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Bismuth sulphide decorated ZnO nanorods heterostructure assembly via controlled SILAR cationic concentration for enhanced photoelectrochemical cells

A A AL-Zahrani, Z Zainal, Z A Talib, H N Lim and A M Holi

1 Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
2 Materials Synthesis and Characterisation laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
3 Imam Abdulrahman bin Faisal University, Eastern Region, Dammam, Saudi Arabia
4 Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
5 Department of Physics, College of Education, University of Al-Qadisiyah, Al-Diwaniyah, Al-Qadisiyah, 58002, Iraq
6 Author to whom any correspondence should be addressed.

E-mail: zulkar@upm.edu.my

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Abstract

The current study investigates Bi2S3 thin films coated on ZnO NRAs with varying cationic concentrations through ionic layer adsorption and reaction (SILAR) technique. XRD patterns reveal that Bi2S3 is successfully synthesised and exhibits orthorhombic structure on the wurtzite ZnO NRAs. The band gap energy (Eg) of Bi2S3/ZnO NRAs shows a notable red shift with increasing cationic concentration. The photocurrent density increases significantly with increasing concentration from 1 mM to 3 mM before decreases at higher concentration due to agglomeration of Bi2S3 NPs and formation of recombination centres. The hybrid photoanode Bi2S3/ZnO NRAs at 3 mM exhibits the highest photocurrent value (1.92 mA cm−2), which is about six times greater than that of plain ZnO NRAs (0.337 mA cm−2). The high photoconversion efficiency value of 1.65% versus 0.5 V Ag A−1g−1C−1l−1 is obtained by Bi2S3/ZnO NRAs (3 mM) in comparison with pristine ZnO NRs, mainly due to the stepwise band alignment edge and significant enhancement of morphological and optical properties. The study reveals that controlling the cationic concentration can potentially improve the photoconversion efficiency.

1. Introduction

Traditional sources of energy such as petroleum, coal and natural gas are non-renewable and are bound to deplete over time. Heavy reliance on these sources may lead to a severe global energy crisis which should be avoided at all cost. One of the best alternatives is to rely on solar energy. Photoelectrochemical cells (PECs) which is the conversion of solar energy into chemical energy have attracted much attention since they were first found by Fujishima and Honda with their experiment using TiO2 as a photoanode [1]. Later, metal oxide-based photoanodes have been heavily revolutionised with successful researches and developments. Among various metal oxides for PECs applications, ZnO has been highly preferred as an alternative to TiO2 for its distinctive characteristics such as moderate band gap energy (3.37 eV), high electron mobility, small electrical resistance, as well as abundancy worldwide [2]. However, ZnO has a critical drawback as its photocurrent production is noticeably limited owing to its relatively large band gap energy leading to restriction in the visible light absorption. With the passage of time, great efforts were strategised including organic dyes doping [3], heterostructure nanocomposite synthesis [4, 5], organic dyes [6] and quantum dots sensitising [7] to overcome these disadvantages. Among them, the synthesis of inorganic-based heterostructure nanorods can be a promising strategy to overcome the ZnO drawback due to the high surface area of the produced composite materials. The arrangement of the band gap energy position of heterostructure is also imperative. The properly-aligned band gap energy in the heterostructure leads to vital enhancement of the photocurrent density in PECs.
since it introduces the fastest and easiest bath of photogenerated electrons. Many narrow band gap metal sulphides such as lead sulphide (PbS) [8], cadmium sulphide (CdS) [9], silver sulphide (Ag2S) [10], copper (I) sulphide (Cu2S) [11,12] and bismuth sulphide (Bi2S3) [13] can be used as a photosensitiser of ZnO NRs. For this purpose, Bi2S3 is selected due to its versatility and possible applications in solar cells [14], photocatalysis [15], photodiode arrays [16], infra-red (IR) spectroscopy and photoelectrochemical cells [17]. Bi2S3 may potentially aid PECs to generate good photocurrent response due to the wide range of visible light absorption (~1.3–1.7 eV), but it can also accelerate the recombination rate of (e– - h+) pairs. Therefore, the combination with ZnO could potentially suppress the recombination rate and substantially improve the PECs performance. In order to assemble Bi2S3 on ZnO nanorods, several approaches have been applied such as hydrothermal method [17, 18], chemical bath deposition (CBD) [19] and, successive ionic layers and adsorption reaction (SILAR) technique [20]. Among them, SILAR technique is the easiest and most cost-effective method to produce Bi2S3 coated on ZnO at ambient temperature. Cationic concentration is one of the important parameters that can affect the amount of deposited Bi2S3 on ZnO NRAs and then the overall photo response of the nanocomposite photodiode. The study reported by [20] revealed that increasing the cationic concentration caused band gap energy blue shift due to the increasing of thickness which reduce the number of defects and decreasing the density of localized state accordingly. Therefore, this study seeks to synthesise a cascade structured of Bi2S3/ZnO NRAs/ITO by varying cationic solution concentrations using SILAR technique purposely to enhance the photoconversion efficiency of ZnO NRs for PEC application.

2. Experimental

2.1. Synthesisation of ZnO nanorods arrays (NRAs)

Highly-oriented perpendicular ZnO nanorods were synthesised at 110 °C for four hours on an indium tin oxide (ITO) substrate by hydrothermal technique as demonstrated in earlier reports [21, 22].

2.2. Synthesisation of Bi2S3/ZnO nanorods arrays

Bi2S3 thin films on ZnO NRAs were synthesised using the SILAR method. Different molarity of bismuth nitrate (Bi(NO3)3) and 0.03 M of sodium sulphide (Na2S) as cationic and anionic precursors solutions were used, respectively. The excess unreacted precursors were removed using de-ionised water (DIW) (18.2 MΩ). The ZnO NRAs was successively immersed for 60 s into the solution containing Bi, followed by rinsing with deionised water. Then, the resultant film was immersed into sulphide solution for 60 s followed by another rinsing in DIW. These four steps were considered as one cycle and each Bi2S3 thin film produced was synthesised for seven cycles. The concentration of Bi(NO3)3 was varied between 1 mM and 10 mM in order to investigate the effect of Bi(NO3)3 concentration on the morphological structure, optical property as well as photoconversion efficiency of Bi2S3/ZnO NRAs/ITO photoanode.

2.3. Characterisation of Bi2S3/ZnO nanorods arrays

The morphological structure and elemental analysis of ZnO NRAs and Bi2S3/ZnO NRAs were examined using field emission scanning electron microscopy (FESEM) and energy dispersive x-ray (EDX) (JEOL JSM-7600F). High-resolution transmission electron microscopy (HRTEM) with selected area (SAED) and electron energy-loss spectroscopy (EELS) modes (Tecnai TF20 x-twin FEI) were used to investigate the structure, crystalline phase, lattice fringe and chemical composition. The crystalline nature of the composite films was examined by x-ray diffraction (XRD) analysis using the Philips PM1730 diffractometer at 40 kV and 40 mA which the data were interpreted using the Panalytical Xpert Highscore software. The scanning range was kept within 20° – 80° with scanning frequency of 5° min–1. Raman spectroscopic analysis was carried out using Alpha 300 R Raman spectrometer (WITec GmbH, Ulm, Germany) at 532 nm laser excitation wavelength and 5 sec of integration time. The x-ray Photoelectron Spectroscopy (XPS) analysis was performed using x-ray Photoelectron Spectroscopy (ULVAC-PHI Quantera II) and Al K-Alpha Monochromatic Source (1486.6 eV) with x-ray beam size of ~100 μm. Absorbance spectra of the produced thin films were measured using the UV–vis spectrophotometer (UV-2600, Shimadzu) with wavelength ranging from 200 nm– 800 nm.

\[
\alpha \ h\nu = A(\ h\nu-E_g)^n
\]  

(1)

where:

- \( \alpha \) is the absorption coefficient,
- \( h\nu \) is the energy of incident photon,
- \( A \) is constant,
- \( E_g \) is the optical band gap energy (eV) and
n value depends on the type of transmission (= ½ and 2 allows direct and indirect transmission respectively). n value is equivalent to ½ as ZnO is a well-known direct band gap semiconductor [23, 24]. The values of $E_g$ for the deposited $Bi_2S_3$/ZnO photoanodes at different cationic precursor concentrations were estimated by deducing the linear portion of $(\alpha h\nu)^2$ versus incident photon energy ($h\nu$) to zero.

The performance analysis of photoelectrochemical cells (PEC) was carried out in a three-electrode electrochemical cells set up that includes the bare ZnO NRAs/ITO and binary heterostructured $Bi_2S_3$/ZnO NRAs/ITO at different cationic concentrations as the semiconductor working electrode, platinum wire as the counter electrode while saturated Ag/AgCl electrode was the reference electrode. The PEC performance was measured using linear sweep voltammetry (LSV) (Autolab PGSTAT204/FRA32 M module) at 20 mVs$^{-1}$ using the binary mixture of 0.1 M Na$_2$S and 0.1 M Na$_2$SO$_3$ as electrolyte solution. All synthesised working electrodes were illuminated using a halogen lamp with 100 mW/cm$^2$ radiation leakage. The estimation for both light and dark currents was done by constantly cutting the irradiation from the light source for every 2 sec at a constant frequency. 

The photoconversion efficiency was calculated based on the following equation [22]:

$$\eta = \frac{J_{ph(1.23 - V_{app})}}{P_{in}} \times 100$$

where:

- $J_{ph}$ ($J_{ph} = J_{light} - J_{dark}$) denotes the obtained photocurrent density (mAcm$^{-2}$),
- $V_{app}$ (V) is employed potential, the normal reversible redox potential reversible redox potential of water electrolysis according to the standard hydrogen electrode (NHE) which is signified as 1.23 V. Meanwhile, $P_{in}$ refers to the power intensity of illumination source (mW/cm$^2$).

3. Results and discussions

X-ray diffraction measurements were done to characterise the crystal structure of bare ZnO NRAs/ITO and ZnO NRAs/ITO decorated with $Bi_2S_3$ as a function of cationic solution concentration. Figure 1 exhibits the x-ray diffraction patterns of bare ZnO NRAs and $Bi_2S_3$/ZnO NRAs prepared at various concentrations of cationic solution between 1 mM and 10 mM range. It can be observed that ZnO NRAs grown via hydrothermal method exhibit a hexagonal wurtzite phase (JCPDS card No. 00-003-0888) while the prepared $Bi_2S_3$/ZnO NRAs/ITO of different concentrations show an orthorhombic structure (JCPDS card No. 03-065-3884) matching the former report by [25, 26]. The distinguishable XRD peaks at (100), (002), (102), (110), (103) and (201) planes matched wurtzite structure phase of ZnO, while the XRD peaks of (114), (025), (044), (202), (240), (072), (173), (302), and (091) matched well with the orthorhombic structure of $Bi_2S_3$. The intensity of diffraction peaks of $Bi_2S_3$ such as (023), (004), (053), (072) and (091) rose with increasing cationic concentration indicating that more $Bi_2S_3$ was deposited on the ZnO NRAs. Apparently, increasing the concentration of Bi ions did not
affect the crystalline nature of ZnO and no impurities were detected in the composites. The outcomes evidently confirmed the successful Bi$_2$S$_3$ formation on the ZnO NRAs.

Figure 2 displays the Raman spectra of ZnO NRAs and Bi$_2$S$_3$/ZnO/ITO at the optimal cationic concentration (3 mM). Many distinct vibration peaks of the synthesised samples situated at 102, 152, 236, 437.5, 480, 710 cm$^{-1}$ can be observed clearly. The two vibration peaks at around 102 and 437.5 cm$^{-1}$ are associated with E$_2$ (low) and E$_1$ (high) phonons vibration modes of ZnO NRAs, respectively [27, 28]. The peak at 575.5 cm$^{-1}$ is ascribed to O$_2$ vacancies and the low intensity of this peak indicates its low defect on the ZnO thin film [13]. Meanwhile, the rest of the peaks located at 152 and 236, 480 and 710 cm$^{-1}$ correspond to Bi$_2$S$_3$ which is in agreement with the Raman peaks as demonstrated by [13, 26, 28].

The XPS analysis was used to explore the chemical components in the heterostructured Bi$_2$S$_3$/ZnO/ITO (optimal sample 3 mM). The binding energy at 284.60 eV was indexed to C 1 s transition in all XPS spectra and used as a reference to standardise the binding energy of other elements in the thin film [29]. The XPS survey profile in figure 3(a) for standard Bi$_2$S$_3$/ZnO/ITO (400°C) shows that the heterostructured photoanode comprised only four elements: Zn, O, Bi and S. The O 1 s profile can be tailored to three distinct peaks which were positioned at 529.64, 531.19 and 532.58 eV, respectively, demonstrating that the sample possessed three distinct O type elements as illustrated in figure 3(c). The peaks at 531.19 eV is attributed to the oxidation state of the element bound with Zn in the crystal lattice of ZnO while the peak at 532.58 eV is correlated to spacious surface of OH$^-$ [30]. Meanwhile, the peak observed at 529.64 eV corresponds to O in Bi$_2$O$_3$. However, x-ray diffraction and Raman analyses were unable to identify the existence of Bi$_2$O$_3$ in the heterostructured photoanode of Bi$_2$S$_3$/ZnO/ITO thin film thus, it is more reasonable to suggest that the formation of Bi$_2$O$_3$ trace was due to water which was used as the solvent for cationic and anionic precursor [30]. The XPS peaks of Zn 2p in figure 3(b) show that there are two peaks located at 1045.06 eV and 1022.02 eV which are attributed to Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$, respectively, proving that Zn exists in Zn$^{2+}$ state [30, 31]. On the other hand, figure 3(d) shows two signals at 158.84 and 163.55 eV which can be ascribed to Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ at 158.84 and 163.55 eV, respectively, verifying the existence of Bi in Bi$^{3+}$ state [29, 32]. Figure 3(a) also shows that two peaks, observed at 162.26 and 160.97 eV can be ascribed to S 2p$_{1/2}$ and S 2p$_{3/2}$, respectively indicating the existence of sulphide species S$^{2-}$ within the thin film.

The morphological surfaces of the bare ZnO NRAs and Bi$_2$S$_3$/ZnO NRAs photoanodes at different concentrations of cationic precursor were analysed using FESEM. Figures 4(a)–(d) illustrate the FESEM images of the plain ZnO NRAs and Bi$_2$S$_3$/ZnO NRAs at 1 mM, 3 mM and 10 mM of cationic precursor, respectively. The bare ZnO NRAs structures are well-aligned and distinct hexagonal phase on ITO substrate with an average diameter $\sim$43.6 ± 2 nm. The Bi$_2$S$_3$ thin film prepared from 1 mM cationic concentration shows non-uniform aggregates with the formation of small grains of Bi$_2$S$_3$ NPs on the top of ZnO NRs and no alteration on the hexagonal wurtzite structure of ZnO NRAs is observed. When the cationic concentration was increased to 3 mM, the Bi$_2$S$_3$ nanoparticles became distinct and covered the entire surface of ZnO NRs uniformly with an average diameter of $\sim$112.35 ± 2 nm. The FESEM images of Bi$_2$S$_3$/ZnO NRAs photoanode at this concentration show better surface porosity, which could enhance the surface area of the
prepared photoanode. As the cationic concentration was increased up to more than 3 mM, the Bi$_2$S$_3$ nanoparticles became clustered together on the ZnO NRs and blocked the spaces between the nanorods. Hence, it can be suggested that 3 mM was the optimum cationic precursor concentration that can provide a large surface area for PEC application.

Figures 5(a), (c) display the selected area electron diffraction (SAED) pattern of bare ZnO NRAs and Bi$_2$S$_3$/ZnO NRs (3 mM), respectively. It was noted that, plain ZnO showed (002) hexagonal wurtzite plane with d-spacing of 0.26 nm. Figure 5(c) demonstrates the polycrystalline nature of Bi$_2$S$_3$/ZnO NRs with 0.26 nm and 0.31 nm of d-spacing allocated to wurtzite ZnO and orthorhombic Bi$_2$S$_3$, respectively.

TEM images of ZnO NRAs and Bi$_2$S$_3$/ZnO NRs (3 mM) are shown in figures 5(b), (d), respectively. The TEM image of bare ZnO in figure 5(b) demonstrates the smooth surface of the rod before the Bi$_2$S$_3$ deposition. After the deposition, uniform distribution of Bi$_2$S$_3$ nanoparticles with an average diameter of around $\sim$7 nm are clearly observed on the surface of ZnO NRAs.

Figure 6 illustrates the HR-TEM image of Bi$_2$S$_3$/ZnO NRs (3 mM) with d-spacing of the plane fringes of 0.26 and 0.31 nm of wurtzite ZnO NRs (002) and orthorhombic Bi$_2$S$_3$ (023), respectively. The TEM image of bare ZnO in figure 5(b) demonstrates the smooth surface of the rod before the Bi$_2$S$_3$ deposition. After the deposition, uniform distribution of Bi$_2$S$_3$ nanoparticles with an average diameter of around $\sim$7 nm are clearly observed on the surface of ZnO NRAs.

The optical properties of the synthesised Bi$_2$S$_3$/ZnO NRAs photoanodes were studied by employing a UV–Vis spectrophotometer at the wavelength ranging from 300 nm-800 nm. Figure 8 displays the absorption
spectra of the uncoated ZnO NRAs and coated Bi$_2$S$_3$/ZnO NRAs/ITO photoanodes prepared from different cationic concentrations (1 mM to 10 mM). It can be noted that ZnO absorbed in the UV range spectrum (≈385 nm). However, the absorption edges of the synthesised photoanodes increased after the deposition of Bi$_2$S$_3$ on the ZnO NRAs. As the cationic concentration increased from 1 to 10 mM, there was a red shift of the absorption edge to the longer wavelengths. As the cationic concentration increased from 1 to 10 mM, the amount of Bi$_2$S$_3$ particles deposited on ZnO NRAs also increased which led to the increment in the nanoparticle size and the reduction in the band gap energy.

When the nanoparticle size was increased, it caused a reduction in the optical band gap energy as demonstrated in the insets of figure 8. This impact, known as ‘quantum confinement effect’ [29], exhibits a comparable behaviour with regard to other materials of such nature [35]. The values of $E_g$ for the deposited Bi$_2$S$_3$/ZnO photoanodes at different cationic precursor concentrations were estimated by deducing the linear portion of $(\alpha h\nu)^2$ versus incident photon energy ($h\nu$) to zero as illustrated in figure 8(B). A significant increase in $E_g$ value was observed with increasing cationic concentration due to the increase quantum confinement effect by increasing amount of deposited Bi$_2$S$_3$ on the ZnO NRAs. The $E_g$ value of Bi$_2$S$_3$/ZnO NRAs/ITO decreased from 3.22 eV to 1.90 eV as the cationic concentration was risen from 1 mM to 10 mM. The calculated values agreed with earlier studies [13]. Furthermore, when the cationic precursor concentration increased, it led to the increase in the thickness of thin film. As a result, the homogeneity of the obtained thin films was increased, the localised state intensity in the band gap was decreased, thus reducing Eg value as reported by [36]. The obtained $E_g$ values are considered optimal values for PEC application, proposing that Bi$_2$S$_3$ is a promising photosensitiser candidate of ZnO NRAs.

4. PEC performance of heterostructured Bi$_2$S$_3$/ZnO NRAs/ITO

The performance of PEC of the assembled Bi$_2$S$_3$/ZnO NRAs as a function of varied concentrations was investigated in a three-electrode configuration cell. The linear sweep voltammogram plots of the Bi$_2$S$_3$/ZnO
NRAs are displayed in figure 9. It is noticed that the photocurrent density ($J_{ph}$) as obtained at $+0.5$ V applied potential increased from 0.337 mA cm$^{-2}$ to 1.92 mA cm$^{-2}$ as the cationic concentration was increased from 0 mM to 3 mM, but then decreased afterwards when prepared using higher concentration of Bi$^{3+}$ cationic precursor.

The photoconversion efficiency of Bi$_2$S$_3$/ZnO NRAs/ITO as a function of cationic concentration at $+0.5$ V applied voltage versus Ag/AgCl rose very significantly with increasing Bi(NO$_3$)$_3$ with the value of 1.65% at 3 mM. Further increment of cationic concentration caused a decrease in the photoconversion efficiency as a

Figure 5. (a), (c) The SAED pattern of plain ZnO NRs and Bi$_2$S$_3$/ZnO NRAs; (b), (d) TEM image of plain ZnO NRs and Bi$_2$S$_3$/ZnO NRAs (optimal sample: 3 mM cationic concentration).

Figure 6. FFT patterns of Bi$_2$S$_3$/ZnO NRAs/ITO attained from the selected area in HRTEM image under scale 5 nm.
result of reduction in the photocurrent density. The calculated photoconversion efficiency at 3 Mm results in a significant improvement in comparison with plain ZnO NRAs (0.25%) as presented in figure 10.

These results could be reflected in terms of two significant factors: the absorption and levels of band alignment of the photoanodes components. As the cationic concentration was increased from 1 mM to 3 mM, the absorption of the incident solar photons increased as illustrated previously and more electron-hole pairs were formed, thus the $J_{ph}$ and $\eta\%$ values increased. In addition, increasing the cationic concentration to 3 mM led to the increment of the photoanode surface area as proven through FESEM images (figure 4).

Moreover, as cationic concentration was increased, the absorption edge showed a red shift, which induced the production of electron-holes pairs that contributed to the significant increase of both $J_{ph}$ and $\eta\%$ values. In contrast, increasing the cationic concentration by more than 3 mM led to a reduction in $J_{ph}$ and $\eta\%$ as demonstrated in table 1. As this performance is primarily ascribed to the increase in the photo generated electron-hole pairs recombination rate in PEC, the excess Bi$_2$S$_3$ nanoparticles acted as the recombination centres [37,38].

Additionally, increasing the concentration of Bi ions by more than 3 mM might cause excessive amount of Bi$_2$S$_3$ being coated which could block the spaces between ZnO NRs and induced the recombination processes. This can lead to reduction in $J_{ph}$ value and also the photoconversion efficiency of the photoanode. Nevertheless, the highest value of photocurrent density was achieved by the sample prepared using 3 mM of Bi(NO$_3$)$_3$ that was almost seven times greater than pure ZnO NRs.

5. Conclusion

Heterostructured Bi$_2$S$_3$/ZnO NRs was synthesised using SILAR method and their properties upon varying the cationic concentrations were examined for photoelectrochemical applications. Significant improvement was...
noted in the photocurrent density of Bi$_2$S$_3$/ZnO NRs (3 mM) with 1.92 mA cm$^{-2}$ and 1.65% of photoconversion efficiency that was seven times greater than bare ZnO NRAs (0.25%). In contrast, when higher cationic concentration of more than 3 mM was employed for synthesising, the photoconversion efficiency was reduced dramatically due to the formation of recombination sites.
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ORCID iDs

A A AL-Zahrani  https://orcid.org/0000-0003-4311-633X
A M Holi  https://orcid.org/0000-0003-2855-952X

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