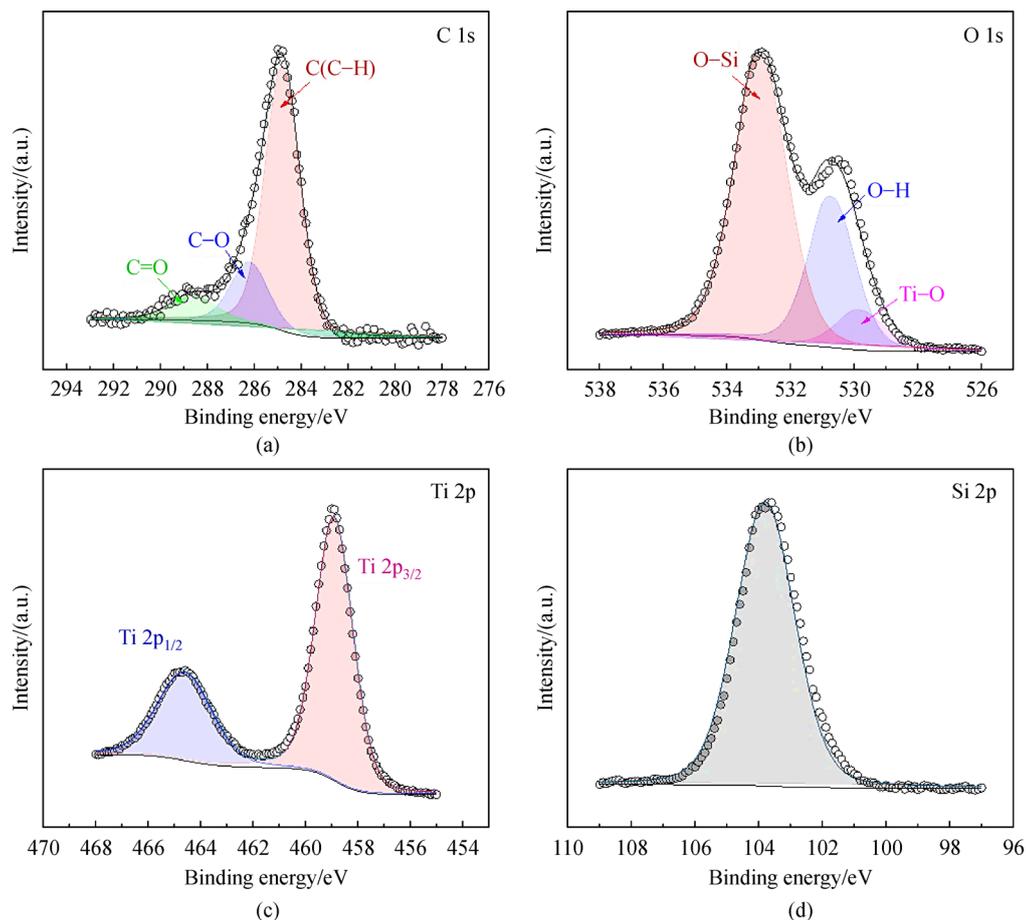


Fig. 4 XPS profile of SiO₂@TiO₂ core-shell nanostructure. (a) C 1s; (b) O 1s; (c) Ti 2p; (d) Si 2p.

to elemental silicon and silicon dioxide. The C 1s peak at the binding energy (BE) value of 284.8 eV is attributed to hydrocarbon mostly related to the residual carbon resulting from the decomposition of the titanium precursor and some surface contamination during the XPS analysis. The O 1s peak could be deconvoluted into three peaks at 529.8, 530.7, and 532.2 eV. These peaks could be assigned to oxygen binding to variable elements such as titanium and silicon, hydrogen of the hydroxyl groups and to carbon. The spin-orbit components of the Ti 2p_{3/2} and Ti 2p_{1/2} peaks were usually deconvoluted into two curves, each at the BE of 458.9 and 464.6 eV, respectively. The separation measured between the maximum of the peaks (5.7 eV) is in agreement with the binding energy separation observed for TiO₂ anatase [28].

Figure 5 presents the Ti 2p and Bi 4f XPS profiles of SiO₂@Bi₂O₃@TiO₂ and SiO₂@TiO₂@Bi₂O₃, and SiO₂@Bi₂O₃ samples, respectively. The results demonstrate that in addition to the Ti element, Bi is also detected in both core-shell reverse configuration samples. An overlap of the peaks of Ti 2p and Bi 4d states are observed. The ratio of Ti is higher for the SiO₂@Bi₂O₃@TiO₂

sample compared to SiO₂@TiO₂@Bi₂O₃, as evidenced by XPS (Figs. 5(a) and 5(c)). The presence of Ti elements for SiO₂@TiO₂@Bi₂O₃ provides information about the thickness of the Bi₂O₃ shell, which should be thinner than 8 nm (as the depth limit analyzed by XPS is up to 8 nm). These results complement the TEM analysis, providing an evidence of the successful coating of the SiO₂@TiO₂ core-shell by the Bi₂O₃ thin overlayer. In addition, the Bi 4f_{7/2} and Bi 4f_{5/2} asymmetric bands are located at the BE at 159.4 and 164.7 eV for all samples, respectively. These orbitals and the separation of 5.3 eV correspond to Bi³⁺ oxide state in pure SiO₂@Bi₂O₃ (Fig. 5(d)), in agreement with Refs. [17,29,30].

3.2 Optical properties

The optical properties were evaluated by recording the UV-visible absorbance spectra of the composites core-shell in the range of 250–800 nm and the results are presented in Fig. 6. As manifested in Fig. 6(a), SiO₂@TiO₂ displays an absorption in the UV range starting from 360 nm, which corresponds to the presence of TiO₂ nanoparticles in its

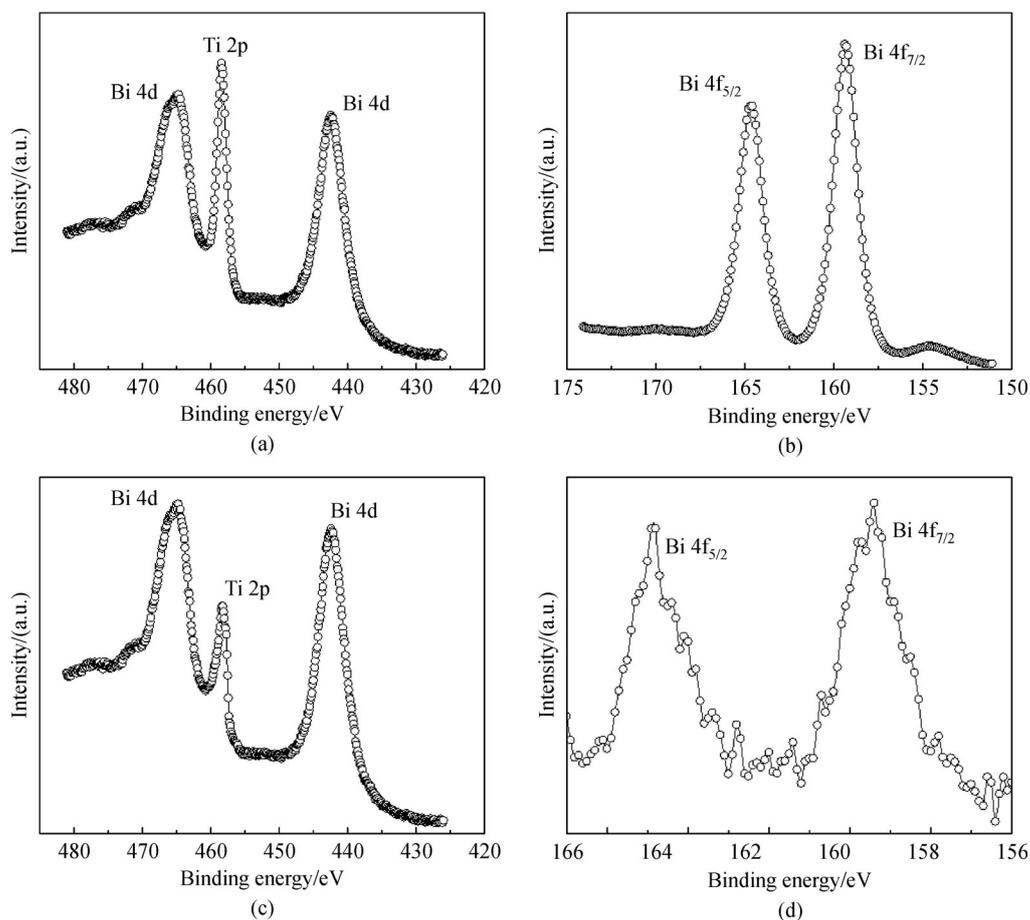


Fig. 5 Ti 2p and Bi 4f XPS profiles.
(a, b) $\text{SiO}_2@Bi_2O_3@TiO_2$; (c) $\text{SiO}_2@TiO_2@Bi_2O_3$; (d) $\text{SiO}_2@Bi_2O_3$.

anatase form [31]. Compared to $\text{SiO}_2@TiO_2$ nanoparticles, the coating core-shell nanostructure with Bi_2O_3 shift the absorption band edge in the visible range. The $\text{SiO}_2@Bi_2O_3$ composite with an absorption edge starting at 550 nm in the visible range is blue-shifted when a TiO_2 layer is coated at the surface. As a result, the $\text{SiO}_2@Bi_2O_3@TiO_2$ composite shows a band edge absorption starting at 420 nm. Likewise, coating the top of $\text{SiO}_2@TiO_2$ with Bi_2O_3 red shift the absorbance edge to 540 nm.

The optical bandgap (E_g) of the nanocomposites were determined using a Tauc plot of modified Kubelka-Munk (KM) function with a linear extrapolation (Fig. 6(b)). The titanium dioxide in the $\text{SiO}_2@TiO_2$ sample operates with a bandgap energy of 3.65 eV. This value is in agreement with the one reported for small sized TiO_2 anatase supported on silica substrate [31,32]. Indeed, the diffusion of the Si element from the silica or the compressive residual stress inhibit the growth of TiO_2 , leading to the small crystallite size. The energy of the bandgap of $\text{SiO}_2@Bi_2O_3$ was 2.21 eV, which is consistent with the bismuth oxide material [33]. The composites $\text{SiO}_2@TiO_2@Bi_2O_3$ and $\text{SiO}_2@$ -

$Bi_2O_3@TiO_2$ showed intermediate bandgap energies of 2.29 eV and 3.17 eV, respectively, which was caused by the existence of TiO_2 .

3.3 Charge carriers dynamics and transition photoresponse of core-shell heterojunctions

The electronic properties of the core-shell heterojunction were studied by means of TRMC as a contactless technique under UV excitation. The TRMC makes it possible to conduct fast photoconductivity measurements to determine the charge carrier mobility and transfer, charge carrier density, and subsequent decay. The signal rising in the first 20 ns is caused by the instrumental response time and the width of the laser pulse. This is followed by a decay, due to a decrease of the density of free charges. Figure 7(a) shows the typical TRMC signal for $\text{SiO}_2@TiO_2$, $\text{SiO}_2@TiO_2@Bi_2O_3$ and $\text{SiO}_2@Bi_2O_3@TiO_2$ core-shell heterojunction after their illumination by the laser pulse emitting at 360 nm. The signal rises from the interaction of the electric field component of the microwaves with mobile charges

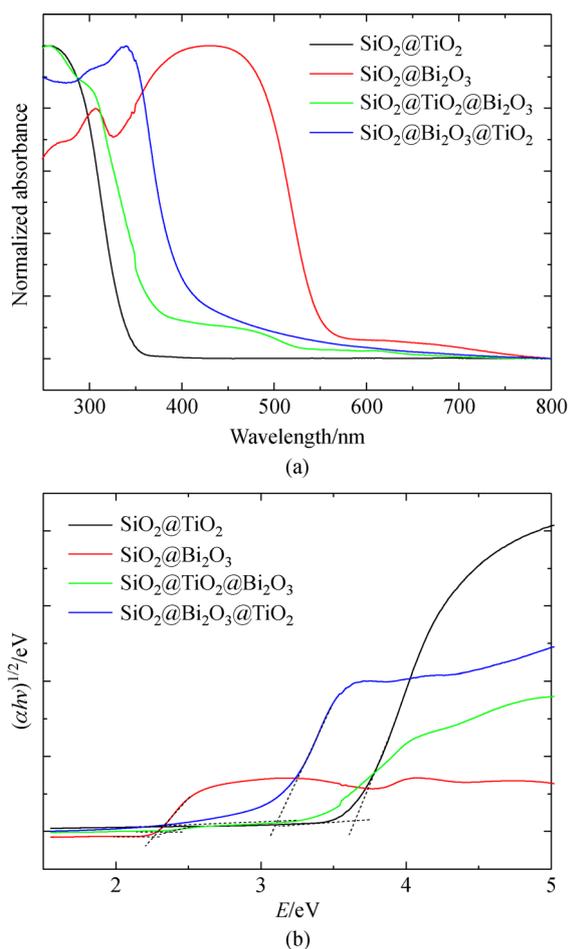


Fig. 6 Optical characterization of variable core-shell systems. (a) UV-visible diffuse reflectance spectra of TiO₂ based core-shell structured composite; (b) plot of transformed Kubelka-Munk function $(\alpha hv)^{1/2}$ vs $E = hv$ (eV).

produced after illumination in the bulk of the photocatalyst, resulting in a change in the real and imaginary conductance [34]. The signal relies mainly on electrons that are more mobile than holes. The results showed different charge carrier density produced after illumination for each samples. The electron density for the SiO₂@TiO₂ nanostructure was found to be very low due to the thinness of TiO₂ photoactive shell or the small crystallite size. As soon as photogenerated electron/hole pairs are produced, they either recombine or are trapped by the surface defects, leading to the nearly zero TRMC signal. The TRMC signal can be divided into three decay stages: charge trapping (τ_{trap}), charge recombination (τ_{rec}), and surface reactions (τ_{surf}) [11]. The trapping time of electrons and holes occurs in an early time (30 ps), and it is accompanied by the fast recombination, occurred during the laser pulse. Both of the trapping and recombination phenomena are considered as the main processes that can explain the decay of the TRMC signals, since the surface reaction occurs at a longer time. During the coupling of TiO₂ and Bi₂O₃, it has been found that the mobility of electrons is sensitive to the design of

the core-shell heterojunction nanostructure. The TRMC signal of SiO₂@Bi₂O₃ is shown in Fig. A1. The results suggest that the decay of the TRMC signals, related to the photocharges, is much faster compared to SiO₂@Bi₂O₃@TiO₂ core-shell. The time constant of electron trapping and recombination can be quantitatively estimated to be $\tau_{\text{trap}} = 0.0815 \mu\text{s}$, $\tau_{\text{rec}} = 0.51296 \mu\text{s}$ and $\tau_{\text{surf}} = 0.51328 \mu\text{s}$, which are faster compared to $\tau_{\text{trap}} = 0.12643 \mu\text{s}$, $\tau_{\text{rec}} = 0.12729 \mu\text{s}$ and $\tau_{\text{surf}} = 1.93922 \mu\text{s}$ for SiO₂@Bi₂O₃@TiO₂ core-shell. The fast recombination of photogenerated charge carriers of SiO₂@Bi₂O₃ leads to a very low photocurrent as evidenced in Fig. A1(b). The insertion of Bi₂O₃ between the silica core and the TiO₂ shell leads to an increase of the charge carrier density. Meanwhile, using Bi₂O₃ as the outer layer shows a small but sensitively higher electron density production and mobility compared to the SiO₂@TiO₂ sample. The results suggest that efficient charge carrier separation and transfer operate regarding the disposition of the layers.

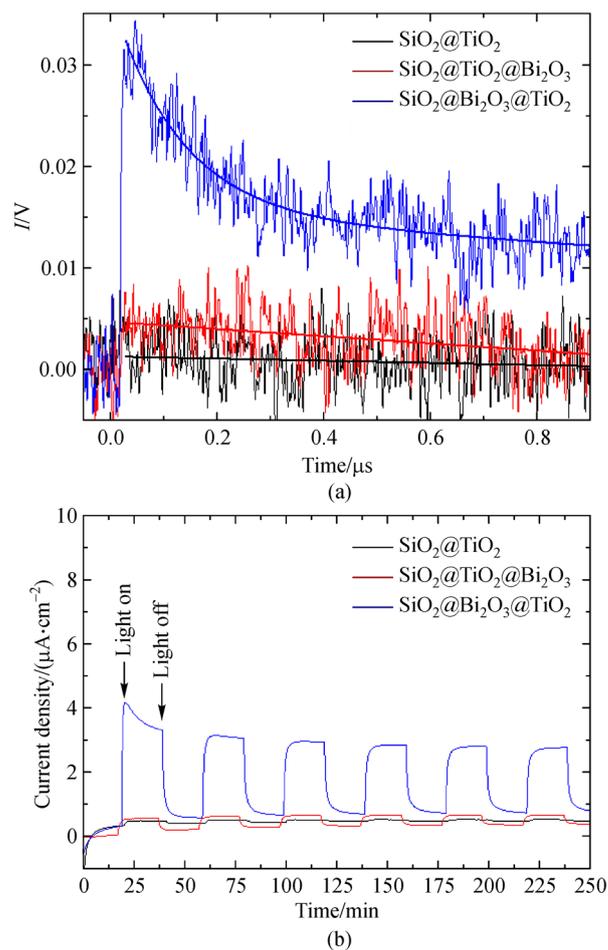


Fig. 7 Charge carriers dynamic and photocurrent response of variable core-shell photocatalysts. (a) TRMC measurements recorded under UV excitation ($\lambda = 360 \text{ nm}$, $I_{\text{ex}} = 1.6 \text{ mJ/cm}^2$); (b) transient photocurrent responses under UV-visible simulated sunlight illumination (AM 1.5 G, 100 mW/cm^2).

The photocurrent-time response of the core-shell nanostructures in on/off cycles under solar light irradiation was further investigated and the results are presented in Fig. 7(b). It can be observed that there was a remarkable increase of the photocurrent when the irradiation was turned on. However, the photocurrent value rapidly decreased as soon as the irradiation was turned off. Combining Bi_2O_3 and TiO_2 in the core-shell heterojunction exhibited an enhanced photocurrent compared to $\text{SiO}_2@\text{TiO}_2$, whose photoresponse is very low ($0.14 \mu\text{A}$). The photocurrent density of $\text{SiO}_2@\text{Bi}_2\text{O}_3@\text{TiO}_2$ ($2.6 \mu\text{A}/\text{cm}^2$) was about 5.2 times higher than that induced in $\text{SiO}_2@\text{TiO}_2@\text{Bi}_2\text{O}_3$ ($0.54 \mu\text{A}/\text{cm}^2$) under solar light irradiation. These results, in agreements with the TRMC signal, indicate that the layout layers are crucial for optimal charge carrier separation and mobility.

3.4 Photocatalytic H_2 generation

The photocatalytic efficiency of the as-prepared core-shell heterojunctions was assessed for hydrogen production from methanoic aqueous solution ($\text{MeOH}/\text{H}_2\text{O}$: 25/75) under UV-visible illumination and presented in Fig. 8(a). In the dark condition, the hydrogen production was not observed. Under UV-visible illumination, $\text{SiO}_2@\text{Bi}_2\text{O}_3$ does not reveal any detectable hydrogen generation. Once coupled to TiO_2 in the core-shell nanostructure, the heterojunction showed variable behaviors toward the hydrogen generation. The highest photocatalytic H_2 generation was observed for $\text{SiO}_2@\text{Bi}_2\text{O}_3@\text{TiO}_2$ heterojunction ($5.6 \mu\text{mol}/(\text{g}\cdot\text{min})$), which was 7 and 13 times higher compared to $\text{SiO}_2@\text{TiO}_2@\text{Bi}_2\text{O}_3$ ($0.8 \mu\text{mol}/(\text{g}\cdot\text{min})$) and $\text{SiO}_2@\text{TiO}_2$ ($0.4 \mu\text{mol}/(\text{g}\cdot\text{min})$), respectively, as shown in Fig. 8(b). This result suggests that the Bi_2O_3 alone is not able to produce hydrogen, but it contributes to the enhancement of the photoactivity of TiO_2 . More importantly, the synergetic effect between Bi_2O_3 and TiO_2 depends on their order on the core-shell heterojunction. These results are in agreement with the TRMC and transition photocurrent results, which is also a correlated to the layout orders of both semiconductors in the core-shell nanostructure.

4 Discussion

The experimental results show that the most active core-shell heterojunction for H_2 generation also showed both the optimal charge carrier separation and the highest photocurrent density. More importantly, these results were dependent on the layout layers of $\text{TiO}_2/\text{Bi}_2\text{O}_3$ in the core-shell nanostructure. To understand the occurrence of the charge carrier transfer in $\text{TiO}_2/\text{Bi}_2\text{O}_3$ core-shell heterojunction, the valence band and conduction band energies were determined. In heterojunction structures, it is crucial

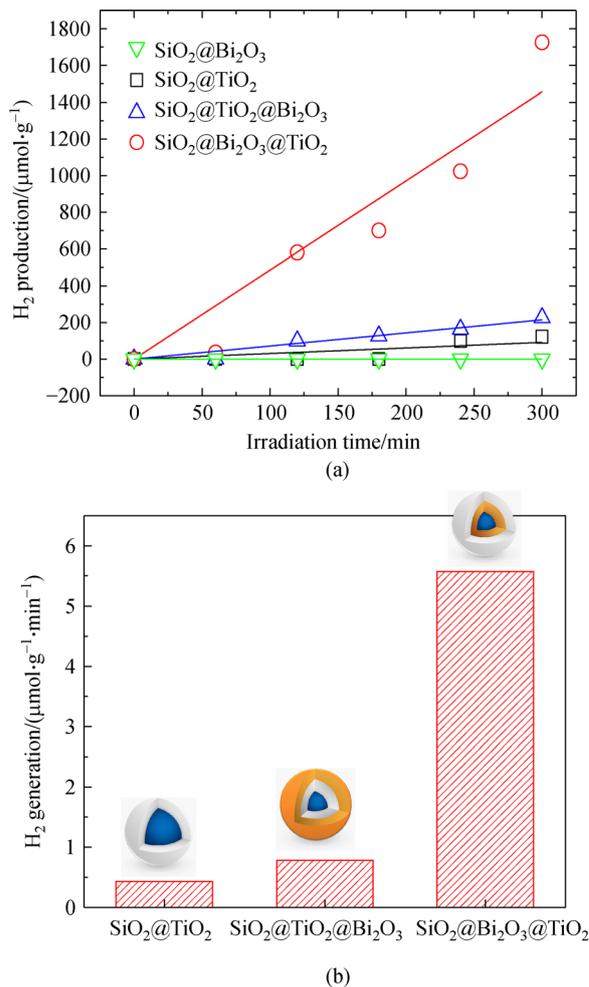


Fig. 8 Photocatalytic characterization of different core-shell heterojunctions during UV-visible irradiation.

(a) Photocatalytic H_2 generation; (b) H_2 production rate.

to identify the highest occupied and the lowest unoccupied electronic levels in each semiconductor. For H_2 evolution, the conduction band (CB) edge should be more negative than the reduction potential of H^+ to H_2 ($E_{\text{H}^+/\text{H}_2} = 0 \text{ V}$ versus NHE at $\text{pH} = 0$). Thus, knowing the optical bandgap energy, obtained from UV-visible DRS spectra, the highest occupied electronic level of the top of the VB and the lowest unoccupied electronic level of the CB of both TiO_2 and Bi_2O_3 can be predicted using the relationship between band edge energies and electronegativity [33] in Eqs. (2) and (3).

$$E_{\text{VB}} = X - E^e + 0.5E_g^e, \quad (2)$$

$$E_{\text{CB}} = X - E^e - 0.5E_g^e, \quad (3)$$

where X is the absolute electronegativity of each semiconductor and defined as the geometric mean of the absolute electronegativity of constituent atoms (X values

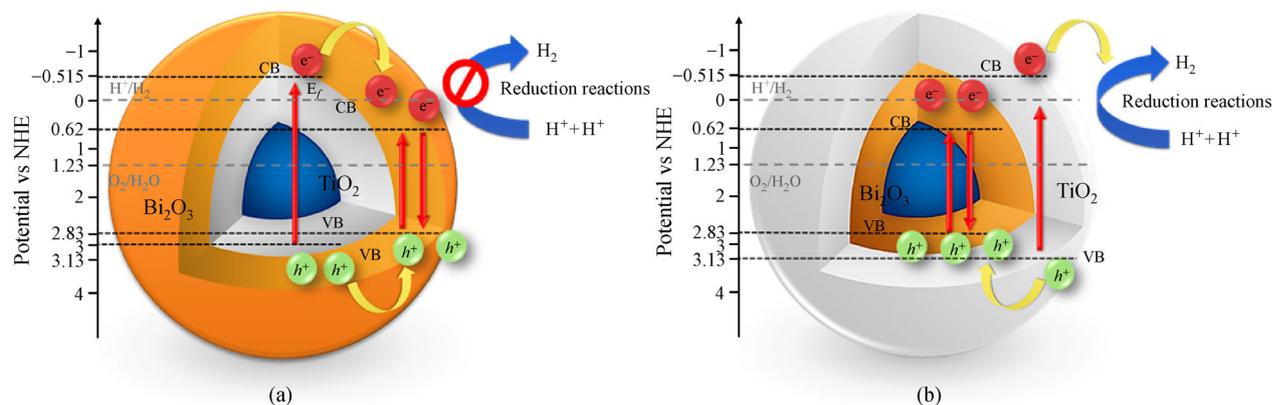


Fig. 9 Diagram of band energy and possible charge separation process for core-shell heterojunctions systems. (a) SiO₂@TiO₂@Bi₂O₃; (b) SiO₂@Bi₂O₃@TiO₂.

for TiO₂ and Bi₂O₃ are 5.81 and 6.23 eV, respectively [33]), E^e is the energy of free electrons on the hydrogen scale (approximately 4.5 eV), E_{VB} is the VB edge potential, E_{CB} is the CB edge potential, and E_g is the bandgap energy for each semiconductor obtained from the UV-visible DRS. The top of the VB and the bottom of the CB of TiO₂ and Bi₂O₃ were 2.83/0.62 eV and 3.13/−0.515 eV, respectively (Figs. 9(a) and 9(b)). The inability of SiO₂@Bi₂O₃ to produce hydrogen is related to the fact that the bottom of the CB of Bi₂O₃ stands at a higher energy than the redox potential of hydrogen. After irradiation of the SiO₂@TiO₂@Bi₂O₃, the photogenerated charge carrier (e^-/h^+) would thermodynamically transfer from TiO₂ to Bi₂O₃ following Type-I band alignment of the core-shell interface, which would prolong the lifetimes of the electrons and then promote the interfacial charge separation (Fig. 9(a)). The charge carrier separation explains very well the increase of both the TRMC signal and the photocurrent density measured for SiO₂@TiO₂@Bi₂O₃, compared to the solely SiO₂@TiO₂. The small increase of the production of hydrogen for this sample could result from the diffusion of energetic electrons produced at the TiO₂ layer, since the bottom CB energy makes Bi₂O₃ thermodynamically unable to reduce hydrogen because the potential of the e^- in the CB of Bi₂O₃ is more positive than the standard redox potential of hydrogen. When the disposition of core-shell heterojunction was changed (SiO₂@Bi₂O₃@TiO₂), making TiO₂ the outer layer, an impressive hydrogen generation was observed. The charge carriers in this system are spatially separated in two semiconductors.

Therefore, there is a possibility of pseudo Type-II band alignment at the core/shell interface, where the hole is delocalized over both the shell and core, and the electron is localized outside the shell (Fig. 9(b)). The photogenerated holes produced at the TiO₂ VB band are accumulated in the Bi₂O₃ VB band, since the bottom of the CB stands at about −0.515 eV versus NHE, leaving the electron at the TiO₂ surface to reduce H⁺ to H[•] efficiently. In this case, Bi₂O₃

acts as a hole transfer layer, favoring the increase of the electron density (TRMC signal and transition photoelectron density) at the TiO₂ surface.

5 Conclusions

In this work, core-shell heterojunctions were prepared by depositing alternatively TiO₂ and Bi₂O₃ by successive sol-gel polycondensation and adsorption precipitation steps. The design of such core-shell heterojunction made it possible to assess selectively the optical, electronic, and photocatalytic properties of the outer layer, i.e., TiO₂ or Bi₂O₃. The best configuration of the core-shell heterojunction was found when Bi₂O₃ was coated with TiO₂. The interfacial charge transfer was found to be affected by the reverse core-shell configuration. The charge carrier transfer for SiO₂@TiO₂@Bi₂O₃ followed Type-I band alignment of the core-shell interface. In the reverse configuration, the separation of charge carriers as well as the photocurrent density and the photocatalytic efficiency were found to be promoted when Bi₂O₃ was deposited below TiO₂, favoring a pseudo-Type II band alignment, as demonstrated by the TRMC and transition photocurrent measurements. Following the disposition of the VB and CB energy of each layer, holes were accumulated in Bi₂O₃ layer leaving electrons free to react for the reduction reaction of hydrogen. The photocatalytic H₂ generation was observed to increase by 7 and 13 times for SiO₂@Bi₂O₃@TiO₂ compared to SiO₂@TiO₂@Bi₂O₃ and SiO₂@TiO₂. This approach can be extended to study the charge carriers transfer in other semiconductors and selectively assess the role playing by each material in order to optimize the efficiency of heterojunctions.

Acknowledgements This work was supported by the public grant overseen by the French National Research Agency (ANR) as part of the “Investissements d’Avenir” program (Labex NanoSaclay, reference: ANR-10-LABX-0035) through project “Z-scheme,” the “Agence Nationale de la Recherche (ANR)” through the UpPhotoCat project, and the “Département de Chimie de

la Faculté des Sciences d'Orsay de l'Université Paris-Saclay" through young researcher grant.

Appendix

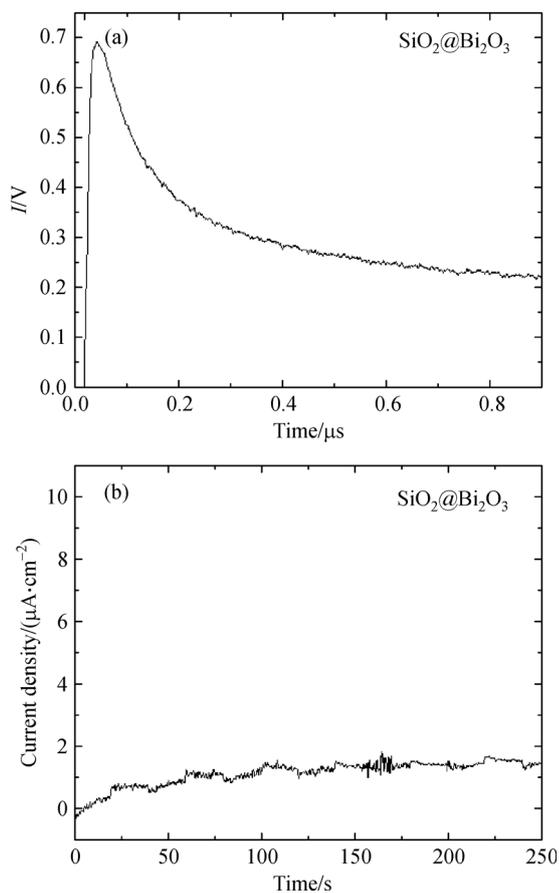


Fig. A1 Charge carriers dynamic and photocurrent response under UV-visible simulated sunlight illumination (AM 1.5 G, 100 mW/cm²) for SiO₂@Bi₂O₃ core-shell.

(a) TRMC signals; (b) transient photocurrent response.

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