



Perspective

Unveiling the impact of interfacially engineered selective V₂O₅ nanobelt bundles with flake-like ZnO and Co–ZnO thin films for multifunctional visible-light water splitting and toxic gas sensing

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HIGHLIGHTS

- Growth of the interfacially matched V₂O₅ nanobelts and flake-like Co–ZnO thin films.
- Combined oxygen bonding at the interface of flake-like Co–ZnO and V₂O₅ nanobelts.
- Surface engineering of V₂O₅/Co–ZnO holds the hydrophilic nature with 63°.
- Surface diffusion improves charge carrier acceleration and visible light harvesting.
- V₂O₅/Co–ZnO outperforms with 42.0 and 10.0 times PEC activity than ZnO and V₂O₅/ZnO.

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ABSTRACT

We report on novel interfacial assembly behavior of V₂O₅ nanobelt bundles (V₂O₅ NBBs) paired with flake-like ZnO (V₂O₅/ZnO) and Co (1.8 at.%)–ZnO (V₂O₅/Co–ZnO) thin films for the first time. This work accomplished highly stable visible-light-driven photoelectrochemical (PEC) water splitting and toxic NO₂ gas sensing. Mainly, charge carrier acceleration ability is associated with the interfacial diffusion behavior between nanobelt and flake-like morphologies. Structural studies revealed strong network formation between predominant ZnO (002) and V₂O₅ (001). Because of nanobelt/flake-like intimate interaction, we fairly established the flake-like ZnO and Co–ZnO morphological features on V₂O₅ NBBs. Accordingly, chemical analysis of V₂O₅/Co–ZnO illustrated a shift in the O 1s peak position towards lower binding energy, which is ascribed to the impressive combined oxygen bonding formation at the interface of Co–ZnO and V₂O₅. Taking advantage of the interfacial interaction and abundant hydrophilicity (63°) of V₂O₅/Co–ZnO, we controllably achieved stable water splitting activity about 21.0 min. In an effort, V₂O₅/Co–ZnO composite outperformed the photocurrent generation with 1.45×10^{-4} A/cm², which is 42.0 times higher than ZnO. Also, V₂O₅/Co–ZnO attained NO₂ gas response (130.0%) at 50 ppm. Comprehensively, nanobelt/flake-like morphological integration serves as a highly stable photoanode in the PEC cell as well as a toxic gas sensor.

1. Introduction

Nowadays, generating sustainable clean energy has become increasing demand due to the destructive depletion of many fossil fuels, including natural gas, petroleum and coal, which is mainly due to the rapid increase of global population and industrialization. To solve the above ecological problems, there is an interesting demand pertained to

develop promising and alternative sustainable clean energy techniques, which can resolve the current public energy crisis. As an emerging technique, photoelectrochemical (PEC) water splitting notably attracted many researchers for sustainable hydrogen (H₂) fuel generation from water. To this end, researchers have been focusing on the development of versatile visible light active materials, which endows water splitting into H₂ and O₂. Specifically, the production of H₂ fuel using the PEC

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water splitting technique through harvesting solar energy is an effective strategy, which is an exceptional way for zero-emission carbon byproducts. For this purpose, Fujishima and Honda first reported the groundbreaking work on TiO_2 as a potential photoanode in the year of 1972 [1]. Despite the remarkable advantage, TiO_2 only absorb a limited UV portion (4%) of solar light because of its band gap falls in the UV region. Thus, several specified semiconducting oxide materials such as ZnO , Fe_2O_3 , SnO_2 and WO_3 etc. have been endeavored to explore the possible PEC activity. Among these, ZnO preferred as an alternative material to the TiO_2 due to its higher electron mobility and lower recombination rate than TiO_2 [2]. Moreover, ZnO exhibits key features such as non-toxicity, abundance, chemical stability and good photocatalytic activity. In this context, ZnO ($E_g = 3.37$ eV) prevails effective PEC performance. But, ZnO is also restricted in the UV region of the solar spectrum. Generally, visible light PEC activity can be accomplished by the transition metal ion doping or making promising hybrid structures. Especially, making of interfacially assembled hybrid structure using semiconductor thin film and nanostructures is an interesting way. In particular, matching of interfacial environment enables visible light response. In such a way, to cultivate the visible light active composite through the improved charge carrier kinetics, integration of rationally designed ZnO and V_2O_5 nanostructures is growing immense interest. Generally, V_2O_5 exhibits a band gap of about 2.3 eV [3,4], which can absorb visible light. Also, it was reported that V_2O_5 is a source for low electrical conductivity, poor microstructure stability, charge trapping states, and high density of surface states [3]. As a result, significant charge carrier recombination limits its ability towards superior photo-conversion efficiency [5]. To overcome these traditional issues, it is necessary to develop the interfacially assembled heterostructure by combining wide band gap semiconducting oxide material, which is representative to inhibit the charge carrier recombination. For instance, the organization of the nanostructure/metal oxide thin film intimate interface is quite an interesting, challenging and novel perspective in the field of optoelectronic devices. Moreover, it discusses the unique surface interfacial interaction properties for achieving superior charge carrier generation and separation. Hence, intimate interfacial interaction was adopted to optimize and extend the visible light absorption during the PEC activity. Therefore, nanostructure/metal oxide thin film morphological features unveiled state-of-the-art material, which facilitates improved charge carrier generation, lifetime and separation. To date, many researchers developed V_2O_5 based composites for diverse applications. Waseem et al. [6] developed $\text{GaN}/\text{V}_2\text{O}_5$ core-shell nanowires for piezoelectric nanogenerators. Nagaraju et al. [7] synthesized $\text{ZnO}/\text{V}_2\text{O}_5$ nanostructured composite thin films for toluene detection. Xie et al. [8] fabricated $\text{TiO}_2/\text{V}_2\text{O}_5$ nanocomposites for arsenic detection. Sahatiya et al. [9] studied the enhanced photodetector performance using V_2O_5 nanowires over MoS_2 nanoflakes. Recently, Liu et al. [10] reported symmetric supercapacitor activity of $\text{V}_2\text{O}_5/\text{rGO}$ composites. Ahirrao et al. [11] revealed the superior electrochemical and supercapacitor activity using V_2O_5 nanowires based graphene composite. Hong et al. [12] studied the enhanced visible light efficiency on Z-scheme $\text{V}_2\text{O}_5/\text{g-C}_3\text{N}_4$ heterojunctions. Su et al. [13] explored the kinetic behaviors of photogenerated charge carriers on $\text{V}_2\text{O}_5\text{-BiVO}_4$ composite. Among these rationally designed composites, $\text{ZnO}/\text{V}_2\text{O}_5$ hybrid structure has been attracted due to its diverse applications including, field emission properties [14], visible light photocatalysis [15–21] and antibacterial activity [22]. At this point, limited findings have been reported to reveal the impact of various V_2O_5 nanostructure interactions with ZnO in the $\text{ZnO}/\text{V}_2\text{O}_5$ composite, which including nanoparticles [14, 20], nanowires [22], shell [23] and shell layer [15]. Motivated by the above morphological integration, we adopted the V_2O_5 nanobelt bundles (V_2O_5 NBBs) interfacial interaction with flake-like ZnO thin films, which significantly reveal the charge carrier generation, separation and transportation properties. Moreover, to further extend the photo-response towards visible light and improve the charge carriers, transition metal ion such as Co^{2+} can be incorporated into the ZnO host

lattice, which is sensitive to succeed the charge carrier generation [24] and acceleration between V_2O_5 and Co-ZnO . In particular, V_2O_5 especially in the form of nanobelt shape brings us significant attention, since the choice of its perfect interaction with sputter-deposited flake-like ZnO and Co-ZnO thin films. This allows the magnitude of intimate interface interaction. Therefore, understanding the interfacial charge carrier transportation relation between (i) ZnO and V_2O_5 in the $\text{V}_2\text{O}_5/\text{ZnO}$ and (ii) Co-ZnO and V_2O_5 in the $\text{V}_2\text{O}_5/\text{Co-ZnO}$ promotes the development of V_2O_5 based visible light PEC active material. Besides, nitrogen dioxide (NO_2) is a hazardous gas to our society, which is expelling from the combustion of fossil fuels and automobiles. Pure V_2O_5 acts as a good NO_2 gas sensor [25]. In such a way, V_2O_5 based metal oxides are also potential candidates to detect the NO_2 gas, such as V_2O_5 decorated SnO_2 [26], $\text{MoO}_3\text{-V}_2\text{O}_5$ composite thin films [27] and $\text{TiO}_2\text{-V}_2\text{O}_5$ nanocrystals [28]. Inspired by the above outcomes, we demonstrated the NO_2 gas sensing using the unique coordination of flake-like Co-ZnO and V_2O_5 NBBs. To the best of our knowledge, there is no previous report on the concept of interfacially assembled $\text{V}_2\text{O}_5/\text{Co-ZnO}$ composite for multifunctional PEC water splitting and toxic NO_2 gas sensing.

Here, we aim to rationally design and highlight the flake-like ZnO and Co-ZnO thin film interfacial interaction with V_2O_5 NBBs using simultaneous RF and DC magnetron sputtering technique. The synthesized $\text{V}_2\text{O}_5/\text{Co-ZnO}$ composite prevailed as a potential photoanode compared to pure ZnO and $\text{V}_2\text{O}_5/\text{ZnO}$. Specifically, the impact of Co incorporation in the ZnO host lattice and Co-ZnO interfacial diffusion interaction with selective V_2O_5 NBBs have been systematically demonstrated, which aims towards the multifunctional PEC water splitting and gas sensing activity.

2. Experimental

2.1. Synthesis of V_2O_5 nanobelt bundles (V_2O_5 NBBs)

To prepare the V_2O_5 NBBs, 10.0 g of commercially available V_2O_5 powder combined with 500 ml of 2 M NaCl in the stirrer at 25°C for the duration of 72 h. Then, the solution has been separated and washed several times in DI water and ethanol by centrifugation process. The above cleaning process leads to achieving the required V_2O_5 NBBs. Next, the solution was left at 80°C in a vacuum oven overnight. Finally, the dried V_2O_5 powder was collected to further spin coat on the ITO substrate. Before the spin coating, the ITO substrates were sequentially subjected to ultrasonication in acetone and IPA. Later, the substrates were placed on the hot plate for 5 min. Finally, the collected V_2O_5 NBBs were used to spin coat on ITO substrates at 3000 rpm for 3 min. The achieved ITO/ V_2O_5 NBBs used to couple with the flake-like ZnO and Co-ZnO thin films.

2.2. Fabrication of $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$

Simultaneous RF and DC magnetron sputtering technique was used to deposit the flake-like ZnO and Co-ZnO thin films on the V_2O_5 NBBs. Fig. 1 represents the schematic diagram of V_2O_5 NBBs coordinated with flake-like ZnO ($\text{V}_2\text{O}_5/\text{ZnO}$) and Co-ZnO ($\text{V}_2\text{O}_5/\text{Co-ZnO}$). Specifically, RF and DC sputter powers of 140 W and 40 W fed to the ZnO (2" dia., 5 N purity) and Co (2" dia., 5 N purity) targets respectively. Here, we selected the optimal DC sputter power of 40 W to incorporate the Co content about 1.8 at.% in the ZnO host lattice [24]. In the sputter chamber, the ITO/ V_2O_5 NBBs was mounted on the rotating substrate, which was considered to achieve fair growth of flake-like thin film morphology. Before the sputtering process, the deposition chamber evacuated to 2×10^{-6} Torr. Then, sputter pressure was maintained at 2×10^{-2} Torr using a mass flow controller under the Ar flow rate of 12 sccm. All the films (ZnO and Co-ZnO) were deposited at room temperature for 30 min. Subsequently, post-deposition annealing has been carried out specifically at 300°C for 2h, which creates further perfect interfacial diffusion interaction between V_2O_5 NBBs and

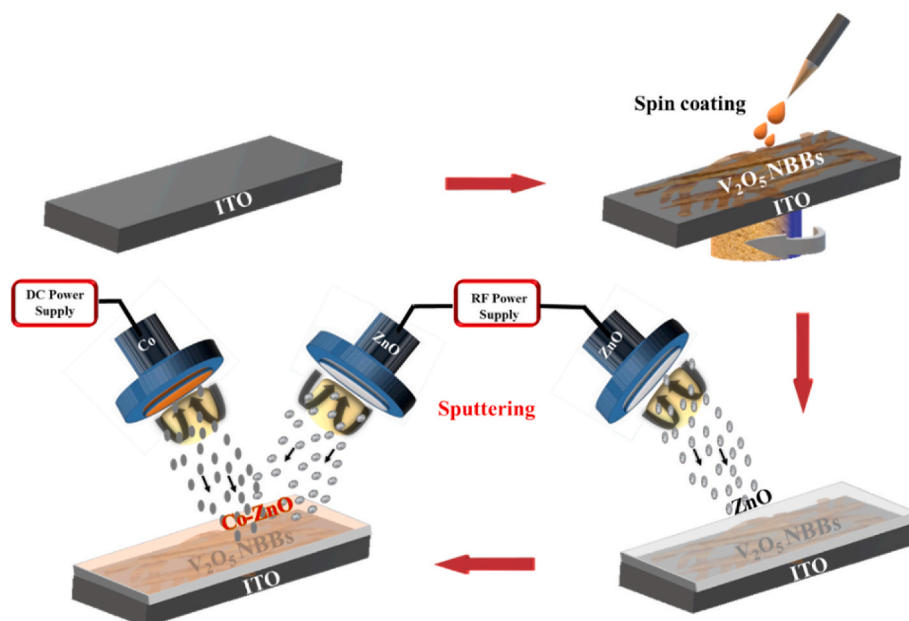


Fig. 1. Schematic representation of V_2O_5/ZnO and $V_2O_5/Co-ZnO$ growth.

sputter-deposited flake-like ZnO and Co (1.8 at.%)–ZnO thin films (Fig. S1). The nanobelt morphological features easily accommodate the flake-like ZnO and Co–ZnO thin films during the annealing process through the interface diffusion. The post-deposition annealed ZnO and Co (1.8 at.%)–ZnO thin films anchored V_2O_5 NBBs further denoted as V_2O_5/ZnO and $V_2O_5/Co-ZnO$ respectively.

The crystal structure of the developed nanobelt/flake-like morphology was analyzed using X-ray diffraction (XRD, X' pert Pro MPD, PANalytical). The surface morphology was recorded using the field emission scanning electron microscopy (FESEM, JEOL, JSM-7500F) and transmission electron microscopy (TEM, Tecnai G2 F30 S-Twin). The chemical binding states were systematically analyzed using the X-ray photoelectron spectroscopy (XPS, K-Alpha thermo electron, UK). Optical properties were carried using Cary 50 Bio spectrophotometer. The water contact angle information was confirmed by the SEO-Phoenix 300 (Model-PHX 300) contact angle analyzer. Mainly, the role of V_2O_5 NBBs on photoelectrochemical water splitting activity was carried using a solar simulator under a UV cutoff filter ($\lambda > 410$ nm) in a standard three-electrode system. PEC performance has been carried out in 0.1 M KOH electrolyte. Typically, 1Sun (100 mW/cm²) light intensity is generated by the solar simulator (Asahi spectra, HAL-320, 300 W) and illuminated towards 1 cm² active surface area. Also, the room temperature gas-sensing performance was measured on the controlling system (GMC 1200) attached with a high precision multimeter (Keithley 2001). The LabVIEW program was used to control the measurements. The target gas NO₂ was maintained at specific concentrations of 10 and 50 ppm, where the air is the carrier gas.

3. Result and discussion

3.1. Structural analysis

XRD technique is employed to analyze the crystallographic phases developed in the pure ZnO and V_2O_5 NBBs assisted flake-like ZnO (V_2O_5/ZnO) and Co (1.8 at.%)–ZnO ($V_2O_5/Co-ZnO$) thin films. Fig. 2 illustrates the crystal phases that existed in the pure ZnO and V_2O_5/ZnO and $V_2O_5/Co-ZnO$ developed on the ITO substrate. Note that all the films expectedly exhibit predominate (002) reflection at $2\theta = 34.54^\circ$ along with weak (101) and (103) reflections at 36.2 and 63.0° respectively, which revealing the formation of ZnO in hexagonal wurtzite

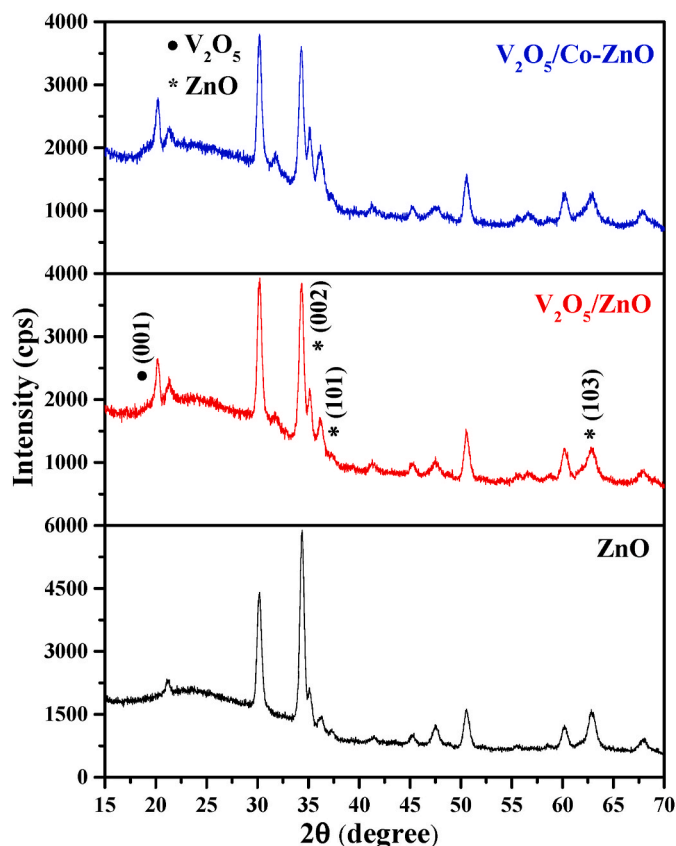


Fig. 2. XRD patterns of ZnO, V_2O_5/ZnO and $V_2O_5/Co-ZnO$.

structured c-axis growth. Upon V_2O_5 assistance (V_2O_5/ZnO), the fundamental peak appeared at a lower diffraction angle of about $2\theta = 20.3^\circ$ corroborates well with the selective (001) phase of V_2O_5 . Such a predominant diffraction peak was also reported for pure V_2O_5 nanobelt bundles [3]. Despite the V_2O_5 NBBs introduced even under the ZnO, the XRD spectrum of V_2O_5/ZnO still ensuing the mixed networks of selective V_2O_5 (001) and predominate ZnO (002) orientations. As observed, the

peak raised at 20.3° demonstrates progressive single-phase V_2O_5 (001) formation, which strongly promotes the compatibility and stabilization of V_2O_5 at the interface of ZnO. It is also noticed that V_2O_5 nanostructures itself act as possible nucleation sites for the improvement of ZnO (101) reflection ($2\theta = 36.20^\circ$) in the V_2O_5 /ZnO. In other words, as the ZnO sputter growth occurred on the V_2O_5 NBBs, ZnO effectively diffused towards the V_2O_5 NBBs and favor for the crystal growth towards (101) direction. As a result, V_2O_5 /ZnO and V_2O_5 /Co-ZnO composites uphold the growth of ZnO (101) reflection along with predominate (002). Further, we expect that there was a concomitant change in the relative intensity of (002) reflection with the Co incorporation into the ZnO host lattice (V_2O_5 /Co-ZnO) compared to V_2O_5 /ZnO, which is a plausible explanation for the successful substitution of Co^{2+} ions for Zn^{2+} ions in the ZnO host lattice and bonding with the neighboring V_2O_5 NBBs. Since the precise growth of Co-ZnO and apparent variation in the relative intensity of ZnO (002) attributed to the ordered intimate interface interaction between ZnO (002) and V_2O_5 (001) directions. Likewise, precise sputter growth of flake-like ZnO and Co-ZnO on V_2O_5 NBBs eventually allows diffusion interaction between ZnO (002) and V_2O_5 (001). In accordance with the above growth directions, full width at half maximum (FWHM) of the predominant ZnO (002) and V_2O_5

(001) reflections were extracted to explore the nanoconfinement in the V_2O_5 /ZnO and V_2O_5 /Co-ZnO composite. Thus, we considered the Scherrer equation to calculate the crystallite size (L). FWHM of the V_2O_5 (001) reflection is about 0.42° in the V_2O_5 /ZnO composite. Whereas, V_2O_5 /Co-ZnO was observed with an increased FWHM of 0.5° . Enlarged (001) reflection of V_2O_5 is also presented in Fig. S2 (a). As a result, the crystallite size of V_2O_5 in the V_2O_5 /ZnO and V_2O_5 /Co-ZnO is about 20.1 and 16.8 nm respectively, which represents the nanoconfinement of V_2O_5 in the V_2O_5 /ZnO and V_2O_5 /Co-ZnO composite. On the other hand, variation in the crystallite size and FWHM of ZnO (002) reflection as a function of V_2O_5 serves to realize the strong interfacial interaction between ZnO (002) and V_2O_5 (001) (Fig. S2 (b)). Regarding the V_2O_5 /Co-ZnO, V_2O_5 nanofeatures are closely promoted near the Co-ZnO compared to the ZnO. Combining the above observations, we account for the perfect interfacial arrangement of flake-like ZnO and Co-ZnO thin films in the vicinity of V_2O_5 NBBs. Thus, the above controllable approach provides a driving force to accelerate the charge carrier interfacial kinetics during PEC activity.

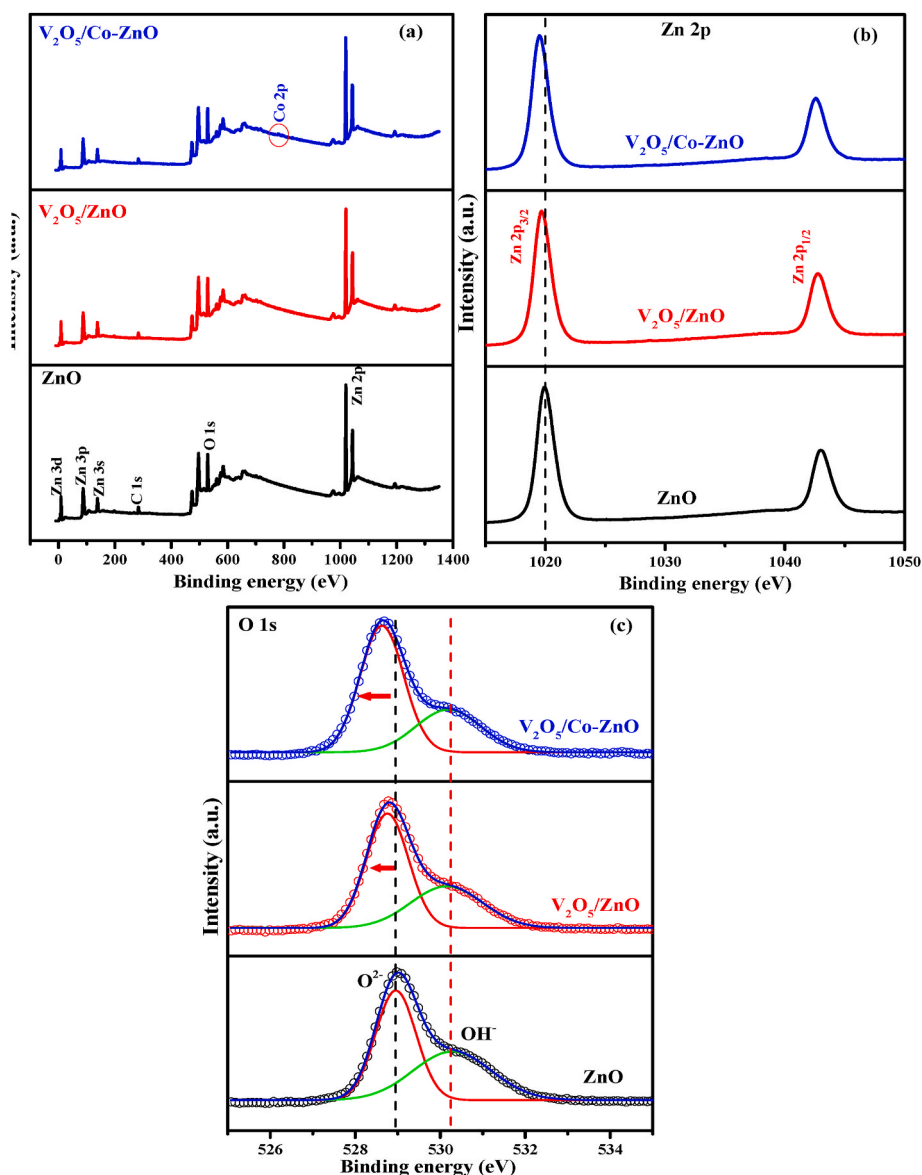


Fig. 3. XPS spectra of ZnO, V_2O_5 /ZnO and V_2O_5 /Co-ZnO: (a) Survey scan (b) Zn 2p. and (c) O 1s levels.

3.2. XPS analysis

Better information over the proposed potentiality of V_2O_5 NBBs assistance and Co incorporation, it is necessary to explore the nature of chemical binding states. Thus, we performed XPS analysis. Fig. 3 (a) displays the survey scan spectra of pure ZnO, V_2O_5/ZnO and $V_2O_5/Co-ZnO$. As can be seen, the photoelectron peaks were assigned to the Zn 3d, Zn 3p, Zn 3s, Zn 2p, C1s, O1s and Co 2p. At this point, the vanadium (V) component is not observed, which explains the strong Zn–O bonds tend to completely develop over the longer surface sections of V_2O_5 NBBs. We believe that the above features are consistent well with the weak V_2O_5 (001) reflection developed along with ZnO (002). However, the weak Co 2p peak is relative to the $V_2O_5/Co-ZnO$ composite following the Co (1.8 at.%) substitution into the ZnO host lattice.

To further assess the impact V_2O_5 NBBs assistance on flake-like ZnO and Co–ZnO thin films, we studied the information of Zn 2p state obtained from the pure ZnO, V_2O_5/ZnO and $V_2O_5/Co-ZnO$. The study on Zn 2p level facilitates a better understanding of interfacial chemical interaction between V_2O_5 NBBs and ZnO flake-like morphology. Thus, we performed high-resolution scan for Zn 2p state (Zn 2p_{3/2} and Zn 2p_{1/2}) as shown in Fig. 3 (b). Typically, in the case of pure ZnO, spin-orbit splitting of Zn 2p level is associated with Zn 2p_{3/2} for 1019.96 eV and Zn 2p_{1/2} for 1042.96 eV. These binding energy values originated with a difference of 23.0 eV, which reflects Zn in the +2 oxidation state. Impressively, for V_2O_5/ZnO , a significant chemical shift in the peak position was observed. Note that the shift is a real contribution from the interfacial interaction between V_2O_5 and ZnO accompanied by the flake-like ZnO diffusion into the V_2O_5 nanobelts during post-annealing treatment. In such a way, V_2O_5/ZnO supplemented a detectable shift in the Zn 2p_{3/2} and Zn 2p_{1/2} levels towards the lower binding energy side and positioned at 1019.63 and 1042.76 eV respectively. Upon cobalt incorporation ($V_2O_5/Co-ZnO$), we further noticed a progressive shift in the Zn 2p_{3/2} (1019.50 eV) and Zn 2p_{1/2} (1042.60 eV) levels. This clear shift is allowing us to confirm the Co incorporation into the ZnO host lattice and unavoidable interaction between V_2O_5 and Co–ZnO. Since, V_2O_5 NBBs functionalization and Co incorporation, the Zn 2p level leads to a significant lower binding energy shift (0.4 eV). It should be emphasized that the above findings are in agreement with the following ideal aspects: (i) potential evolution of electronic interaction, (ii) structural organization and (iii) near-surface presence of flake-like ZnO and Co–ZnO thin films over the V_2O_5 NBBs.

Fig. 3 (c) displays the high-resolution O 1s scan spectra of ZnO, V_2O_5/ZnO , and $V_2O_5/Co-ZnO$. It is a challenge to explain the O 1s spectra of composite structure because stronger interaction exists between V_2O_5 NBBs and flake-like ZnO. As compared to pure ZnO, V_2O_5/ZnO and $V_2O_5/Co-ZnO$ were observed with a lower binding energy shift, which envisages the strengthened V_2O_5 NBBs assistance and Co incorporation. As it can be seen, the O 1s spectra of ZnO deconvoluted into a dominating peak at 528.8 eV, which is associated with the lattice oxygen (O^{2-}) in the Zn–O [29]. The secondary peak originated at a higher binding energy of 530.5 eV corresponding to the hydroxyl groups (OH^-) adsorbed on the ZnO surface [24]. Indeed, we also observed a significant shift in the lattice oxygen peak towards the lower angle side about 0.33 eV and no notable shift in the shoulder peak (hydroxyl peak) with the addition of V_2O_5 NBBs (V_2O_5/ZnO) and Co incorporation ($V_2O_5/Co-ZnO$). Considering the V_2O_5/ZnO composite, the fact that the formation of combined oxygen bonding with Zn in ZnO and V in V_2O_5 at the interface of V_2O_5/ZnO reinforces shift in the O 1s peak position towards lower angle side. In all of these, the O1s peak of $V_2O_5/Co-ZnO$ further shifted towards the lower binding energy side, indicating the betterment in the combined oxygen bonding proportion between Co–ZnO and V_2O_5 compared to V_2O_5/ZnO . Yan et al. [30] also reported such binding energy shifts towards the lower angle side due to the formation of cross-linking Zn–O–Ti bonds in the ZnO/TiO₂ heterostructure. In other words, hybridization strength occurs between the incorporated Co^{2+} ions in the ZnO and oxygen in the V_2O_5 at the interface of

$V_2O_5/Co-ZnO$. These parameters significantly impact on the electronic band structure and also provides oxygen bonding evolution at the interface of $V_2O_5/Co-ZnO$. Further, we demonstrated the weak vanadium V 2p_{3/2} peak relative to the V_2O_5/ZnO and $V_2O_5/Co-ZnO$ composites, which show the existence of two minor components at 515.5 eV and 517.0 eV (Figs. S3(a–b)). In the organization of V_2O_5/ZnO and $V_2O_5/Co-ZnO$, peaks developed at 517.0 eV corresponding to the characteristic V^{5+} state on the vanadium surface [17,31] and additional peak at 515.5 eV assigned to the lower oxidation state V^{4+} . As proof of interfacial interaction between V_2O_5 and Co–ZnO, the binding energy difference between predominate O 1s peak and V 2p_{3/2} is about 13.3 eV. On the other hand, it is considered as a variation in the chemical state of V_2O_5 into VO_2 at the interface of ZnO. In detail, it illustrates the successful interfacial interaction between two oxide materials (V_2O_5/ZnO and $V_2O_5/Co-ZnO$), which provides another determining factor for achieving improved charge carrier generation and separation. We further studied the high-resolution scan of Co 2p, which developed in the $V_2O_5/Co-ZnO$ composite (Fig. S3(c)). As can be seen, Co 2p resolved into Co 2p_{3/2} and Co 2p_{1/2}, which were positioned at 791.0 and 796.3 eV respectively [32]. The above peak positions indicate Co in Co^{2+} state and perfectly substituted for Zn^{2+} in the $V_2O_5/Co-ZnO$ composite. Overall, specific binding energy shift criteria and interfacial interaction serve to realize the superior PEC activity.

3.3. Surface morphology

To observe the nanobelt interface functionalization with flake-like morphology, we employed the FESEM analysis. Fig. 4(a–c) (i–iv) provides clear nanobelt/flake-like morphological features and EDAX spectra of pure ZnO, V_2O_5/ZnO and $V_2O_5/Co-ZnO$. Firstly, as synthesized pure V_2O_5 NBBs at different magnifications were presented in Fig. S4 (a) (i–iii). These morphological features realize that individual V_2O_5 nanobelts are highly aggregated, which leads to the formation of nanobelt bundles. As it can be seen in Fig. 4(b and c) (i–iii), geometric isotropy of flake-like ZnO and Co–ZnO thin films on V_2O_5 NBBs, which serve as dominating factor for achieving progressive interaction trend between nanobelts and flake-like morphology. Specifically, in the initial state of V_2O_5 nanobelts, the average diameter of the individual nanowire is about 120 nm (Fig. S4 (b)(i)). Upon introduction of sputtered ZnO and Co–ZnO, (i) evolution of uniform flake-like thin film morphology oriented over the surface of V_2O_5 NBBs and (ii) V_2O_5 nanobelts completely bonded and buried under the flake-like ZnO and Co–ZnO thin films. At such conditions, the diameter of the overlapped composition significantly increased to 314 nm (Fig. S4 (b)(ii–iii)). Benefiting from the post-deposition annealing, the orientation of the flake-like ZnO and Co–ZnO thin film morphology strongly involved throughout the vicinity of V_2O_5 NBBs. Indeed, elemental analysis confirms the clear existence of impressive uniform V_2O_5 distribution under the flake-like ZnO and Co–ZnO thin films (Fig. 4(a–c) (iv)). In this way, well-aligned V_2O_5/ZnO and $V_2O_5/Co-ZnO$ further strengthened the apparent surface interfacial connection between flake-like (ZnO and Co–ZnO) and (V_2O_5) nanobelt morphologies. On the other hand, to support the above surface interfacial interaction in the complex structure, we recorded the elemental mapping for all samples (Fig. S5). Considering the observed elemental mapping assignments, clear interfacial interaction is originated between flake-like and nanobelt morphologies, which further confirmed the preferential diffusion aligned between flake-like (ZnO and Co–ZnO) thin film morphology and V_2O_5 NBBs. Finally, the response of sputtering and post-deposition annealing processes presumed a direct link to amplifying the flake-like ZnO and Co–ZnO thin film diffusion towards the vicinity of V_2O_5 NBBs. This interfacial stability gained special attention to robust PEC activity. It will be discussed later section in the PEC water splitting analysis.

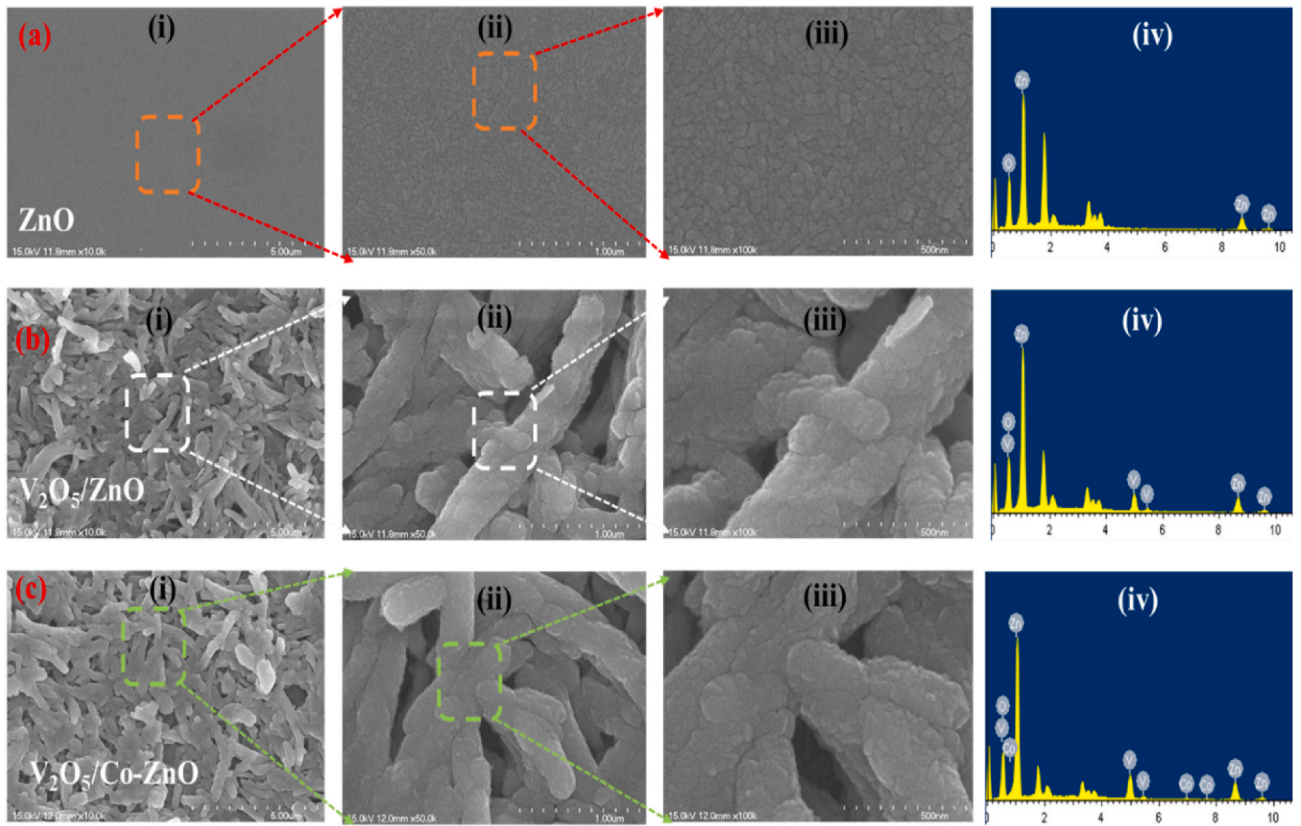


Fig. 4. Low-, high-resolution FESEM images and EDX spectra of (a) ZnO, (b) V₂O₅/ZnO and (c) V₂O₅/Co-ZnO.

3.4. TEM analysis

To further validate the above mentioned intimate interfacial

interaction phenomenon, we performed TEM analysis. Firstly, we carried out a focused ion beam (FIB) technique, which is useful to view the individual thin film layer information in the well-aligned V₂O₅/ZnO and

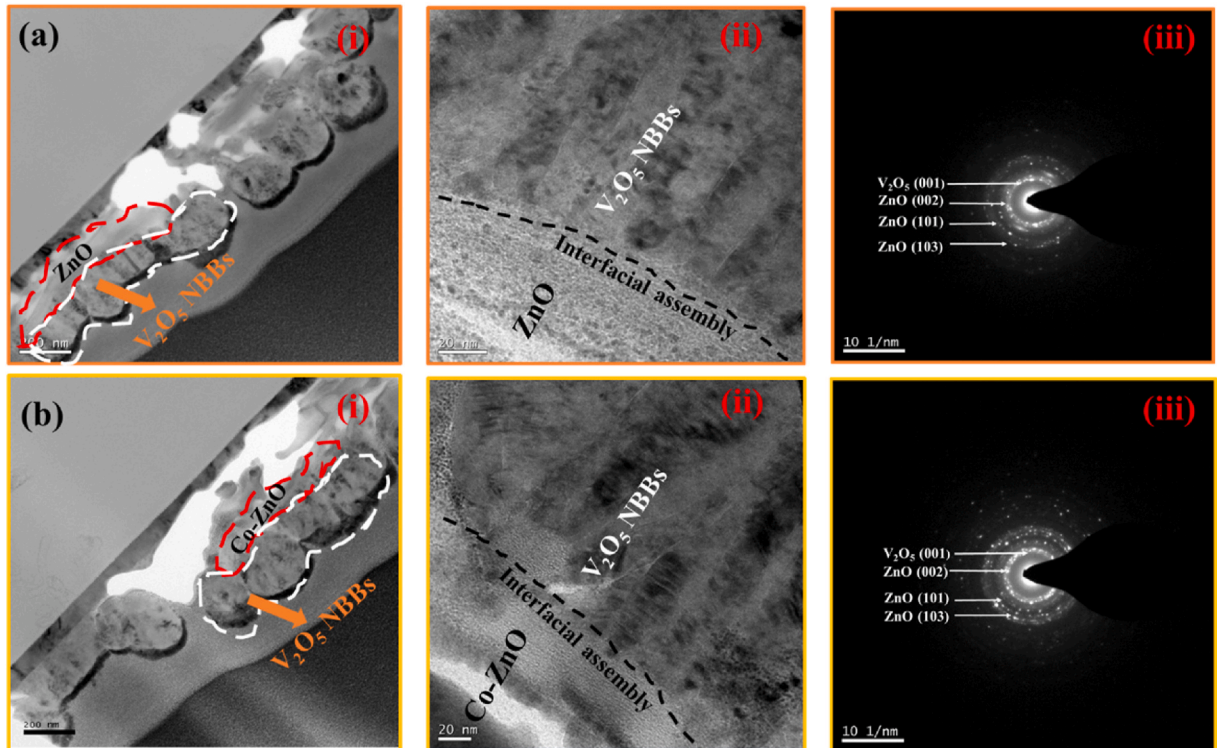


Fig. 5. TEM microstructure, interfacial assembly and SAED pattern of (a) V₂O₅/ZnO and (b) V₂O₅/Co-ZnO.

$\text{V}_2\text{O}_5/\text{Co-ZnO}$ composite developed on the ITO substrate (Fig. S6 (a-b) (i)). Later, in view of the interfacial assembly fact, detailed TEM microstructure, high-resolution TEM and SAED pattern of $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ have been systematically studied. Fig. 5(a and b) (i) display the typical TEM cross-section microstructure view of $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ composites. We note that the V_2O_5 NBBs perfectly combined with the ZnO and Co-ZnO thin films. Nevertheless, the above morphological features are in good agreement with the above FESEM observations. Another interesting phenomenon is that significant interface diffusion interactions favoring the development of well-coordinated $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ composites (Fig. 5(a and b) (ii)). In agreement with the above findings, HRTEM images also illustrated the sensitive surface interface interaction between V_2O_5 NBBs and flake-like morphology (Fig. S6 (a-b) (ii)). To prove that, we interpreted the formation of predominate V_2O_5 (001) and ZnO (002) lattice fringes by means of corresponding SAED pattern of $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ (Fig. 5(a and b) (iii)). As observed from the above results, TEM analysis further addresses well with the evidence of clear surface interfacial interaction between nanobelt bundles and flake-like thin films, which is a proper choice to accelerate the charge carrier generation, transportation and separation during PEC activity.

3.5. Water contact angle analysis

Furthermore, the water contact angle is the degree of surface reaction to evaluate the potential impact with the electrolyte during PEC activity [33] and property of the surface that strongly demonstrates the sensitization of incident photons. It is interesting to note that the water contact angle greatly influences a few nanometers of the developed photoanode [34]. Based on the above phenomena, we further interpreted the surface evolution properties of pure ZnO, $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ using water contact angle analysis (Fig. S7). As can be seen from Fig. S7, appropriate decrement in the contact angle signifies the strong evidence of V_2O_5 NBBs intimate interaction with flake-like ZnO and Co-ZnO thin films. Since the formation of flake-like morphology, pure ZnO is presumed to exhibit a water contact angle of about 90° . Here, it is important to highlight that pure V_2O_5 NBBs exhibited superhydrophilicity with a water contact angle of 32° (inset of Fig. S4 (b) (i)). Thus, we expect that the integration of nanobelts with flake-like morphology sustains the development of hydrophilic nature. It is assumed that superhydrophilic V_2O_5 NBBs interaction with flake-like ZnO ($\text{V}_2\text{O}_5/\text{ZnO}$) maintained betterment in the water contact angle about 75° , which further signifies the constructive interconnection between nanobelt bundles and flake-like morphological features. Surprisingly, as the formation of Co-ZnO ($\text{V}_2\text{O}_5/\text{Co-ZnO}$), the corresponding surface morphology architecture further influenced the water contact angle (63°). Because of stable flake-like Co-ZnO thin film growth significantly involved on the V_2O_5 NBBs. Eventually, the $\text{V}_2\text{O}_5/\text{Co-ZnO}$ composite greatly influenced the surface reactivity compared to the $\text{V}_2\text{O}_5/\text{ZnO}$. Therefore, in the context of a surface interfacial assembly, the unique microstructure of $\text{V}_2\text{O}_5/\text{ZnO}$ (75°) and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ (63°) accord with the excellent hydrophilic nature and beneficial for the electrolyte interaction during PEC activity. Thus, the above results mainly due to the initial development of flake-like ZnO and Co-ZnO thin film morphological features and effective diffusion towards the vicinity of V_2O_5 NBBs, which acts as underlying factors for achieving superior PEC activity.

3.6. Optical properties

Apart from the above parameters, interfacial interaction directly impacts on the optical properties. Because of the interfacial interaction, we can envisage the direct link between optical properties and PEC water splitting activity. Generally, optical transmittance behavior is closely related to the charge carrier generation entities to achieve superior PEC activity. In other words, narrowing the band gap of nanobelt/

flake-like composite excels the incident light absorption. Thus, the quantitative determination of PEC water splitting activity can be monitor as a function of the optical band gap. The specific variation in the optical transmittance and absorption edge of ZnO, $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ shown in Fig. S8 (a). Considering that pure ZnO has flake-like morphology, it is reasonable to exhibit a sharp absorption edge below 400 nm. This fact is explained by the characteristic property of ZnO under the UV region. According to the V_2O_5 NBBs integration ($\text{V}_2\text{O}_5/\text{ZnO}$), obvious changes in the electronic structure reflecting the substantial shift in the absorption edge towards the visible region. Moreover, interfacial diffusion is believed to play an essential role in switching the absorption edge. As it can be observed from the figure, the absorption edge completely extended towards the visible region of $\text{V}_2\text{O}_5/\text{Co-ZnO}$. Therefore, this result is comprised of a stable interfacial interaction trend between V_2O_5 and Co-ZnO. As expected, $\text{V}_2\text{O}_5/\text{Co-ZnO}$ guarantees the development of more sensitive groups on the V_2O_5 NBBs, which quickly responds to the incident visible light. The involvement of selective V_2O_5 NBBs and Co substitution initiates a contributing pathway to achieve superior PEC water splitting activity. Because of the unique interface, strong visible light absorption was addressed by the $\text{V}_2\text{O}_5/\text{Co-ZnO}$ compared to the pure ZnO and $\text{V}_2\text{O}_5/\text{ZnO}$. To further clarify the interfacial diffusion, we extracted the band gap from Tauc's expression, which responsible for the variation in the optical band gap. The direct optical band gap (E_g) can be estimated from the optical absorption coefficient (α) using the following relationship [35],

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

where A is the proportionality constant and $h\nu$ is the incident photon energy. By extrapolating the linear portion of plots $(\alpha h\nu)^2$ vs. $(h\nu)$ to $(\alpha h\nu)^2 = 0$, the above expression provides the direct band gap information of ZnO, $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ (Fig. S8(b)). The extrapolation plots revealed that ZnO exhibits its characteristic band gap of about 3.2 eV. As expected, $\text{V}_2\text{O}_5/\text{ZnO}$ heterostructure highlighted with a reduced band gap (2.98 eV). Similar band gap tuning was also observed for ZnO/ V_2O_5 composite thin films [7]. Observing more carefully, the reduced band gap demonstrates the interfacial interaction and diffusion between layered flake-like ZnO and V_2O_5 NBBs, which effectively alter the electronic structure of the combined structure ($\text{V}_2\text{O}_5/\text{ZnO}$). Admittedly, it clearly explains the credibility of successful intimate interaction between flake-like ZnO and V_2O_5 NBBs. When Co doping occurs in the ZnO host lattice ($\text{V}_2\text{O}_5/\text{Co-ZnO}$), the band gap value is further reduced to 2.75 eV. From the concomitant V_2O_5 NBBs assistance and Co doping, we can address the stable surface interaction between flake-like Co-ZnO and V_2O_5 NBBs, which are the driving force for band gap tuning and strengthened visible light absorption for achieving superior PEC water splitting activity.

3.7. Photoelectrochemical (PEC) activity

To further figure out the impact of the above-mentioned potentiality of inherent interfacial assembly involved in the nanobelt/flake-like composite, we addressed the PEC water splitting activity by comparing the linear sweep voltammetry (I-V), amperometric I-t, Tafel plots and electron impedance spectroscopy (EIS) studies of pure ZnO, $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$. All these parameters were carried out under 0.1 M of KOH electrolyte. After checking the above parameters, the interfacially integrated nanobelt/flake-like composite validates significant development in the photocurrent generation and stability.

To quantify the ability of stable interfacial interaction on the concept of progressive charge carrier generation, we measured the linear sweep voltammetry (I-V) from -1 to +1 V. The charge carrier acceleration mainly depends on the electron transportation and separation at the of nanobelt/flake-like interface. Fig. 6 (a) depicts the I-V analysis of ZnO, $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ under chopped 1 Sun irradiation at an

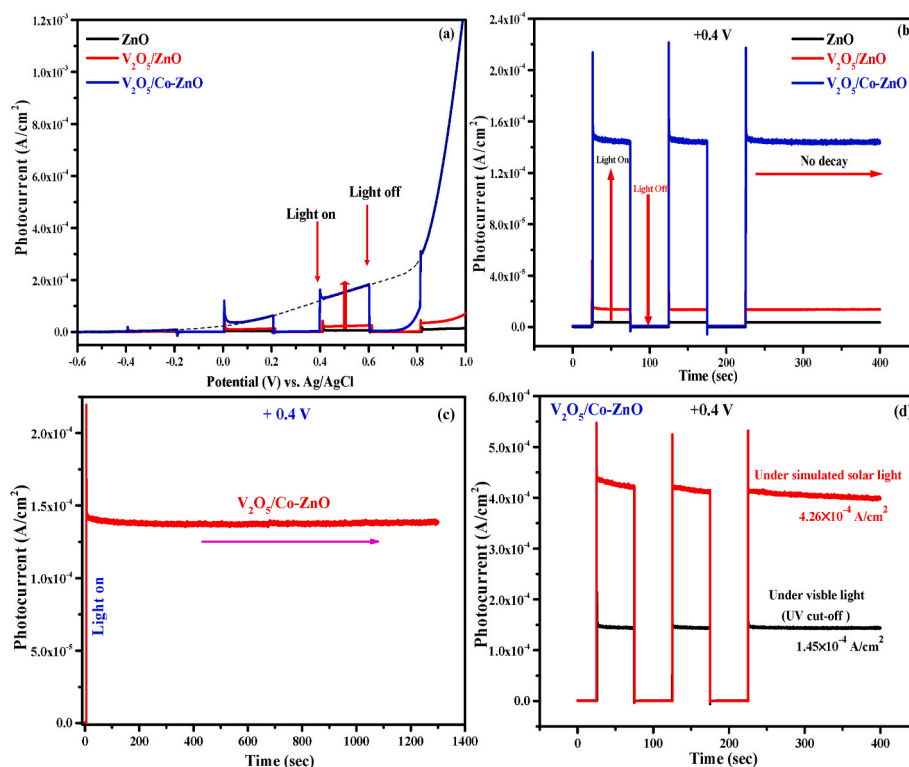


Fig. 6. Visible light PEC properties of ZnO, $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$: (a) Chopped light linear sweep voltammogram (I–V), (b) amperometric I–t studies at +0.4 V (c) highly photostable $\text{V}_2\text{O}_5/\text{Co-ZnO}$ for 21 min and (d) photocurrent generation comparison of $\text{V}_2\text{O}_5/\text{Co-ZnO}$ under simulated solar light and visible light (UV cut-off) conditions.

interval of +0.2 V. We emphasize that photocurrents progressively increased in the following order of $\text{V}_2\text{O}_5/\text{Co-ZnO} > \text{V}_2\text{O}_5/\text{ZnO} > \text{ZnO}$. As a consequence, we note that linear increment in the photocurrents primarily associated with the following parameters: (i) V_2O_5 nanobelts assistance, (ii) Co incorporation into the ZnO host lattice and (iii) strong interfacial interaction and diffusion between the nanobelts and flake-like thin films. Especially, the achieved interfacial interaction act as a successful parameter to account for charge carrier acceleration. As can be seen from Fig. 6 (a), pure ZnO exhibits insignificant photocurrents even under the light state. After the intimate interaction of V_2O_5 NBBs with ZnO and Co-ZnO, photocurrents significantly boosted. The first required factor to satisfy the improved photocurrents is the presence of active V_2O_5 NBBs networks buried and interconnected with the flake-like ZnO. As a result, the composite (nanobelt/flake-like) structure allows improved charge carrier separation, which favors photoelectron transportation from ZnO to V_2O_5 . Secondly, once the flake-like Co-ZnO sputter growth on V_2O_5 nanobelt networks, the V_2O_5 nanobelt surface further strengthens insights into the stable interaction during progressive coverage of Co-ZnO, which excels superior charge carrier generation and transportation from Co-ZnO to V_2O_5 . At the same time, under the impact of Co doping, Co^{2+} ions are associated with ZnO host lattice and experiences decrement in the band gap energy. Therefore, the presence of interfacially anchored Co-ZnO on V_2O_5 NBBs significantly extends the visible light absorption, which yields superior photocurrent generation compared to $\text{V}_2\text{O}_5/\text{ZnO}$. Moreover, V_2O_5 NBBs are effectively surrounded by the active Co-ZnO flakes, which strengthens the evidence of stable $\text{V}_2\text{O}_5/\text{Co-ZnO}$ interface. Keeping all the above factors, relatively high interfacial interaction is achieved by the $\text{V}_2\text{O}_5/\text{Co-ZnO}$ composite, which is preferable for achieving superior photocurrent generation and separation towards the counter electrode. On the other hand, I–V spectra of ZnO, $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ under dark and light states (without chopped light) presented in Fig. S9 (a), which is precisely matched with the chopped I–V spectra. From the

dealings of above I–V findings, the well-organized $\text{V}_2\text{O}_5/\text{Co-ZnO}$ hybrid structure crucially suggests the superior PEC water splitting activity due to the selective interfacial diffusion raised between the V_2O_5 NBBs and flake-like Co-ZnO thin film morphological features.

It is considered that the interfacial diffusion assembly of the nanobelt/flake-like is anticipated to achieve durability and photostability. At first, photostability was extensively recognized as a crucial parameter to explain the characteristic details of the nanobelt/flake-like interface. The monotonic constructive support of V_2O_5 NBBs with flake-like ZnO and Co-ZnO demonstrate the considerable intimate interfacial interaction. Thus, to ascertain more insights into the interfacial assembly, we assessed amperometric I–t studies for 400 s at a lower bias voltage of +0.4 V under chopped light conditions (Fig. 6 (b)). As seen in the figure, the potential nature of V_2O_5 NBBs assistance and Co doping are helping tools to estimate the prompt light response and reproducible photocurrents. The results indicate that the inherent increment in the photocurrent generation is experienced by the strong interfacial interaction between nanobelt and flake-like morphologies. The achieved transient photocurrents at +0.4 V were in good agreement with the I–V analysis (Fig. 6 (a)). Besides, the hydrophilic nature observed by the $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ contributes easy access to the electrolyte. Thus, we compared the photocurrent generation of ZnO, $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co-ZnO}$ relative to the well maintained hydrophilic surfaces as shown in Fig. S9 (b). This outcome is mainly due to interfacial diffusion. Thus, it is extensively established that interface interaction more efficient for reproducible photocurrents and stable PEC activity. As described above, charge carrier stability can be evaluated by the strong relationship between V_2O_5 NBBs and Co-ZnO. Therefore, the $\text{V}_2\text{O}_5/\text{Co-ZnO}$ composite exhibit a chemically bonded nature. In depth, light absorption extended towards the visible region, which can be interpreted by the successful Co incorporation into the ZnO host lattice. In comparison, photoanodes illuminated under visible light (UV cut-off), $\text{V}_2\text{O}_5/\text{Co-ZnO}$ composite yielded superior photocurrents about $1.45 \times$

10^{-4} A/cm² compared to V₂O₅/ZnO (1.42×10^{-5} A/cm²) and ZnO (3.4×10^{-6} A/cm²) at a specific lower bias voltage of +0.4 V. Here, successful doing of Co²⁺ ions into the ZnO host lattice gives deep insights into the charge carrier generation and their separation towards the conduction band of V₂O₅. In this respect, the merits of the V₂O₅/Co-ZnO composite interface consist of no decay in the photocurrent separation, which accounts for the successful development of highly stable photoanode under visible light. In turn, optimized V₂O₅/Co-ZnO providing superior charge carrier generation and separation. Accordingly, V₂O₅/Co-ZnO outperforms the photocurrent generation about 42.0 and 10.0 times higher than pristine ZnO and V₂O₅/ZnO respectively. On the other hand, V₂O₅/ZnO advancing the photocurrent generation about 4.0 times than pristine ZnO. It strongly suggests that enhanced and reproducible photocurrents mainly due to the effective role of abundant visible light absorption [36]. Moreover, the prolonged photocurrent generation of V₂O₅/Co-ZnO photoanode under visible light also measured for 21.0 min, it indicates a highly stable nature without attenuation of photocurrents (Fig. 6 (c)). In addition, we compared the PEC activity of V₂O₅/Co-ZnO under simulated solar light and visible light (UV cut-off solar light) (Fig. 6 (d)). It should be highlighted that the photocurrents generated in both total solar spectrum and UV cut-off solar light conditions were about 4.26×10^{-4} A/cm² and 1.45×10^{-4} A/cm² respectively. Based on Fig. 6 (d), we concluded that the V₂O₅/Co-ZnO composite was completely tuned as a visible light active material. Specifically, visible light active Co-ZnO harvests the majority portion of visible light present in the solar spectrum, which effectively separates and transfers the electrons towards V₂O₅. Moreover, we compared the photocurrent generation based on the role of V₂O₅ based composites for PEC water splitting applications in Table 1. In this approach, the above results reflect that the V₂O₅/Co-ZnO photoanode provides a specific interfacial assembly feature, which is the most relevant parameter to fulfill the stable and reproducible PEC water splitting activity.

To gain more potential prospects, we studied the electrochemical impedance spectroscopy (EIS) analysis. With the subsequent triggering of photocurrent generation (I-V and I-t studies), charge carrier kinetic efficiency is quantitatively consistent well with the EIS analysis and Tafel plots (Figs. S10(a-b)). Accordingly, the EIS spectra of ZnO, V₂O₅/ZnO and V₂O₅/Co-ZnO under the light state is presented in Fig. S10 (a). It revealed that the difference was sustained in the semicircle radius in the order of ZnO > V₂O₅/ZnO > V₂O₅/Co-ZnO. Thus, regarding the possible interfacial charge transfer resistance between the Co-ZnO and V₂O₅ NBBs drastically decreased in comparison with the ZnO and V₂O₅/ZnO. Therefore, concomitant V₂O₅ NBBs assistance and Co incorporation prevailed constructive interfacial assembly in the V₂O₅/Co-ZnO composite. Overall, during the charge carrier generation and separation processes, reduced interfacial resistance was retained by the V₂O₅/Co-ZnO photoanode compared to ZnO and V₂O₅/ZnO.

By considering the above superior charge carrier separation at suppressed recombination of PEC performance, we believe that there is clear evidence of interfacial interaction between nanobelt bundles and flake-like morphology. This outcome is significantly influenced by the

electrical resistivity, charge carrier generation, separation and transportation during PEC activity. Thus, considerable development of visible light active V₂O₅/Co-ZnO composite can be modulated by the V₂O₅ NBBs intimate interfacial interaction with the flake-like Co-ZnO thin films.

3.8. Proposed PEC water splitting mechanism

To understand the visible light PEC water splitting based on the interfacially assembled V₂O₅/ZnO and V₂O₅/Co-ZnO photoanodes for achieving superior charge carrier generation, separation and transportation, we proposed a charge transport mechanism and presented in Fig. 7. We emphasized that charge carrier separation efficiency is mainly induced by the intimate interaction between the two layers, which directly influence the PEC water splitting activity. At the same time, electrostatic interaction between the hole transport material (V₂O₅) and electron transport materials (ZnO and Co-ZnO) in the complex structure of V₂O₅/ZnO and V₂O₅/Co-ZnO regulates the overall PEC activity. As illustrated in the schematic diagram, we inferred that the V₂O₅/Co-ZnO combination generates superior photocurrents compared to V₂O₅/ZnO. Under light illumination, remarkable charge carrier separation occurs by the V₂O₅/Co-ZnO matrix. Subsequently, the photogenerated electrons move from the conduction band of Co-ZnO to the conduction band of V₂O₅ [16,17,20], which indicates V₂O₅/Co-ZnO composite exhibits lower recombination rate. Besides, combined oxygen bonding with Zn and V at the interface of V₂O₅ and ZnO is another important factor, which results in the acceleration of photogenerated electrons from Zn-O to the V₂O₅ NBBs. Whereas, Co-ZnO generates superior charge carriers in the V₂O₅/Co-ZnO composite, which effectively drifts towards the V₂O₅ NBBs compared to V₂O₅/ZnO. Consequently, the lifetime of the photogenerated electrons significantly improved, which strengthen the prolonged H₂ production at the counter electrode (platinum). On the other hand, holes effectively migrate from the valence band of V₂O₅ NBBs to the valence band of Co-ZnO, which involves oxygen generation at the working electrode. Moreover, the feasibility of interfacial interaction between nanobelt morphology of V₂O₅ and flake-like morphology of Co-ZnO prevails superior intimate surface interaction for extending the visible light absorption, charge carrier generation, separation and transportation.

3.9. NO₂ gas sensing of V₂O₅/Co-ZnO

Further, we assessed the toxic NO₂ gas sensing capability based on the existing interfacial assembly between V₂O₅ and Co-ZnO in the developed V₂O₅/Co-ZnO composite. Initially, we developed the V₂O₅/Co-ZnO composite on the ITO substrate and then conducted the room

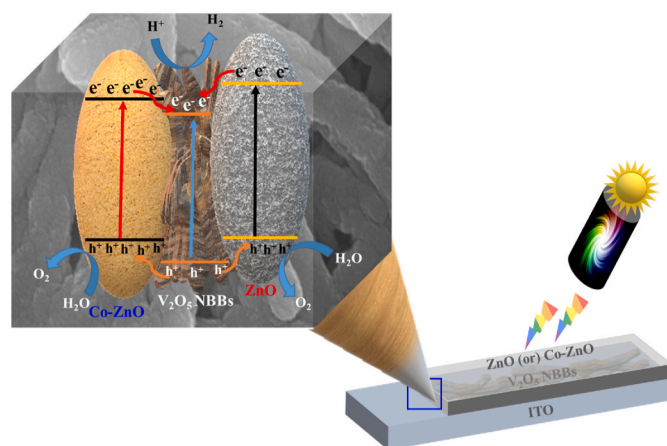


Fig. 7. Schematic charge carrier transport mechanism of V₂O₅/ZnO and V₂O₅/Co-ZnO under visible light.

Table 1

Summary of various V₂O₅ based composites for PEC water splitting applications.

Photoelectrode	Photocurrent	V vs. Ag/AgCl (or) RHE	Electrolyte	Ref
TiO ₂ /V ₂ O ₅	80 μ A/cm ²	1.23 V vs. RHE	—	[37]
ZnO/V ₂ O ₅	1.21 mA/cm ²	1.23 V vs. RHE	0.5 M Na ₂ SO ₄	[23]
V ₂ O ₅ /BiVO ₄	0.268 mA/cm ²	1.23 V vs. Ag/AgCl	0.1 M Na ₂ SO ₄	[38]
V ₂ O ₅ /g-C ₃ N ₄	0.12 μ A/cm ²	—	—	[12]
V ₂ O ₅ /Ni(OH) ₂	10 mA/cm ²	39 mV vs. RHE	1 M KOH	[39]
V ₂ O ₅ /ZnO	1.42×10^{-5} A/cm ²	0.4 V vs. Ag/AgCl	0.1 M KOH	In this work
V ₂ O ₅ /Co-ZnO	1.45×10^{-4} A/cm ²	0.4 V vs. Ag/AgCl	0.1 M KOH	In this work

temperature gas-sensing performance. Fig. 8 presents the response curve of $V_2O_5/Co-ZnO$ to NO_2 gas at low concentrations of 10 and 50 ppm. As shown in the figure, the evidence of interfacial diffusion assembly achieved between V_2O_5 NBBs and flake-like $Co-ZnO$ prevailed to get clear and large response signal under various NO_2 concentrations. The response of the $V_2O_5/Co-ZnO$ sensor calculated by following the expression,

$$\text{Response (\%)} = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \times 100 \quad (2)$$

where R_T and R_0 are the electrical resistance of the $V_2O_5/Co-ZnO$ composite under target gas NO_2 and its initial resistance respectively. Interestingly, the response to 50 ppm concentration of NO_2 reaches to 130.0% than 25.0% at a low concentration of 10 ppm. Under the ambient conditions, oxygen molecules easily adsorbed and extract electrons from the surface of buried V_2O_5 nanobelts and flake-like $Co-ZnO$ thin films, resulting in the formation of oxygen ions (O^- or O_2^-) and processes to surface electron depletion. It is well known that when the sensor is exposed to the NO_2 gas, it behaves like a strong oxidizing gas due to the absorbed O_2^- onto the composite surface and extract more electrons from a nearby surface [40], this phenomenon offers further decrement in the electron concentration of $V_2O_5/Co-ZnO$ composite. Moreover, the development of the depletion region can be observed under the NO_2 gas. In such a way, the sensor resistance gradually increases under the exposure of NO_2 gas. The detailed gas sensing mechanism based on the interfacial assembly developed in the $V_2O_5/Co-ZnO$ composite is presented in Fig. S11. The gas sensing mechanism can be explained from the following expressions [41],

In air,



In NO_2



All the above findings prove that the $V_2O_5/Co-ZnO$ is also suitable and active for the toxic NO_2 gas sensing applications at 10 and 50 ppm concentrations.

4. Conclusions

In this work, the effectiveness of selective V_2O_5 NBBs intimate surface interaction with flake-like ZnO (V_2O_5/ZnO) and Co (1.8 at.%) ZnO ($V_2O_5/Co-ZnO$) thin films was successfully explored, which possesses immense attention towards highly stable visible light PEC water splitting activity. In addition to PEC activity, $V_2O_5/Co-ZnO$ composite strengthened as a potential toxic NO_2 gas sensor at room temperature. This study strongly suggests that post-annealing is crucial for interfacial diffusion between nanobelt bundles and flake-like morphological features. Because of the unique interfacial interaction between V_2O_5 NBBs and $Co-ZnO$, $V_2O_5/Co-ZnO$ composite was highlighted with structural, morphological, chemical and optical changes compared to pure ZnO and V_2O_5/ZnO . Based on the promising interfacial diffusion, $V_2O_5/Co-ZnO$ is advantageous for the formation of a strong nanobelt/flake-like morphological interface. Specifically, we observed binding energy shift of O1s spectra of $V_2O_5/Co-ZnO$ due to the interaction effect originated from the interfacial oxygen bonding between $Co-ZnO$ and V_2O_5 NBBs. More importantly, the capability of unique $V_2O_5/Co-ZnO$ composite delivered outstanding reproducible and stable visible light photocurrents about $1.45 \times 10^{-4} \text{ A/cm}^2$ at a lower bias voltage of +0.4 V compared to the V_2O_5/ZnO ($1.42 \times 10^{-5} \text{ A/cm}^2$) and ZnO ($3.4 \times 10^{-6} \text{ A/cm}^2$). The photocurrents observed by the $V_2O_5/Co-ZnO$ in both simulated solar light and visible light (UV cut-off solar light) conditions are about 4.26×10^{-4} and $1.45 \times 10^{-4} \text{ A/cm}^2$ respectively, which

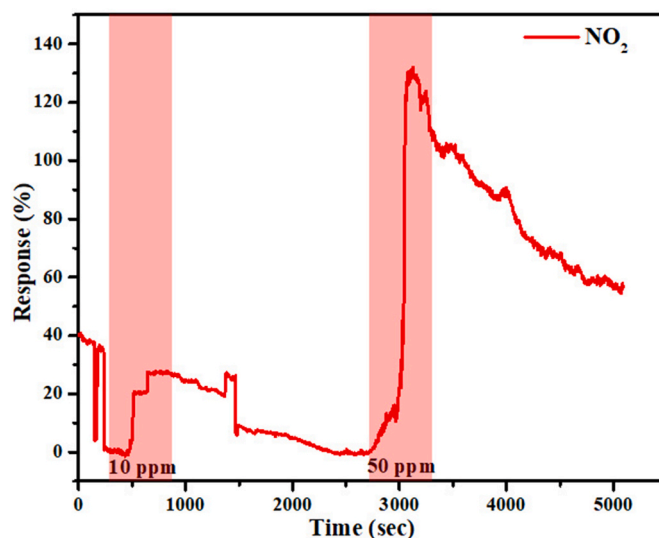


Fig. 8. NO_2 gas response of $V_2O_5/Co-ZnO$ composite at 10 and 50 ppm concentrations.

strongly reveals the visible light active nature of $V_2O_5/Co-ZnO$ composite. Also, the reason behind the highly stable and superior PEC activity is related to the suppressed interfacial charge transfer resistance and abundant hydrophilicity during PEC activity. Moreover, $V_2O_5/Co-ZnO$ was deemed as a reliable NO_2 gas sensor up to 130.0% response at 50 ppm concentration. In conclusion, combining the above exceptional properties of interfacially assembled $V_2O_5/Co-ZnO$ not only elucidates insights into the highly stable visible-light-driven PEC water splitting (for 21.0 min) but also provides motivating toxic NO_2 gas sensing (130.0%) applications.

CRediT authorship contribution statement

Adem Sreedhar: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft. **I. Neelakanta Reddy:** Formal analysis. **Qui Thanh Hoai Ta:** Formal analysis. **Thanh Hoang Phuong Doan:** Formal analysis. **Jaesool Shim:** Formal analysis. **Jin-Seo Noh:** Validation, Supervision, Review & Editing, Writing - review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2020.229081>.

References

- [1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature* 238 (1972) 37–38, <https://doi.org/10.1038/238037a0>.
- [2] M. Ghorbani, H. Abdizadeh, M. Taheri, M.R. Golobostanfard, Enhanced photoelectrochemical water splitting in hierarchical porous ZnO /Reduced graphene oxide nanocomposite synthesized by sol-gel method, *Int. J. Hydrogen Energy* 43 (2018) 7754–7763, <https://doi.org/10.1016/j.ijhydene.2018.03.052>.

- [3] I.N. Reddy, A. Sreedhar, C.V. Reddy, M. Cho, D. Kim, J. Shim, Facile synthesis and characterization of V_2O_5 nanobelt bundles containing plasmonic Ag for photoelectrochemical water splitting under visible light irradiation, *Ceram. Int.* 45 (2019) 23333–23340, <https://doi.org/10.1016/j.ceramint.2019.08.033>.
- [4] K. Schneider, M. Lubecka, A. Czaplá, V_2O_5 thin films for gas sensor applications, *Sensor. Actuator. B Chem.* 236 (2016) 970–977, <https://doi.org/10.1016/j.snb.2016.04.059>.
- [5] M. Shahid, I. Shaker, S.-J. Yang, D.J. Kang, Facile synthesis of core-shell SnO_2/V_2O_5 nanowires and their efficient photocatalytic property, *Mater. Chem. Phys.* 124 (2010) 619–622, <https://doi.org/10.1016/j.matchemphys.2010.07.023>.
- [6] A. Waseem, M.A. Johar, M.A. Hassan, I.V. Bagal, J.S. Ha, J.K. Lee, S.W. Ryu, Effect of crystal orientation of GaN/V_2O_5 core-shell nanowires on piezoelectric nanogenerators, *Nanomater. Energy* 60 (2019) 413–423, <https://doi.org/10.1016/j.nanoen.2019.03.075>.
- [7] P. Nagaraju, Y. Vijayakumar, M.V.R. Reddy, U.P. Deshpande, Effect of vanadium pentoxide concentration in ZnO/V_2O_5 nanostructured composite thin films for toluene detection, *RSC Adv.* 9 (2019) 16515–16524, <https://doi.org/10.1039/c9ra02356a>.
- [8] L. Xie, P. Liu, Z. Zheng, S. Weng, J. Huang, Morphology engineering of V_2O_5/TiO_2 nanocomposites with enhanced visible light-driven photofunctions for arsenic removal, *Appl. Catal. B Environ.* 184 (2016) 347–354, <https://doi.org/10.1016/j.apcatb.2015.11.014>.
- [9] P. Sahatiya, C.S.K. Reddy, S. Badhulika, Discretely distributed 1D V_2O_5 nanowires over 2D MoS_2 nanoflakes for an enhanced broadband flexible photodetector covering the ultraviolet to near infrared region, *J. Mater. Chem. C* 5 (2017) 12728–12736, <https://doi.org/10.1039/c7tc05036d>.
- [10] H. Liu, W. Zhu, D. Long, J. Zhu, G. Pezzotti, Porous V_2O_5 nanorods/reduced graphene oxide composites for high performance symmetric supercapacitors, *Appl. Surf. Sci.* 478 (2019) 383–392, <https://doi.org/10.1016/j.apsusc.2019.01.273>.
- [11] D.J. Ahirrao, K. Mohanapriya, N. Jha, V_2O_5 nanowires-graphene composite as an outstanding electrode material for high electrochemical performance and long-cycle-life supercapacitor, *Mater. Res. Bull.* 108 (2018) 73–82, <https://doi.org/10.1016/j.materresbull.2018.08.028>.
- [12] Y. Hong, Y. Jiang, C. Li, W. Fan, X. Yan, M. Yan, W. Shi, In-situ synthesis of direct solid-state Z-scheme $V_2O_5/g-C_3N_4$ heterojunctions with enhanced visible light efficiency in photocatalytic degradation of pollutants, *Appl. Catal. B Environ.* 180 (2016) 663–673, <https://doi.org/10.1016/j.apcatb.2015.06.057>.
- [13] J. Su, X.X. Zou, G.D. Li, X. Wei, C. Yan, Y.N. Wang, J. Zhao, L.J. Zhou, J.S. Chen, Macroporous $V_2O_5-BiVO_4$ composites: effect of heterojunction on the behavior of photogenerated charges, *J. Phys. Chem. C* 115 (2011) 8064–8071, <https://doi.org/10.1021/jp200274k>.
- [14] H. Yin, C. Song, Z. Wang, B. Guo, K. Yu, V_2O_5 nanoparticles grown on ZnO nanowires for enhanced field emission properties, *Appl. Surf. Sci.* 345 (2015) 256–263, <https://doi.org/10.1016/j.apsusc.2015.03.162>.
- [15] C.W. Zou, Y.F. Rao, A. Alyamani, W. Chu, M.J. Chen, D.A. Patterson, E.A. Emanuelsson, W. Gao, Heterogeneous lollipop-like V_2O_5/ZnO array: a promising composite nanostructure for visible light photocatalysis, *Langmuir* 26 (2010) 11615–11620, <https://doi.org/10.1021/la101324e>.
- [16] H. Yin, K. Yu, C. Song, R. Huang, Z. Zhu, Synthesis of Au-decorated $V_2O_5@ZnO$ heteronanostructures and enhanced plasmonic photocatalytic activity, *ACS Appl. Mater. Interfaces* 6 (2014) 14851–14860, <https://doi.org/10.1021/am501549n>.
- [17] J. Aliaga, N. Cifuentes, G. González, C. Sotomayor-Torres, E. Benavente, Enhancement photocatalytic activity of the heterojunction of two-dimensional hybrid semiconductors ZnO/V_2O_5 , *Catalysts* 8 (2018) 1–13, <https://doi.org/10.3390/catal8090374>.
- [18] R. Saravanan, V.K. Gupta, E. Mosquera, F. Gracia, Preparation and characterization of V_2O_5/ZnO nanocomposite system for photocatalytic application, *J. Mol. Liq.* 198 (2014) 409–412, <https://doi.org/10.1016/j.molliq.2014.07.030>.
- [19] P. Shukla, J.K. Shukla, Facile sol-gel synthesis and enhanced photocatalytic activity of the V_2O_5 -ZnO nanoflakes, *J. Sci. Adv. Mater. Devices* 3 (2018) 452–455, <https://doi.org/10.1016/j.jsamd.2018.09.005>.
- [20] H. Yin, K. Yu, J. Hu, C. Song, B. Guo, Z. Wang, Z. Zhu, Novel photoluminescence properties and enhanced photocatalytic activities for V_2O_5 -loaded ZnO nanorods, *Dalton Trans.* 44 (2015) 4671–4678, <https://doi.org/10.1039/c5dt00015g>.
- [21] M. Aslam, I.M.I. Ismail, T. Almelbi, N. Salah, S. Chandrasekaran, A. Hameed, Enhanced photocatalytic activity of V_2O_5 -ZnO composites for the mineralization of nitrophenols, *Chemosphere* 117 (2014) 115–123, <https://doi.org/10.1016/j.chemosphere.2014.05.076>.
- [22] H. Sun, Z. Yang, Y. Pu, W. Dou, C. Wang, W. Wang, X. Hao, S. Chen, Q. Shao, M. Dong, S. Wu, T. Ding, Z. Guo, Zinc oxide/vanadium pentoxide heterostructures with enhanced day-night antibacterial activities, *J. Colloid Interface Sci.* 547 (2019) 40–49, <https://doi.org/10.1016/j.jcis.2019.03.061>.
- [23] T.F. Hou, M.A. Johar, R. Boppella, M.A. Hassan, S.J. Patil, S.W. Ryu, D.W. Lee, Vertically aligned one-dimensional ZnO/V_2O_5 core-shell hetero-nanostructure for photoelectrochemical water splitting, *J. Energy Chem.* 49 (2020) 262–274, <https://doi.org/10.1016/j.jechem.2020.02.004>.
- [24] A. Sreedhar, I.N. Reddy, Q.T. Hoai Ta, G. Namgung, E. Cho, J.S. Noh, Facile growth of novel morphology correlated Ag/Co-doped ZnO nanowire/flake-like composites for superior photoelectrochemical water splitting activity, *Ceram. Int.* 45 (2019) 6985–6993, <https://doi.org/10.1016/j.ceramint.2018.12.198>.
- [25] A.A. Mane, A.V. Moholkar, Effect of film thickness on NO_2 gas sensing properties of sprayed orthorhombic nanocrystalline V_2O_5 thin films, *Appl. Surf. Sci.* 416 (2017) 511–520, <https://doi.org/10.1016/j.apsusc.2017.04.097>.
- [26] W.C. Ko, K.M. Kim, Y.J. Kwon, H. Choi, J.K. Park, Y.K. Jeong, ALD-assisted synthesis of V_2O_5 nanoislands on SnO_2 nanowires for improving NO_2 sensing performance, *Appl. Surf. Sci.* 509 (2020) 144821, <https://doi.org/10.1016/j.apsusc.2019.144821>.
- [27] A.A. Mane, S.A. Nikam, A.V. Moholkar, NO_2 gas sensing properties of sprayed composite porous $MoO_3-V_2O_5$ thin films, *Mater. Chem. Phys.* 216 (2018) 294–304, <https://doi.org/10.1016/j.matchemphys.2018.05.043>.
- [28] M. Epifani, E. Comini, R. Díaz, C. Force, P. Siciliano, G. Faglia, TiO_2 colloidal nanocrystals surface modification by V_2O_5 species: Investigation by 47,49 Ti MAS-NMR and H_2 , CO and NO_2 sensing properties, *Appl. Surf. Sci.* 351 (2015) 1169–1173, <https://doi.org/10.1016/j.apsusc.2015.06.080>.
- [29] A. Antony, P. Poornesh, I.V. Kityk, G. Myronchuk, G. Sanjeev, V.C. Petwal, V. P. Verma, J. Dwivedi, A study of 8 MeV e-beam on localized defect states in ZnO nanostructures and its role on photoluminescence and third harmonic generation, *J. Lumin.* 207 (2019) 321–332, <https://doi.org/10.1016/j.jlumin.2018.11.043>.
- [30] X. Yan, C. Zou, X. Gao, W. Gao, ZnO/TiO_2 core-brush nanostructure: processing, microstructure and enhanced photocatalytic activity, *J. Mater. Chem.* 22 (2012) 5629–5640, <https://doi.org/10.1039/c2jm15477c>.
- [31] M. Laurenti, M. Castellino, D. Perrone, A. Asvarov, G. Canavese, A. Chiolerio, Lead-free piezoelectrics: V^{3+} to V^{5+} ion conversion promoting the performances of V-doped Zinc Oxide, *Sci. Rep.* 7 (2017) 41957, <https://doi.org/10.1038/srep41957>.
- [32] A. Sreedhar, I.N. Reddy, Q.T. Hoai Ta, E. Cho, J.S. Noh, Highly supportive hydrogen peroxide as a hole scavenger to improve the visible light water splitting activity of flake-like Co-doped ZnO thin films, *Sol. Energy* 191 (2019) 151–160, <https://doi.org/10.1016/j.solener.2019.08.070>.
- [33] C. Meng, B. Wang, Z. Gao, Z. Liu, Q. Zhang, J. Zhai, Insight into the role of surface wettability in electrocatalytic hydrogen evolution reactions using light-sensitive nanotubular TiO_2 supported Pt electrodes, *Sci. Rep.* 7 (2017) 41825, <https://doi.org/10.1038/srep41825>.
- [34] M. Taylor, A.J. Urquhart, M. Zelzer, M.C. Davies, M.R. Alexander, Picoliter water contact angle measurement on polymers, *Langmuir* 23 (2007) 6875–6878, <https://doi.org/10.1021/la070100j>.
- [35] J. Tauc, A. Menth, States in the gap, *J. Non-Cryst. Solids* (1972), [https://doi.org/10.1016/0022-3093\(72\)90194-9](https://doi.org/10.1016/0022-3093(72)90194-9).
- [36] C. Wang, Y. Feng, L. Cai, X. Yang, J. He, W. Yan, Q. Liu, Z. Sun, F. Hu, Z. Xie, T. Yao, S. Wei, $ZnO@S$ -doped ZnO core/shell nanocomposites for highly efficient solar water splitting, *J. Power Sources* 269 (2014) 24–30, <https://doi.org/10.1016/j.jpowsour.2014.06.066>.
- [37] Y.J. Kwon, W.C. Ko, S. Kang, K.M. Kim, Y.K. Jeong, Surface passivation of highly stable TiO_2/V_2O_5 photocatalyst by atomic layer deposited- Al_2O_3 , *Appl. Surf. Sci.* 507 (2020) 145128, <https://doi.org/10.1016/j.apsusc.2019.145128>.
- [38] C.S. Yaw, Q. Ruan, J. Tang, A.K. Soh, M.N. Chong, A Type II n-n staggered orthorhombic V_2O_5 /monoclinic clinobisvanite $BiVO_4$ heterojunction photoanode for photoelectrochemical water oxidation: fabrication, characterisation and experimental validation, *Chem. Eng. J.* 364 (2019) 177–185, <https://doi.org/10.1016/j.cej.2019.01.179>.
- [39] A. Meena, M. Ha, S.S. Chandrasekaran, S. Sultan, P. Thangavel, A.M. Harzandi, B. Singh, J.N. Tiwari, K.S. Kim, Pt-like hydrogen evolution on a $V_2O_5/Ni(OH)_2$ electrocatalyst, *J. Mater. Chem. A* 7 (2019) 15794–15800, <https://doi.org/10.1039/c9ta03627j>.
- [40] G. Namgung, Q.T.H. Ta, W. Yang, J.S. Noh, Diffusion-driven Al-doping of ZnO nanorods and stretchable gas sensors made of doped ZnO nanorods/Ag nanowires bilayers, *ACS Appl. Mater. Interfaces* 11 (2019) 1411–1419, <https://doi.org/10.1021/acsami.8b17336>.
- [41] C.W. Zou, J. Wang, W. Xie, Synthesis and enhanced NO_2 gas sensing properties of ZnO nanorods/ TiO_2 nanoparticles heterojunction composites, *J. Colloid Interface Sci.* 478 (2016) 22–28, <https://doi.org/10.1016/j.jcis.2016.05.061>.