Realization of electrolyte interface effect on Bi$_2$Te$_3$ implanted flake-like ZnO thin films for understanding the highly stable PEC water splitting under simulated solar light and visible light

Adem Sreedhar and Jin-Seo Noh
Department of Nano-Physics, Gachon University, 1342 Seongnamdaero, Sujeong-gu, Seongnam-si, Gyeonggi-do 461-701, Republic of Korea
E-mail: jinseonoh@gachon.ac.kr

Keywords: thin films, Intimate interface interaction, Ionic conductivity, ZnO, Bi$_2$Te$_3$, PEC activity

Abstract
This study aimed to rationally design the novel Bi$_2$Te$_3$ implanted ZnO (Bi$_2$Te$_3$@ZnO) thin films using simultaneous RF and DC magnetron sputtering technique. Herein, we explored the electrolyte interface effect (0.1 M of KOH, KCl, Na$_2$SO$_3$, and Na$_2$SO$_4$) on ZnO and Bi$_2$Te$_3$@ZnO towards highly stable PEC water splitting activity for the first time. Specifically, morphological evolution and electrolyte ion diffusion properties play a crucial role in realizing the prolonged charge carrier lifetime. Moreover, Bi$_2$Te$_3$@ZnO is highlighted with unique nanocone-shaped morphology compared to flake-like ZnO. Also, constructive interfacial interaction was observed between Bi$_2$Te$_3$ and ZnO. As a result, Bi$_2$Te$_3$@ZnO demonstrated superior and highly stable photocurrents in the KOH electrolyte compared to KCl, Na$_2$SO$_3$, and Na$_2$SO$_4$ electrolytes. Precisely, Bi$_2$Te$_3$@ZnO triumphed highly stable photocurrents about $7.93 \times 10^{-4}$ A cm$^{-2}$ compared to ZnO ($6.02 \times 10^{-4}$) at +0.4 V under solar light in KOH electrolyte. Accordingly, Bi$_2$Te$_3$@ZnO achieved remarkable photoconversion efficiency ($\eta$) about 0.65 %, which is enabled by the strengthened intimate interaction between Bi$_2$Te$_3$ and ZnO. Furthermore, we compared the PEC activity under visible light (UV cut-off solar light). These results highlighted that the photoconversion efficiency difference between Bi$_2$Te$_3$@ZnO and ZnO (about 4 times) under visible light is relatively higher than solar light (1.3 times) in KOH. Thus, we proposed different charge carrier generation mechanisms of Bi$_2$Te$_3$@ZnO under solar and visible light. Therefore, intimate interfacial interaction, surface modification, ion diffusion and photoelectrode-electrolyte interaction are key parameters to enhance the PEC activity. Overall, rational design of the transition metal oxide/thermoelectric material interface using Bi$_2$Te$_3$@ZnO composite paves a new path towards highly stable photoanode during PEC water splitting activity in the KOH electrolyte environment.

1. Introduction

Nowadays, the rapid increase of the global population and economy causes drastic depletion of current fossil fuel reserves, which is also connected to various environmental issues. Thus, we should concern about the development of sustainable clean energy for our future generations. In this direction, conversion of abundantly available renewable solar energy into storable hydrogen (H$_2$) fuel paid immense attention, which guideline clean and carbon-free environment to our society. For this purpose, photoelectrochemical (PEC) water splitting has been adopted as a promising energy conversion technique, which dissociates water into hydrogen (H$_2$) and oxygen (O$_2$) by utilizing renewable solar energy. Specifically, to make an efficient PEC water splitting system, stable photoelectrode and selective electrolyte environment are necessary. Taking advantage of the pioneering report on PEC water splitting using TiO$_2$ [1], various semiconducting oxide materials (WO$_3$, ZnO, Fe$_2$O$_3$, and CuO) have been explored. Later, plasmonic Au nanoparticles were also developed on TiO$_2$ nanotubes to study the PEC water splitting [2]. Recently,
Sb$_2$Se$_3$ has been considered as a photo-absorber with a band gap of 1.1 eV in solar cell applications [3]. Also, the dual-function of CdCl$_2$ treated SnO$_2$ in Sb$_2$Se$_3$ also benefited for solar cell applications [4]. Moreover, Sb$_2$Se$_3$ exhibited an efficient charge carrier transport mechanism as a prominent absorber in the solar cell [5]. Another narrow band gap Cu$_2$ZnSnS$_4$ (1.5 eV) also considered for hydrogen production under visible light [6]. Despite the above selective metal oxides, narrow band gap materials and thermoelectric materials, bismuth telluride (Bi$_2$Te$_3$) is a popular thermoelectric material [7–9], which is considered as a novel photoactive material. Recent studies elevated the advantage of Bi$_2$Te$_3$ in graphene-based nanocomposites [10]. Specifically, Bi$_2$Te$_3$ exhibits strong broadband absorption due to its band gap of about 0.17 eV [11–14]. As a thermoelectric behavior of Bi$_2$Te$_3$, Bi$_2$Te$_3$ generates electricity from waste heat, which ensuring a new strategy to improve the charge carrier generation in the field of optoelectronic devices [7, 15]. Based on the above features, Zhao et al [16] explained the thermoelectric transport behavior of micrometer thick Bi$_2$Te$_3$ films. Very recently, Ren et al [17] fabricated Au particle decorated Bi$_2$Te$_3$ towards photoelectrochemical-type photodetector (solid–solid–liquid joint). Further, intimate interfacial interaction between Bi$_2$Te$_3$ and CoNiMo strengthened the PEC water splitting activity under visible light [18]. Moreover, unique marigold flower-shaped Bi$_2$Te$_3$ thin films distinctly boosted the electrochemical and surface deformation properties [19]. However, the rational design of the novel semiconducting oxides–thermoelectric material interface is interesting for achieving stable and superior PEC water splitting activity. Owing to the above benefits, exploring the intimate interfacial interaction between transparent conducting oxide and Bi$_2$Te$_3$ in the field of optoelectronic devices is a challenging task. In the view of charge carrier generation, Chen et al [7] effectively studied the dye-sensitized solar cell performance of Bi$_2$Te$_3$/TiO$_2$ composite. Also, Patil et al [20] introduced the Bi$_2$Te$_3$ quantum dots on TiO$_2$ micro flowers to improve the photoelectrochemical performance. In addition to TiO$_2$, ZnO is noted as suitable optoelectronic material and extensively studied, but its band gap also confines to the UV region. Nickel-doped ZnO structures tune the PEC water splitting towards visible light [21]. However, possible interfacial interaction between ZnO and Bi$_2$Te$_3$ must be addressed to make visible light active. Until now, limited attempts have been made on a combination of Bi$_2$Te$_3$ and ZnO (Bi$_2$Te$_3$ nanosheet/ZnO nanoparticle and Bi$_2$Te$_3$ nanotube/ZnO) in the field of optoelectronic devices [22, 23]. Thus, strategic experimental techniques are necessary to strengthen the intimate interfacial interaction and achieve a visible response. For this, we followed the promising simultaneous RF and DC magnetron sputtering technique to rationally design the Bi$_2$Te$_3$ implanted ZnO thin films (Bi$_2$Te$_3$@ZnO). Specifically, we focused on strengthening intimate interfacial interaction between Bi$_2$Te$_3$ and ZnO using a conventional sputtering technique. Usually, Bi$_2$Te$_3$ implantation itself permits a potential pathway for electron transportation [23]. In such a way, progressive interfacial interaction between Bi$_2$Te$_3$ and ZnO provides unique heterojunction characteristics, charge carrier generation and transportation properties. In particular, the below-mentioned factors greatly influence the overall PEC water splitting of Bi$_2$Te$_3$@ZnO: (i) intimate interaction between Bi$_2$Te$_3$ and ZnO (ii) surface modification (iii) prolonged electron pathway of Bi$_2$Te$_3$ throughout the composite and (iv) fast kinetic behavior of thermoelectrically converted charge carriers. On the other hand, a selective electrolyte environment at the interface of developed photoelectrode is one of the effective ways to improve the PEC water splitting activity [24]. It is worthy to state that electrolytes with different ionic mobility and minimized solution resistance greatly influence the overall water splitting activity [25]. Thus, understanding the electrolyte interaction at the interface of developed photovoltaic is a complicated process but offers the insights into stable charge carrier kinetics during PEC activity. Therefore, optimization of electrolyte ion diffusion and transfer properties highly beneficial for achieving long-term stability. To the best of my knowledge, the electrolyte interfacial effect (KOH, KCl, Na$_2$SO$_4$ and Na$_2$SO$_3$) on novel Bi$_2$Te$_3$@ZnO was demonstrated for the first time.

This report comprehensively evaluates the intimate interfacial interaction between nanocone-shaped Bi$_2$Te$_3$ and flake-like ZnO and photoelectrode–electrolyte interface effect for achieving superior PEC water splitting activity under simulated solar light and visible light conditions. Specifically, we focused on possible factors for achieving superior and stable PEC water splitting activity of ZnO and Bi$_2$Te$_3$@ZnO electrodes in 0.1 M of KOH, KCl, Na$_2$SO$_4$ and Na$_2$SO$_3$ electrolytes. These results highlighted that the potential PEC system can be achieved under selective KOH and Na$_2$SO$_3$ electrolyte environments through their effective ion diffusion and transportation properties at minimized solution resistance compared to KCl and Na$_2$SO$_4$ electrolytes.

2. Experimentation and characterization

Pure ZnO and Bi$_2$Te$_3$ (3.3 wt.%) implanted ZnO (Bi$_2$Te$_3$@ZnO) thin films were successfully fabricated on ITO glass substrates using simultaneous RF and DC magnetron sputtering technique. To grow the pure ZnO and Bi$_2$Te$_3$@ZnO thin films, 5N purity and 2° dia. of ZnO and Bi$_2$Te$_3$ sputter targets were positioned at 45° to the rotating substrate. Prior to the deposition, the sputter chamber was evacuated to 2 $\times$ 10$^{-6}$ Torr using turbomolecular and rotary pump combination. To achieve the optimized film growth, ZnO and Bi$_2$Te$_3$ targets were sputtered at an optimized working pressure of 2 $\times$ 10$^{-3}$ Torr and Ar flow rate of 12 sccm. Here, RF and DC sputter power of 140 and 4 W simultaneously applied to the ZnO and Bi$_2$Te$_3$ targets respectively. As displayed in
Figure 1. Schematic representation of the ZnO and Bi$_2$Te$_3$@ZnO growth process.

Table 1. Deposition conditions maintained during the growth of ZnO and Bi$_2$Te$_3$@ZnO.

| Sputter Targets          | ZnO (5N purity, 2" dia.) | Bi$_2$Te$_3$ (5N purity, 2" dia.) |
|-------------------------|--------------------------|----------------------------------|
| Base pressure           | $2 \times 10^{-6}$ Torr  | $2 \times 10^{-2}$ Torr           |
| Sputter pressure        | ZnO (RF-140 W)           | Bi$_2$Te$_3$ (DC-4 W)            |
| Deposition temperature  | Bi$_2$Te$_3$ (30 min)    |                                  |
| Deposition time         | Bi$_2$Te$_3$ (1 min @ after 1, 10 and 13 min of ZnO) |
| Post-deposition annealing | 300 °C for 2 h        |                                  |

Figure 1, the Bi$_2$Te$_3$ target shutter arbitrarily opened for 3 times (total 3 min) at every 1, 10 and 13 min deposition of ZnO. After that, pure ZnO and Bi$_2$Te$_3$@ZnO films were annealed at 300 °C for 2 h to achieve progressive interfacial interaction between ZnO and Bi$_2$Te$_3$. The detailed deposition conditions are listed in Table 1. The nanocone-shaped Bi$_2$Te$_3$ (3.3 wt.%) implanted ZnO thin films further labeled as Bi$_2$Te$_3$@ZnO.

Structural properties were studied by the X-ray diffraction (XRD, Rigaku, Smart Lab) analysis. The morphological transformation under Bi$_2$Te$_3$ implantation was revealed using field emission scanning electron microscopy (FESEM, JEOL, JSM-7500F). UV-vis absorption spectra recorded in a Cary 50 Bio spectrophotometer. To obtain the wettability information, water contact angle measurement was examined by SEO-Phoenix 300 (Model-PHX 300) contact angle analyzer. In particular, the effectiveness of Bi$_2$Te$_3$ implantation and interfacial interaction on PEC water splitting activity was demonstrated under simulated solar light and visible light (UV cut-off) in a standard three-electrode PEC cell. In all experiments, 1Sun (100 mW cm$^{-2}$) illuminated towards 1 cm$^2$ active surface area using a solar simulator (Asahi spectra, HAL-320, 300 W). Specifically, $I$–$V$ and $I$–$t$ measurements systematically monitored using the computer–controlled DY2300 potentiostat, which interfaced with ZnO and Bi$_2$Te$_3$@ZnO working electrodes, Ag/AgCl reference electrode and platinum (Pt) counter electrode. Photoelectrode-electrolyte interfacial effect studied at 0.1 M of KOH, KCl, Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolytes.

3. Result and discussions

3.1. Structural properties

To ensure the Bi$_2$Te$_3$ implantation and intimate interfacial interaction between Bi$_2$Te$_3$ and ZnO, reliable crystal structure information was studied by the XRD analysis. The corresponding XRD patterns of pure ZnO and Bi$_2$Te$_3$@ZnO thin films deposited on the ITO glass substrate shown in Figure 2. From figure 2, the predominant
diffraction peak (002) prevailed at $2\theta = 34.4^\circ$ well matched with the hexagonal wurtzite structured ZnO [26]. Apart from the (002) reflection, relatively weak diffraction peaks were observed. These peaks were related to the ITO glass substrate. Interestingly, no sign of peaks related to the Bi$_2$Te$_3$, which signifies that Bi$_2$Te$_3$@ZnO is a composite with the integration of thin layer-by-layer Bi$_2$Te$_3$ intermediate to the ZnO. As shown in figure 2, the Bi$_2$Te$_3$@ZnO composite delivers significant variation in the intensity of the (002) reflection compared to the pure ZnO, which is governed by the constructive interfacial interaction between Bi$_2$Te$_3$ and ZnO. Further insights into the Bi$_2$Te$_3$ implantation are obtained from the full width at half maximum (FWHM). The FWHM of the Bi$_2$Te$_3$@ZnO (002) becomes wider (0.44°) compared to the pure ZnO (0.4°), which ascribed to the nanostructural changes in the Bi$_2$Te$_3$@ZnO. Besides that, the appearance of the above structural changes also suggests that ZnO acts as nucleation site to promote the nanocone-shaped Bi$_2$Te$_3$ during the sputtering process. As for the trend of the above features, Bi$_2$Te$_3$ diffusion can alter the crystal and electronic structure of ZnO. Obviously, the above beneficial effects define the versatile role of Bi$_2$Te$_3$ implantation towards sensible intimate interaction between Bi$_2$Te$_3$ and flake-like ZnO. Combining the above evidence, linear diffusion of Bi$_2$Te$_3$ into ZnO create the constructive Bi$_2$Te$_3$@ZnO composite, which is preferable for use in the PEC cells.

3.2. Morphological studies

To elucidate the impact of Bi$_2$Te$_3$ implantation on morphological evolution, field emission scanning electron microscopy (FESEM) was carried out. Figure 3 displays the morphological evolution due to the Bi$_2$Te$_3$ implantation. As clearly shown in figure 3(a) (i–iii), the ZnO thin film delivers an interesting trend of flake-like morphology. Remarkably, upon Bi$_2$Te$_3$ implantation, most of the flake-like ZnO transformed to nanocone-shape (figure 3(b) (i–iii)). It is evident that the successful diffusion of nanocone-shaped Bi$_2$Te$_3$ networks towards the flake-like ZnO. Inset of figure 3(a)–(b) (iii) signifies the growth of flake-like ZnO and nanocone-shaped Bi$_2$Te$_3$@ZnO. To gain a deeper insight into the morphological transformation of Bi$_2$Te$_3$@ZnO, the nanocone-shaped surface features of pure Bi$_2$Te$_3$ also presented in figure S1(a) (available online at stacks.iop.org/MRX/8/016405/mmedia). Park et al [27] also observed such cone-shaped morphology of Bi$_2$Te$_3$ nanoparticles. In-depth, the above morphological features confirmed the compatibility of nanocone-shaped Bi$_2$Te$_3$ at the interface of flake-like ZnO, which may also cause grain boundary effect in the Bi$_2$Te$_3$@ZnO and lattice distortion in the ZnO host lattice. Therefore, it is expected that the internal diffusion of nanocone-shaped Bi$_2$Te$_3$ towards ZnO shows a significant variation in the particle size of the Bi$_2$Te$_3$@ZnO. The reconstruction of surface morphology emerges as a dominant feature at the electrolyte interface during PEC water splitting activity. Figures S1(b)–(c) shows the high-magnification FESEM images of pure ZnO and Bi$_2$Te$_3$@ZnO, which validates the flake-like and nanocone-shaped morphology. From the high magnified FESEM images, it is found that flake-like ZnO exhibited with flake sizes ranging from 20 to 50 nm. Whereas Bi$_2$Te$_3$@ZnO was clearly modulated the particle size in the order of 20 nm. This is recognized as the consequence of a diffused Bi$_2$Te$_3$ framework into the ZnO for modulating the particle size of the resultant Bi$_2$Te$_3$@ZnO. The variation in the FWHM of Bi$_2$Te$_3$@ZnO (002) reflection also supports the variation in the particle size. Insights of Bi$_2$Te$_3$ existence in the ZnO also observed by the cross-sectional SEM images of pure ZnO and Bi$_2$Te$_3$@ZnO as shown in figure S2. The
appearance of pure ZnO promoted with consistent flake-like morphological features (figure S2(a)). In the case of Bi2Te3@ZnO, we find out the perfectly fitted layer-by-layer growth of Bi2Te3 between ZnO (figure S2(b)). At this condition, EDX spectra confirmed the Bi2Te3 content about 3.3 wt.% in the resultant Bi2Te3@ZnO (figure 3(b) (iv)). Such a lower concentration of Bi2Te3 was also observed by the Bi2Te3/TiO2 composite for dye-sensitized solar cell applications [7]. Besides, a piece of imperative morphological information also illustrated using elemental mapping analysis of ZnO and Bi2Te3@ZnO (figure S3). For pure ZnO, Zn and O elements were clearly observed (figure S3(a)). Notably, Bi and Te are uniformly evenly distributed along with Zn and O throughout the Bi2Te3@ZnO surface (figure S3(b)). Therefore, pronouncing from the above trends of morphological evolution, cross-section layer-by-layer SEM images and EDX mapping, we can speculate that the structural integrity boosted in the Bi2Te3@ZnO composite through the distinguished intimate interaction between flake-like ZnO and nanocone-shaped Bi2Te3. Hence, the effect of morphological transformation triggers the photoelectrode-electrolyte interaction during PEC water splitting activity.

### 3.3. XPS studies

Encouraged by the above constructive surface interfacial interaction between ZnO and Bi2Te3, XPS analysis is also required to further strengthen the chemical bonding interaction. Thus, to access the dependence of Bi2Te3 on the chemical properties of the Bi2Te3@ZnO, X-ray photoelectron spectroscopy (XPS) analysis was studied. Figures 4(a)–(c) displays the XPS survey scan and narrow scan spectra (Zn 2p and O 1s) of pure ZnO and Bi2Te3@ZnO thin films. According to the survey scan spectra, we can notice that both ZnO and Bi2Te3@ZnO display the characteristic peaks of Zn (Zn 3d, Zn 3p, Zn 3s and Zn 2p) and O (O 1s) as shown in figure 4(a). There are no peaks related to the Bi and Te in the Bi2Te3@ZnO, which suggests the Bi2Te3 as a thin layer buried under the ZnO. In other words, Bi2Te3 existed in lower content with less thickness. This is a coincidence with the XRD results with no peaks related to the Bi2Te3@ZnO. To identify the chemical interaction further clearly between ZnO and Bi2Te3 in the Bi2Te3@ZnO composite, we have studied variation in the characteristic Zn 2p and O 1s levels of pure ZnO and Bi2Te3@ZnO. Figure 4(b) shows the narrow scan spectra of Zn 2p level, which is composed of Zn 2p3/2 and Zn 2p1/2 due to spin-orbit splitting. As can be seen in figure 4(b), Zn 2p3/2 and Zn 2p1/2 positions were located at 1019.7 and 1042.8 eV with a binding energy difference of 23.1 eV confirming the Zn in Zn2+ state [28]. However, if we consider the strength of Bi2Te3 interaction in the Bi2Te3@ZnO, the Zn 2p3/2 and Zn 2p1/2 peaks positions were shifted to the lower binding side and positioned at 1019.3 and 1042.4 eV, which guarantees the effective surface and chemical interaction between Bi2Te3 and ZnO. The evidence can be found in deconvoluted O 1s peak into lattice oxygen (O2−) and hydroxy group (OH−) as shown in figure 4(c). The observed O2− and OH− peak positions of Bi2Te3@ZnO shifted to a lower binding energy side compared to the pure ZnO because of interfacial interaction. The chemical interaction capability of the Bi2Te3@ZnO composite is significant when considering the linear variation in the binding energy of Zn 2p and O 1s states towards the lower side. These constructive features will undoubtedly influence the charge carrier generation and transportation properties during PEC water splitting activity.
3.4. Optical properties

Optical absorption is another important parameter that supports the PEC activity of the developed Bi$_2$Te$_3$@ZnO photoelectrode based on the remarkable capability of Bi$_2$Te$_3$ interaction with ZnO. Figure 5 shows the variation in the optical absorption and band gap of pure ZnO and Bi$_2$Te$_3$@ZnO. As it can be seen in figure 5(a), the observable redshift in the optical absorption edge in the Bi$_2$Te$_3$@ZnO compared to ZnO. As discussed above, substantial morphological transformation and integration by the Bi$_2$Te$_3$@ZnO strongly defined an apparent shift in the optical absorption edge. Moreover, the lower content of Bi$_2$Te$_3$ leads to clear grain boundary interaction with ZnO. Since the particle size is affected by the Bi$_2$Te$_3$ implantation, we suggest variation in the optical absorption of Bi$_2$Te$_3$@ZnO. From the above perspective, Bi$_2$Te$_3$@ZnO achieves superior light-harvesting ability compared to ZnO. Further, the optical band gap can be estimated from the following Tauc’s expression [29],

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$  \hspace{1cm} (1)

where $E_g$ represents the optical band gap, A is the proportionality constant and $h\nu$ is the incident photon energy and $\alpha$ is the optical absorption coefficient. By extrapolating the linear portion of $(\alpha h\nu)^2$ versus $(h\nu)$ to $(\alpha h\nu)^2 = 0$, we can estimate the band gap energy of ZnO and Bi$_2$Te$_3$@ZnO. Indeed, pure ZnO showed a band gap of about 3.21 eV [25]. Whereas well-organized Bi$_2$Te$_3$@ZnO observed with a reduced band gap of 3.17 eV as presented in figure 5(b). Hence, variation in the band gap strongly dependent on the constructive (i) grain boundary interfacial interaction between Bi$_2$Te$_3$ and ZnO, (ii) variation in the electronic structure of ZnO and (iii) and morphological evolution, which reasonably consisted well with the SEM results. The above features provide the superior visible-light-harvesting ability of Bi$_2$Te$_3$@ZnO.

3.5. Water contact angle analysis

Intending to determine the consistent impact of Bi$_2$Te$_3$ interaction with ZnO, we further investigated the wettability test. The wettability test provides crucial information about the surface interaction strength between the developed electrode and electrolyte to achieve superior PEC water splitting activity. Thus, water contact
angle information of pure ZnO and Bi$_2$Te$_3$@ZnO was studied (figure S4). Encouraged by the flake-like morphological features, ZnO prevailed with a water contact angle of 85°. Surprisingly, we found remarkable variation in the water contact angle of Bi$_2$Te$_3$@ZnO (52°), which is mainly due to the formation of nanocone-shaped morphological features. In particular, Bi$_2$Te$_3$@ZnO signifies the hydrophilic nature and improved surface interaction strength with the electrolyte compared to pure ZnO. Additionally, the flake-like morphology of ZnO and nanocone morphology of Bi$_2$Te$_3$@ZnO observed with different interaction strengths at the interface of water. Under the above constructive features, Bi$_2$Te$_3$@ZnO provides a significant influence on developing the electrode-electrolyte interface and redox reaction compared to ZnO. Meng et al [30] explained the importance of electrolyte-electrode interaction strength as one of the fundamental surface properties to achieve superior redox reaction during the electrochemical reaction. As clearly distinguished from the water contact angle analysis, it is believed that grain growth modification through the Bi$_2$Te$_3$ implantation is sensitive to the selective electrolyte. Thus, PEC water splitting activity highly dependent on the surface morphological features of the developed electrode. It will be discussed in the later section.

3.6. PEC water splitting activity

Existence of the impact of Bi$_2$Te$_3$ implantation on progressive photoelectrode-electrolyte interfacial interaction and stable charge carrier generation, PEC water splitting activity was carried out in various electrolytes (KOH, KCl, Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolytes (0.1 M)). At the same time ion-conducting behavior of the electrolyte significantly influence the charge transportation processes. Also, the light-harvesting ability of the developed photoelectrode greatly influences the overall PEC activity [31]. It is plausible that electrolyte resistance accelerates ion diffusion and migration [32]. Moreover, reduced ion accumulation on the photoelectrode results
in improved PEC activity. Thus, it is reasonable to evaluate the principal strength of incident light and electrolyte environment near the developed photoelectrode. The incident light utilization efficiency of Bi$_2$Te$_3$@ZnO can be evaluated based on the Bi$_2$Te$_3$ layers [33]. Therefore, to establish the strengthened photoelectrode-electrolyte interface, we monitored the PEC studies (linear sweep voltammetry (I–V), amperometric I-t and photoconversion efficiency ($\eta$)) of ZnO and Bi$_2$Te$_3$@ZnO under (i) simulated solar light, (ii) visible light (UV cut-off solar light) and (iii) various electrolytes.

3.6.1. Electrolyte interface effect on ZnO and Bi$_2$Te$_3$@ZnO under simulated solar light

To reveal the characteristic ion diffusion and transfer properties of selective electrolytes at the interface of developed photoelectrode, PEC activity was studied in KOH, KCl, Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolytes under simulated solar light. Particularly, it has been emphasized that Bi$_2$Te$_3$ implantation and ion diffusion are promising tools to analyze the charge carrier generation and photostability of ZnO and Bi$_2$Te$_3$@ZnO. All of the improved PEC activity is greatly influenced by the reduced recombination rate and narrow band gap [34].

To promote the solar light-harvesting capacity of ZnO and Bi$_2$Te$_3$@ZnO, a batch of I–V and I-t have been acquired in KOH and KCl electrolytes (figures 6(a)–(d)). It is found that superior photocurrent generation by the Bi$_2$Te$_3$@ZnO in KOH electrolyte compared to KCl, which is mainly due to the increased ion diffusion, transfer and minimized solution resistance of KOH [35]. Surprisingly, one interesting observation is that the photocurrents energetically triggered at a negative bias voltage of $-0.4$ V in KOH medium and $-0.3$ V in KCl medium (figures 6(a) and (c)). Accordingly, there is no saturation of photocurrents throughout the sweeping potential [28, 36]. Encouraged by the above features, these results suggest that K$^+$ ions in the KOH electrolyte significantly participated in the PEC water splitting activity and forming a constructive photoelectrode-electrolyte interface than in KCl. As expected, because of progressive intimate interaction between Bi$_2$Te$_3$ and ZnO, the light absorption capacity of Bi$_2$Te$_3$@ZnO is superior compared to the pure ZnO. This means the improvement in the photocurrent density comes from the characteristic thermoelectric behavior of Bi$_2$Te$_3$. Here, Bi$_2$Te$_3$ partially converts waste heat into electricity and offers the to achieve superior PEC activity [20]. The incident light on the developed Bi$_2$Te$_3$@ZnO electrode creates some thermal energy and heat generation, which is called waste heat. Mechanistic investigations highlighted that Bi$_2$Te$_3$ not only converts the waste heat into...
electricity but also enhances the charge transfer properties as an efficient photoreaction catalyst, suggesting the thermoelectric behavior of Bi$_2$Te$_3$. Thus, we suggest superior PEC activity of the Bi$_2$Te$_3$@ZnO undoubtedly originated from (i) thermoelectric electron generation of Bi$_2$Te$_3$ (ii) improved electrolyte ion diffusion, (iii) improved electrolyte interaction (iv) minimized solution resistance and (v) electron transportation from ZnO to Bi$_2$Te$_3$. Under these constructive features, Bi$_2$Te$_3$@ZnO yielded superior photocurrents about $7.93 \times 10^{-4}$ A cm$^{-2}$ in KOH electrolyte (figure 6(a)) compared to KCl ($2.95 \times 10^{-4}$ A cm$^{-2}$)(figure 6(c)), which is also higher than pure ZnO. This indicated that above factors emphasize the precise role of rationalized Bi$_2$Te$_3$ implantation and selective electrolyte environment (KOH).

Following the stability of pure ZnO and Bi$_2$Te$_3$@ZnO photoelectrode as a function of ion transport and interaction behavior, amperometric I-t studies also recorded under the light on/off conditions for 400 sec. It is worth noting that ZnO and Bi$_2$Te$_3$@ZnO thin films prevailed highly stable, reproducible photocurrents with prolonged electron lifetime in KOH electrolyte (figure 6(b)). We also emphasize that Bi$_2$Te$_3$@ZnO provided superior photocurrents in KCl electrolyte like in KOH. But rapid decay in the photocurrents was observed, which indicates the reduced Cl$^-\textit{i}ons transfer during PEC activity (figure 6(d)). Despite the interfacial interaction between Bi$_2$Te$_3$ and ZnO, potential ion diffusion and transfer properties of KOH electrolyte are quite necessary to achieve superior and highly stable PEC water splitting activity.

Further insights into the electrolyte interface effect of ZnO and Bi$_2$Te$_3$@ZnO was studied in Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolytes. The corresponding I–V (−1 to +1) and I-t characteristics (+0.4 V) of pure ZnO and Bi$_2$Te$_3$@ZnO under solar light shown in figures 7(a)–(d). Under the light state, Bi$_2$Te$_3$@ZnO generated superior photocurrents about $5.6 \times 10^{-4}$ A cm$^{-2}$ in Na$_2$SO$_3$ medium compared to Na$_2$SO$_4$ medium-$2.27 \times 10^{-4}$ A cm$^{-2}$. Whereas pure ZnO generated $4.19 \times 10^{-4}$ and $1.57 \times 10^{-4}$ A cm$^{-2}$ in Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolytes respectively (figures 7(a) and (c)). As shown in figure 7(b), considering the hole scavenging behavior of SO$_3^{2-}$ ions present in the Na$_2$SO$_3$ electrolyte, we achieved the stable and superior photocurrents by the Bi$_2$Te$_3$@ZnO [37]. It is obvious that photogenerated holes effectively oxidize the SO$_3^{2-}$ ions at the photoelectrode surface. Thus, the collective effects of SO$_3^{2-}$ ions and intimate interfacial interaction enabled the reliable PEC water splitting activity by the Bi$_2$Te$_3$@ZnO.

In contrast, drastic photocurrent decay and discontinuous reproducibility were observed in the Na$_2$SO$_4$ electrolyte (figure 7(d)) over 400 sec, which is due to the reduced ionic strength of SO$_3^{2-}$ ions compared to SO$_4^{2-}$. The above
results validate another convincing result on charge carrier generation under electrolyte interface effect. Overall, electrolyte ion movement and interaction with the developed electrode drive the overall water splitting activity.

In comparison, it is commonly accepted that Bi$_2$Te$_3$@ZnO achieved superior PEC activity than ZnO in all electrolytes. Specifically, ZnO and Bi$_2$Te$_3$@ZnO photoelectrodes highlighted with highly stable (KOH), stable (Na$_2$SO$_3$) and decayed photocurrent tendency (KCl and Na$_2$SO$_4$) under various electrolytes, which revealed the electrolyte interaction strength at the interface of ZnO and Bi$_2$Te$_3$@ZnO. Another convincing point is that the ion accumulation feature was significantly suppressed at the interface of photoelectrode-electrolyte, which inevitably improved the charge separation and transport properties.

### 3.6.2. Electrolyte interface effect on ZnO and Bi$_2$Te$_3$@ZnO under visible light

Since the Bi$_2$Te$_3$ has an excellent visible light response (UV cut-off solar light) than ZnO, Bi$_2$Te$_3$@ZnO offers promising PEC activity under strategic thermoelectric behavior. This property is generally reliable to demonstrate the superior charge carrier generation and transportation. To highlight the importance of thermoelectric behavior of Bi$_2$Te$_3$, we compared the I–V and I-t characteristics of ZnO and Bi$_2$Te$_3$@ZnO under KOH and KCl electrolytes (figures 8(a)–(d)). Especially, the fact that K$^+$ ions in KOH electrolyte benefit for notable ion conductivity and transfer. On the other hand, intimate interaction strength between Bi$_2$Te$_3$ and ZnO further supports the charge transportation after adsorption of KOH electrolyte near the Bi$_2$Te$_3$@ZnO. The results show that Bi$_2$Te$_3$@ZnO promotes a strong visible light absorption than pure ZnO in both KOH and KCl electrolyte environments. Due to the superior thermoelectric generation behavior from Bi$_2$Te$_3$, the Bi$_2$Te$_3$@ZnO hybrid system can generate superior charge carriers under visible light. As explained earlier, KOH electrolyte provides minimized solution resistance and strengthened K$^+$ ion diffusion capacity. Benefiting from the above phenomenon, Bi$_2$Te$_3$@ZnO strongly suggests preservable superior charge carrier generation and separation. It is found that the Bi$_2$Te$_3$@ZnO generated photocurrents about 1.67 × $10^{-5}$ A cm$^{-2}$ in KOH medium compared to KCl (1.29 × $10^{-5}$ A cm$^{-2}$). A similar trend was also observed by the ZnO (KOH-4.4 × $10^{-6}$ A cm$^{-2}$ and KCl-5.3 × $10^{-7}$ A cm$^{-2}$) (figures 8(a) and (c)) at +0.4 V. On the other hand, the coordination of interconnected Bi$_2$Te$_3$ in the Bi$_2$Te$_3$@ZnO promotes the highly accessible electron
transportation path. Therefore, our observations suggest that Bi$_2$Te$_3$ generates superior thermoelectric charge carriers than ZnO (photoinduced) under visible light. Subsequently, thermoelectric charge carriers (Bi$_2$Te$_3$) and photoexcited charge carriers (ZnO) combine and effectively participate in the overall PEC water splitting activity. Previous reports on Bi$_2$Te$_3$ nanosheet/ZnO nanoparticle composite [22] and Bi$_2$Te$_3$ nanotube/ZnO nanoparticle composite [23] also reported such electron transportation kinetics of Bi$_2$Te$_3$ for DSSC applications. Because of the layer-by-layer formation of Bi$_2$Te$_3$ superior PEC activity can be maintained under visible light. To further understand the above phenomenon in more detail, we measured the amperometric $I$-$t$ studies under the light on/off states at $+0.4$ V for $400$ sec (figures 8(b) and (d)). In the case of KOH electrolyte (figure 8(b)), stable and superior photocurrents were observed by the Bi$_2$Te$_3$@ZnO, which is ascribed to the favorable diffusion of Bi$_2$Te$_3$ electrons towards the ITO substrate. In the case of KCl (figure 8(d)), sharp photocurrent decay was observed. Thus, it is worthwhile to point out the Bi$_2$Te$_3$ interfacial interaction with ZnO and selective electrolyte environment for prompting the PEC activity under superior and stable charge carrier generation.

Encouraged by the above results, we further explored and assessed the dependence of Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolytes on charge carrier generation of ZnO and Bi$_2$Te$_3$@ZnO under visible light (figures 9(a)–(d)). One interesting observation is that the Na$_2$SO$_3$ electrolyte interface highlighted with stable and superior photocurrent generation compared to the Na$_2$SO$_4$ electrolyte. Under the light state, established interaction between Bi$_2$Te$_3$ and ZnO in the Bi$_2$Te$_3$@ZnO prevailed superior photocurrent density about $3.97 \times 10^{-5}$ A cm$^{-2}$ in Na$_2$SO$_3$ electrolyte than Na$_2$SO$_4$ (1.23 $\times 10^{-5}$ A cm$^{-2}$) at $+0.4$ V. Whereas ZnO yielded insignificant photocurrents about $3.86 \times 10^{-6}$ and $5.3 \times 10^{-7}$ A cm$^{-2}$ in Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolytes respectively (figures 9(a) and (c)). Unlike in the KOH and KCl electrolytes, there is a dissimilar trend in the photocurrent generation throughout the sweeping potential. We find out that Na$_2$SO$_3$ electrolyte significantly hinders the charge carrier recombination compared to Na$_2$SO$_4$ electrolyte, which is reliable to demonstrate the improved charge carrier separation of the PEC system [37]. As mentioned before, SO$_3^{2-}$ anions effectively scavenge the holes and create SO$_4^{2-}$ ions. Accordingly, Bi$_2$Te$_3$@ZnO prevailed highly stable and reproducible

Figure 9. Visible light PEC properties of ZnO and Bi$_2$Te$_3$@ZnO in Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolytes: (a), (c) linear sweep voltammogram (I–V) and (b), (d) amperometric $I$–$t$ studies.
photocurrents under Na₂SO₃ electrolyte environment (figure 9(b)). As for Na₂SO₄ electrolyte, obvious photocurrent decay was observed by the Bi₂Te₃@ZnO (figure 9(d)).

From the above observations, rationally designed Bi₂Te₃@ZnO yielded superior, highly stable, and reproducible photocurrents (in visible and solar light) under a selective KOH electrolyte interaction compared to other electrolytes (KCl, Na₂SO₃ and Na₂SO₄). In our results, there is no saturation of photocurrent generation in the KOH electrolyte compared to other counterparts. As displayed in figure 6(a) and figure 8(a), photocurrents linearly increased with the sweeping potential. Thus, the intrinsic light-harvesting capacity of pure ZnO and Bi₂Te₃@ZnO under solar and visible light conditions derived from the photoconversion efficiency (\(\eta\)) using the following expression [38, 39]

\[
\eta = \frac{J}{V_{app}} - \frac{1}{I_{light}} \times 1.23
\]

where \(J\) is the achieved photocurrent density, \(V_{app}\) represents the applied bias voltage versus Ag/AgCl and \(I_{light}\) is the intensity of incident light (100 mW cm⁻²). Figure 10(a) shows the photoconversion efficiency (\(\eta\)) of pure ZnO and Bi₂Te₃@ZnO under solar light. Because of intimate interaction between Bi₂Te₃ and ZnO, superior photoconversion efficiency has been achieved by the Bi₂Te₃@ZnO about 0.65 %, which is higher than pure ZnO (0.5 %) at +0.4 V. Whereas, under visible light condition, Bi₂Te₃@ZnO ensured with 0.016 % compared to pure ZnO (0.004 %) at +0.6 V (figure 10(b)). Under the appreciable interfacial interaction between Bi₂Te₃ and ZnO in the Bi₂Te₃@ZnO and selective electrolyte interface environment (KOH), Bi₂Te₃@ZnO successfully dissociated the water into H₂ and O₂ under solar light as shown in figure 10(c). Therefore, considering the strategic merit of Bi₂Te₃ implantation, we listed the magnitude of photocurrent generation and photoconversion efficiency under simulated solar light and visible light (UV cut-off) of pure ZnO and Bi₂Te₃@ZnO in table 2.

Comprehensively, photoconversion efficiency difference between ZnO and Bi₂Te₃@ZnO under visible light (4 times) is higher than that of simulated solar light (1.3 times), which suggesting the acceleration of thermoelectric property of Bi₂Te₃ under visible light. Further, the specific relationship between water contact angle and photocurrent generation is also noteworthy to comprehend the surface evolution of Bi₂Te₃@ZnO.
Table 2. Photocurrent generation and photoconversion efficiency ($\eta$) of ZnO and Bi$_2$Te$_3$@ZnO in KOH electrolyte under solar and visible light.

| Material          | Photocurrent density (A cm$^{-2}$) | Photoconversion efficiency ($\eta$) % |
|-------------------|-----------------------------------|--------------------------------------|
|                   | Simulated solar light | Visible light | Simulated solar light | Visible light |
|                   | +0.4 V | +0.6 V | +0.4 V | +0.6 V | (+0.4 V) | (+0.6 V) |
| ZnO               | 6.02 × 10$^{-4}$ | 7.85 × 10$^{-5}$ | 4.4 × 10$^{-6}$ | 6.48 × 10$^{-6}$ | 0.5 | 0.004 |
| Bi$_2$Te$_3$@ZnO  | 7.93 × 10$^{-4}$ | 1.0 × 10$^{-3}$ | 1.67 × 10$^{-3}$ | 2.58 × 10$^{-3}$ | 0.65 | 1.3 times | 0.016 | 4 times |

(Bi$_2$Te$_3$ implantation) and photoelectrode-electrolyte interface interaction (figure S5). Thus, the relatively superior visible light response and stable PEC water splitting activity achieved by the Bi$_2$Te$_3$@ZnO can be explained by the surface modification and constructive photoelectrode-electrolyte interface interaction under selective KOH electrolyte.

As shown in the above results, both the electrolyte engineering effect and rational design of Bi$_2$Te$_3$ implanted ZnO thin films significantly realize the charge carrier stability under favorable features of ion diffusion and intimate interaction between Bi$_2$Te$_3$ and ZnO. Despite that, Bi$_2$Te$_3$@ZnO provides constructive bonding force between Bi$_2$Te$_3$ and ZnO, which prevails the superior PEC stability [40]. Thus, the photoelectrode based on a selective photoelectrode-electrolyte interface meets the requirement of long-term stability of Bi$_2$Te$_3$@ZnO and disclosed the PEC activity trend: KOH > Na$_2$SO$_3$ > KCl > Na$_2$SO$_4$. The long-term stability of Bi$_2$Te$_3$@ZnO was also recorded for 15 min under solar and visible light, which reveals the long-term stability of Bi$_2$Te$_3$@ZnO under constructive KOH environment (figure S6). Our previous results were also consistent well with the above tendency in the PEC water splitting activity of Co-ZnO thin films [25].

3.7. Proposed charge transport mechanism under simulated solar light and visible light

To explain the thermoelectric behavior of Bi$_2$Te$_3$ on charge carrier generation and its intimate interaction with flake-like ZnO, two kinds of charge transport mechanisms were proposed under simulated solar and visible light conditions. Firstly, under simulated solar light, ZnO generated considerable photoinduced electrons under the influence of characteristic UV light. It must be noted that the ZnO electrons eventually moves towards the Bi$_2$Te$_3$. Due to the fact, the potential thermoelectric behavior of Bi$_2$Te$_3$ converts the waste heat in the Bi$_2$Te$_3$@ZnO into electricity [7]. This phenomenon facilitates an alternative electron transportation path through the interconnected Bi$_2$Te$_3$ in the Bi$_2$Te$_3$@ZnO. In other words, Bi$_2$Te$_3$ generates electrons based on their Seebeck effect to convert the waste heat into electricity to improve the charge carrier density [23]. As a result, distinctly generated photoinduced charge carriers (ZnO) and thermoelectric electrons (Bi$_2$Te$_3$) combine and provides a strong reason in favor of superior PEC water splitting activity (figure 11(a)). Genuinely, the Bi$_2$Te$_3$@ZnO dissociate the water into H$_2$ and O$_2$ as illustrated in the photo image (figure 10(c)). It has been found that involvement of the Bi$_2$Te$_3$ under visible light (UV cut-off solar light) significantly exceeds and generates more thermoelectric charge carriers compared to photoinduced charge carriers (ZnO). In such a way, figure 11(b) depicts the precise thermoelectric behavior of Bi$_2$Te$_3$ in the resultant Bi$_2$Te$_3$@ZnO. These observations needed to stress the exceeded thermoelectric electrons under visible light compared to solar light. Overall, Bi$_2$Te$_3$@ZnO composite validated superior solar light and visible light response under selective KOH electrolyte. Thus, the proposed charge transportation mechanism reveals the versatile thermoelectric behavior of Bi$_2$Te$_3$ under visible light for quantification of charge carrier generation and transportation, which meets the requirements of stable photoelectrode material in the PEC system.

4. Conclusions

In summary, the photoelectrode/electrolyte interface mechanism of the layer structured Bi$_2$Te$_3$@ZnO was successfully investigated. The effects of novel nanocone-shaped Bi$_2$Te$_3$ implantation into flake-like ZnO and electrolyte interface effect were evaluated and elucidated to achieve the highly stable PEC water splitting activity under solar and visible light. Firstly, we considerably improved the apparent intimate interaction and diffusion between Bi$_2$Te$_3$ and ZnO in the Bi$_2$Te$_3$@ZnO. Secondly, ZnO and Bi$_2$Te$_3$@ZnO photoelectrode interaction demonstrated at various KOH, KCl, Na$_2$SO$_3$ and Na$_2$SO$_4$ electrolyte interfaces. The observed correlation between Bi$_2$Te$_3$ and ZnO, surface transformation and selective electrolyte (KOH) proved the ability of Bi$_2$Te$_3$@ZnO to achieve highly stable and superior PEC activity under both simulated solar light ($7.93 \times 10^{-4}$ A cm$^{-2}$) and visible light ($1.67 \times 10^{-3}$ A cm$^{-2}$). Despite that, selective KOH electrolyte highlighted with minimized solution resistance, lower ion accumulation and better ion transfer compared to...
other electrolytes, which initiated to development of the ideal PEC system. Finally, these findings reveal that electrolyte ion diffusion and transportation properties are considered as prime factors to determine the overall PEC activity of Bi$_2$Te$_3$@ZnO under constructive intimate interaction between Bi$_2$Te$_3$ and ZnO. Therefore, the constructive interfacial properties of Bi$_2$Te$_3$@ZnO with various electrolytes attributed to the development of a stable photoelectrode/electrolyte interface for achieving stable PEC water splitting activity under solar and visible light in KOH electrolyte.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2019R1A2C1008746).

ORCID iDs

Adem Sreedhar  https://orcid.org/0000-0002-8379-6133

References

[1] Fujishima A and Honda K 1972 Electrochemical photolysis of water at a semiconductor electrode Nature 238 37–8
[2] Qi W, Wang N, Chen X and Liang H 2020 Plasmon-assisted partially reduced TiO$_2$ nanotube arrays for photoelectrochemical water splitting Mater. Res. Express 6 125069
[3] Cao Y, Zhu X, Chen H, Zhang X, Zhou J, Hu Z and Pang J 2019 Towards high efficiency inverted Sb$_2$Se$_3$ thin film solar cells Sol. Energy Mater. Sol. Cells 200 109945
[4] Zhou J, Zhang X, Chen H, Tang Z, Meng D, Chi K, Cai Y, Song G, Cao Y and Hu Z 2020 Dual-function of CdCl$_2$ treated SnO$_2$ in Sb$_2$Se$_3$ solar cells Appl. Surf. Sci. 534 147632
[5] Cao Y, Zhu X, Jiang J, Liu C, Zhou J, Ni J, Zhang J and Pang J 2020 Rotational design of charge carrier transport layers for optimal antimony trisulfide solar cells and its integration in tandem devices Sol. Energy Mater. Sol. Cells 206 110279
[6] Wang J, Zeng X, Zhao Y and Zhang W 2020 Preparation and photocatalytic properties of Cu$_2$ZnSnS$_4$ for H$_2$ production Mater. Res. Express 7 095902
[7] Chen T, Guai G H, Gong C, Hu W, Zhu J, Yang H, Yan Q and Li C M 2012 Thermoelectric Bi$_2$Te$_3$-improved charge collection for high-performance dye-sensitized solar cells Energy Environ. Sci. 5 6294–8
[8] Mamur H, Bhuiyan M R A, Korkmaz F and Nil M 2018 A review on bismuth telluride (Bi$_2$Te$_3$) nanostructure for thermoelectric applications Renew. Sustain. Energy Rev. 82 4159–69
[9] Ivanov O and Yaprintsev M 2018 Mechanisms of thermoelectric efficiency enhancement in Lu-doped Bi$_2$Te$_3$ Mater. Res. Express 5 015905
[10] Ahmad K, Wan C, Al-Eshaikh M A and Kadachi A N 2019 Enhanced thermoelectric effect of Bi2Te3-based graphene nanocomposites Appl. Surf. Sci. 474 2–8
[11] Wang Z, Li M, Yang L, Zhang Z and Gao X P A 2017 Broadband photovoltaic effect of n-type topological insulator Bi2Te3 films on p-type Si substrates Nano Res. 10 1872–9
[12] Qiao H E et al 2015 Broadband photodetectors based on graphene–Bi2Te3 heterostructure ACS Nano 9 1886–94
[13] Islam S, Mishra J K, Kumar A, Chatterjee D, Ravishankar N and Ghosh A 2019 Ultra-sensitive graphene–bismuth telluride nano-wire hybrids for infrared detection Nanoscale 11 1579–86
[14] Yue Z, Chen Q, Sahu A, Wang X and Gu J 2017 Photo-oxidation-modulated refractive index in Bi2Te3 thin films Mater. Res. Express 4 126403
[15] Patil P B, Mali S S, Kondalkar V V, Mane R M, Patil P S, Hong C K and Bhosale P N 2015 Morphologically controlled electrodeposition of fern shaped Bi2Te3 thin films for photoelectrochemical performance J. Electroanal. Chem. 758 178–90
[16] Zhao D, Chen J, Ren Z, Chen J, Song Q, Zhang Q, Chen N and Jiang Y 2020 Thermoelectric transport and magnetoresistance of electrochemically deposited Bi2Te3 films at micrometer thickness Ceram. Int. 46 3339–44
[17] Ren X, Zheng W, Qiao H, Ren L, Liu S, Huang Z, Qi X, Wang Z, Zhong J and Zhang H 2020 Enhanced photoresponse behavior of Au@Bi2Te3-based photoelectrochemical-type photodetector at solid-solid-liquid joint interface Mater. Today Energy 16 100401
[18] Yin K, Cui Z D, Zheng X R, Yang X J, Zhu S L, Li Z Y and Liang Y Q 2015 A Bi2Te3@CoNiMo composite as a high performance bifunctional catalyst for hydrogen and oxygen evolution reactions J. Mater. Chem. A 3 22770–80
[19] Thorat J B, Mohite S V, Madake S B, Suryavanshi R D, Rajpure K Y, Shinde T J, Fulari V J and Shinde N S 2019 Electrochemical and surface deformation studies on electrodeposited nanostructured Bi2Te3 thin films Opt. Laser Technol. 113 384–93
[20] Patil P B, Mali S S, Kondalkar V V, Mane R M, Patil P S, Hong C K and Bhosale P N 2015 Bismuth telluride quantum dot assisted titanium oxide microcavities for efficient photoelectrochemical performance Mater. Lett. 159 177–81
[21] Reddy I N, Sreedhar A, Venkata Reddy C, Cho M, Kim D and Shim J 2019 Nickel-doped ZnO structures for efficient water splitting under visible light Mater. Res. Express 6 055517
[22] Wan K, Wu F, Dou Y, Yang L and Mao C 2016 Enhance the performance of dye-sensitized solar cells by Bi2Te3 nanosheet/ZnO nanoparticle composite photoanode J. Alloys Compd. 680 373–80
[23] Dou Y, Wu F, Fang L, Liu G, Mao C, Wan K and Zhou M 2016 Enhanced performance of dye-sensitized solar cell using Bi2Te3 nanotube/ZnO nanoparticle composite photoanode by the synergistic effect of photovoltaic and thermoelectric conversion J. Power Sources 307 181–9
[24] Ding C, Zhou X, Shi J, Yan P, Wang Z, Liu G and Li C 2015 Abnormal effects of cations (Li+, Na+, and K+) on photoelectrochemical and electrocatalytic water splitting J. Phys. Chem. B 119 5360–6

Sreedhar A, Jung H, Kwon H, Yi J, Sohn Y and Gwag J S 2017 Novel composite ZnO/TiO2 thin film photoanodes for enhanced visible-light-driven photoelectrochemical water splitting activity J. Electroanal. Chem. 804 92–8
[26] Tauc J and Menth A 1972 States in the gap J. Non. Cryst. Solids 8–10 569–85
[27] Meng C, Wang B, Gao Z, Liu Z, Zhang Q and Zhai J 2017 Insight into the role of surface wettability in electrocatalytic hydrogen evolution reactions using light-sensitive nanotubular TiO2 supported Pt electrodes Sci. Rep. 7 41185
[28] Afroz K, Moniruddin M, Bakranov N, Kudaibergenov S and Nuraje N 2018 A heterojunction strategy to improve the visible light water splitting activity of flake-like Co-doped ZnO thin films Sol. Energy 191 151–60
[29] Park J W, Nguyen S T, Luan Y and Noh J S 2016 Crystalline bismuth telluride nanoparticle grown by a magnetically assisted physical method Mater. Des. 110 449–55
[30] Sreedhar A, Jung H, Kwon H, Yi J, Sohn Y and Gwag J S 2017 Novel composite ZnO/TiO2 thin film photoanodes for enhanced visible-light-driven photoelectrochemical water splitting activity J. Electroanal. Chem. 804 92–8
[31] Tauc J and Menth A 1972 States in the gap J. Non. Cryst. Solids 8–10 569–85
[32] Meng C, Wang B, Gao Z, Liu Z, Zhang Q and Zhai J 2017 Insight into the role of surface wettability in electrocatalytic hydrogen evolution reactions using light-sensitive nanotubular TiO2 supported Pt electrodes Sci. Rep. 7 41185
[33] Afroz K, Moniruddin M, Bakranov N, Kudaibergenov S and Nuraje N 2018 A heterojunction strategy to improve the visible light sensitive water splitting performance of photocatalytic materials J. Mater. Chem. A 6 21696–718 splitting
[34] Shirinagawa T and Takehara T 2017 Towards versatile and sustainable hydrogen production through photoelectrochemical water splitting: Electrolyte engineering Chem. Sus. Chem. 10 1318–36
[35] Cao Y, Zhu X, Tong X, Zhou J, Ji J, Zhang J and Pang J 2020 Ultrathin microcrystalline hydrogenated Si/Ge alloyed tandem solar cells towards full solar spectrum conversion Front. Chem. Sci. Eng. 14 997–1005
[36] Abdell-Sattar M K and Taha M 2020 Electronic structures and optoelectronic properties of ATiOPO4 (A = H, Li, Na, K, Rb, Cs, Fr, NH4, Ag) compounds and their applications in water splitting, CO2 reduction, and photo-degradation Mater. Res. Express 7 045501
[37] Shirinagawa T, Ng M T K and Takehara T 2017 Electrolyte engineering towards efficient water splitting at mild pH Chem. Sus. Chem. 10 4155–62
[38] Hernández S, Cauda V, Hidalgo D, Farias Rivera V, Manfredi D, Chiodoni A and Pirri F C 2014 Fast and low-cost synthesis of 1D ZnO/TiO2 core–shell nanoarrays: characterization and enhanced photo-electrochemical performance for water splitting J. Alloys Compd. 615 S530–7
[39] Guo S, Zhao X, Zhang W and Wang W 2018 Optimization of electrolyte to significantly improve photoelectrochemical water splitting performance of ZnO nanoarrays Mater. Sci. Eng. B 227 129–35
[40] Sharma M D, Mahala C and Basu M 2020 Sensitization of vertically grown ZnO 2D thin sheets by MoS2 for efficient charge separation process towards photoelectrochemical water splitting reaction Int. J. Hydrogen Energy 45 12272–82
[41] Wang C et al 2014 ZnO@S-doped ZnO core/shell nanocomposites for highly efficient solar water splitting J. Power Sources 269 24–30
[42] Wu Q, Yao T, Sheng M, Shi J and Lv F 2019 Amorphous Co-W-P grown on carbon cloth as a bifunctional catalytic electrode for water splitting Mater. Res. Express 6 115507