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Highlights

- A novel composite photoanode of Mo-doped $\text{ZnV}_2\text{O}_6/\text{rGO}$ was fabricated for PEC.
- DFT calculations revealed that the hole mobility is remarkably affected by Mo ions.
- Bulk doping and surface modification synergistically facilitate OER kinetics.
- Maximum IPCE of 17% at 370 nm was achieved.
- The discussed charge transfer process can aid the design of new photoelectrodes.

Mo-doped ZnV₂O₆/Reduced Graphene Oxide Photoanodes for Solar Hydrogen Production

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Abstract

We report the fabrication and characterization of molybdenum (Mo)-doped ZnV_2O_6 /reduced graphene oxide (rGO) composite and its use as photoanode for photoelectrochemical (PEC) hydrogen production. Compared to pure ZnV_2O_6 , Mo ions act as electron donor in the ZnV_2O_6 :Mo lattice increasing charge carrier concentration and subsequently mobility in the bulk by the polaron transport. We measured the hole transfer efficiency for the pure and Mo-doped ZnV_2O_6 electrodes and revealing a substantial increase from 16 to 25 %. The mechanism of enhanced photoactivity of Mo-doped ZnV_2O_6 was studied by density functional theory calculations. Moreover, electrochemical impedance spectroscopy measurements show that graphene modification improves carrier separation and transfer across the electrode/electrolyte interface. Therefore, the combination of the two strategies triggers a synergistic enhancement in PEC performance in terms of incident photon-to-current efficiency, which is 17% at 370 nm, being 4.5- and 3.6-times greater than those of pristine ZnV_2O_6 and ZnV_2O_6 :Mo photoanodes, respectively. With photocurrent onset potentials of 0.6 V and photocurrent densities of 2.07 mA/cm^2 at 1.23 V vs. RHE, ZnV_2O_6 :Mo/rGO photoanodes are of interest for the design of high performance PEC visible-light-induced water-splitting devices.

KEYWORDS: *Photoanode, Doping effect, Reduced graphene oxide, Charge transfer, Solar water splitting*

1. Introduction

Solar-to-chemical energy conversion through photoelectrochemical (PEC) splitting of water is an attractive approach for addressing environmental and energy challenges [1-3]. Hence, following the first report this concept has been studied extensively [4]. Generally, this process involves three stages, including photon absorption by a semiconductor to produce electronically excited states of electron-hole pairs, followed by their separation and then transport to drive the hydrogen evolution reaction (HER) H^+/H_2 ($2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$) and oxygen evolution reaction (OER) $\text{O}_2/\text{H}_2\text{O}$ ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$) [5]. Compared with HER, OER is a more complex reaction as it is a four-electron, four-proton process. The standard single semiconductor structure in which an *n*-type semiconductor (photoanode) or a *p*-type semiconductor (photocathode) is employed with a metal counter electrode to drive the reduction or oxidation half-reactions allows to evaluate simply the performance of a new material for photoelectrochemical devices [6,7].

In terms of thermodynamic requirements, an ideal photoanode for hydrogen production must possess an adequate band gap to absorb a large portion of the solar spectrum and have suitable band edge positions to straddle the water oxidation potential [8]. Theoretically, a semiconductor with a band gap of just 1.23 eV can drive water splitting. However, in terms of kinetic requirements a bandgap of at least 1.8 eV is needed due to significant energy losses such as the oxygen evolution overpotential and the device operating voltage [7]. Higher charge carrier mobility could facilitate O_2 evolution by the photoanode due to lower overpotential and increase the energy conversion efficiency [9]. Furthermore, the material must be stable against photocorrosion (photo-oxidative decomposition or dissolution) in the electrolyte under illumination and made of abundant elements to make it low cost and sustainable [10]. Among numerous studied compounds, metal oxides such as TiO_2 [11], WO_3 [12], BiVO_4 [13] and Fe_2O_3

[14] have been widely investigated as *n*-type semiconductors for OER. However, it is highly desirable to develop semiconductors with optimal photophysical and chemical characteristics to overcome the limitations of currently available materials for water splitting. In the past few years, metal vanadates such as NiV_2O_6 [15], $\text{Cu}_3\text{V}_2\text{O}_8$ [16], $\text{Mn}_2\text{V}_2\text{O}_7$ [17] and $\text{Fe}_2\text{V}_4\text{O}_{13}$ [18] have shown potential as efficient light absorbers for PEC applications. However, rapid electron-hole recombination occurring in the bulk and at the surface is a general concern, unless a large overpotential is applied to drive the kinetically rate-limiting OER [19]. To improve the conductivity of the photoanode materials, considerable efforts have been recently devoted to suppress charge recombination. Doping elements [20] and using nanostructured architectures [21] are common strategies to promote charge transfer by amplifying donor density and shortening the pathway of photoexcited electrons/holes to the surface.

Recently, we investigated theoretically the fundamental properties of monoclinic ZnV_2O_6 and found that it meets all photophysical requirements for use in solar water splitting [22]. Subsequently we synthesized a nanocomposite of ZnV_2O_6 hybridized with reduced graphene oxide (rGO) via a facile hydrothermal approach [23]. The combination of a nanomaterial with two-dimensional carbon sheets is considered as a drastic strategy to enhance the photoactivity for various applications [24-26]. Having observed an efficient photocatalytic performance of $\text{ZnV}_2\text{O}_6/\text{rGO}$ for the degradation of Rhodamine B, we evaluate this nanocomposite as potential photoanode for solar water splitting. In the meantime, the effect of molybdenum doping on the structural and optical properties of ZnV_2O_6 was comprehensively explored. To better understand the intrinsic mechanism of enhanced PEC performance of Mo-doped vanadates, the fundamental properties were studied using an *ab initio* technique based on density functional theory (DFT)

calculations. We believe the combination of bulk doping by Mo ions and surface modification by rGO can lead to a synergetic effect to enhance PEC hydrogen production.

2. Experimental

2.1. Material synthesis and film preparation

All chemicals and materials were purchased from Sigma-Aldrich and used as received. The $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ nanocomposite was synthesized via a facile hydrothermal route. At first, 35 mg graphene oxide (GO, made using the modified Hummer's method [27,28]) was dispersed in 75 mL deionized water using a high intensity ultrasonication for 30 min. Then, 0.549 g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (2.5 mmol), 0.561 g NH_4VO_3 (4.8 mmol), 0.048 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.2 mmol) and 0.1 g sodium dodecyl benzene sulfonate (SDBS, as surfactant) were added. After 30 min stirring, the suspension was autoclaved at 220 °C for 4 h. To collect the dark yellow $\text{ZnV}_{1.92}\text{Mo}_{0.08}\text{O}_6\text{/rGO}$ nanocomposite, the resulting homogeneous suspension was centrifuged and washed with 1:1 ethanol-deionized (DI) water mixture and then dried at 110 °C for 2 h. The undoped $\text{ZnV}_2\text{O}_6\text{/rGO}$ nanocomposite was also synthesized using the same procedure without sodium molybdate dehydrate and using 5 mmol NH_4VO_3 . Thin film photoanodes were prepared by electrophoretic deposition on fluorine-doped tin oxide (FTO) glasses as described previously [23]. Briefly, a solution containing 30 mg of the respective powders and 20 mg iodine in 10 mL acetone was prepared by sonication. FTO substrates were washed in acetone and DI water mixture and dried with nitrogen. Afterwards, electrophoretic deposition was carried out in a two-electrode configuration by applying a bias voltage of 40 V between the FTO substrate and a Pt electrode for 3 min. The photoanode was subsequently annealed at 300 °C for 30 min.

2.2. Characterizations and measurements

X-ray diffraction (XRD) patterns were collected using a France Intel. (EQuinox 3000) Diffractometer equipped with Cu K α radiation. UV-Vis absorption and Raman spectra were acquired using a UV-Vis spectrophotometer (JENWAY6715 UV-vis) with an integrating sphere attachment and a Bruker SENTERRA dispersive microscope, respectively. Film morphology was imaged using a field emission scanning electron microscope (FE-SEM; model Mira3) equipped with an energy-dispersive X-ray spectroscopy (EDS) operated at an accelerating voltage of 15 kV. Surface area and pore size distribution were analyzed by a multipoint Brunauer-Emmett-Teller (BET) method using nitrogen adsorption/desorption isotherm measurements at 400 °C. The photoelectrochemical properties were measured on a VersaSTAT4 potentiostat in a standard three-electrode configuration using the prepared samples as the working electrode, a Pt foil as the counter electrode, and Ag/AgCl (saturated KCl) as reference electrode. All potentials in this work were converted into that versus the RHE for ease of comparison according to Eq 1:

$$E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl \text{ vs } NHE} + 0.0591 \text{ pH} \quad (\text{Eq. 1})$$

where the $E_{Ag/AgCl \text{ vs } NHE}$ is 0.1976 V at 25 °C. The illuminated areas were 0.28 cm² and all photocurrent experiments were conducted in a 0.1 M sodium borate buffer solution (pH= 9.2). For some measurements, 0.1 M Na₂SO₃ was added as a hole scavenger. Illumination (100 mW cm² AM 1.5G) was achieved with a Newport light source and the light response was recorded through a chopped light linear sweep voltammetry (LSV). For incident photon-to-current efficiency (IPCE) measurements, monochromatic light was produced using an Oriel Cornerstone

130 monochromator and the output was measured with a photodiode detector. The IPCE value at any specific wavelength was calculated using the following equation:

$$IPCE = \frac{1239.8 \times I}{\lambda \times P} \quad (\text{Eq. 2})$$

where I , P and λ are the measured photocurrent density and the measured light power density at the specific wavelength and the incident wavelength, respectively. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis were performed using a commercial three-electrode Autolab system (PGSTAT302N) and a solution containing sodium borate buffer. EIS measurements were conducted at an amplitude of 10 mV over a frequency range of 0.1 Hz to 100 kHz in 0.1 M Na₂SO₃.

2.3. Models and computational details

Since quantum mechanics describes and explains chemical bonds in a material, the fundamental properties can be simulated by solving the Schrodinger equation for the electrons in that structure. In this research, the calculations were carried out using a first principle plane wave pseudo-potential technique based on DFT with Cambridge Serial Total Energy Package (CASTEP) module in Materials Studio [29]. The electronic exchange correlation interactions were processed at the generalized gradient approximation (GGA) level, employing the Perdew-Burke-Ernzerhof (PBE) functional [30]. We used the structural data from ref. [31] as initial input for the calculations. However, the geometric optimization of ZnV₂O₆ was performed before single point energy calculations using the dispersion correction based on Tkatchenko and Scheffler's (TS) model [32]. The structural model of Mo-doped ZnV₂O₆ was also constructed by

substituting one V atom in a relaxed cell containing 33 atoms. Brillouin-zone integrations were performed using Monkhorst and Pack k -point meshes ($3 \times 3 \times 2$) to obtain the accurate density of the electronic states [33]. The self-consistent field tolerance and the convergence criterion of total force acting on each atom were set at 10^{-6} eV/atom and less than 0.01 eV/Å, respectively. Moreover, the maximum displacement was 10^{-4} nm while the upper limit of stress was 0.02 GPa.

3. Results and discussion

The XRD patterns of ZnV_2O_6 and Mo-doped ZnV_2O_6 powders are illustrated in Fig. 1a. The patterns exhibit the well defined peaks of the monoclinic ZnV_2O_6 phase for both samples according to JCPDS No. 74-1262. In addition, no diffraction peaks for MoO_3 are observed for Mo-doped ZnV_2O_6 . However, close inspection reveals a slight shift of all diffraction peaks towards lower angles for Mo-doped ZnV_2O_6 compared with pristine ZnV_2O_6 where Zn^{2+} ions are octahedrally coordinated and the V^{5+} ions have an irregular octahedral coordination [34]. According to Vegard's law, if the molybdenum ions (with slightly larger ionic radius rather than vanadium ions) substitute for V^{5+} may result in the lattice distortion observed as a shift in the diffraction pattern towards lower angles [35,36]. The unit cell volumes were obtained 197.6 and 199.1 Å³ for pure and doped ZnV_2O_6 , respectively confirming the lattice expansion after Mo substitution. Figure 1b displays absorption spectra acquired from ZnV_2O_6 and Mo-doped ZnV_2O_6 . Both as-synthesized samples strongly absorb in the visible region with an absorption edge at about 480 nm. Moreover, the Tauc plot derivatives for indirect transitions are presented in the inset of Fig. 1b. Both ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$ exhibit a bandgap of about 2.5 eV, consistent with the yellow color of the samples.

Fig. 1. (a) XRD patterns and (b) UV-Vis absorbance spectra of ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$ (inset: the corresponding Tauc plots)

The BET surface area and the pore size distributions for $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ composite were obtained by N_2 adsorption-desorption isotherm measurements (Fig. 2a). The sample exhibits a type IV isotherm with a hysteresis loop, which is a typical characteristic of inhomogeneous mesopores due to the interstitial space between the nanoparticles and the rGO sheets [37]. The corresponding pore size distribution, calculated from desorption data by the Barrette Joynere-Halenda (BJH) method is shown in the inset of Fig. 2a. In comparison with undoped composite [23], the $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ has a relatively higher surface area ($87.26 \text{ m}^2 \text{ g}^{-1}$) and the pore diameter due to the change in crystallinity conditions in the presence of dopant ions. Figure 2b displays the Raman spectrum recorded to further confirm the presence of the dopants and rGO in the prepared $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ composite. The obtained Raman bands are in complete agreement with previous studies for ZnV_2O_6 [38]. However, a slight shift towards lower wavenumbers was observed for the doped sample suggesting that the Mo with a larger ionic radius (59 pm) partially substitutes the V (54 pm) in the ZnV_2O_6 lattice [39]. The observed red shift in Raman spectrum for the doped sample shows that frequency of phonons interacting with the incident photon decreased due to the tensile strain imposed on the lattice in the presence of Mo ions. The two

additional peaks around 1330 and 1590 cm^{-1} are typically assigned to the disordered carbon (*D* band) and graphitic structure (*G* band) of rGO sheets, respectively. The *D* band originates from the breathing mode of the sp^3 -hybridized carbon atoms due to the structural defects, while the *G* band corresponds to the in-plane vibrational mode of the sp^2 -hybridized carbon atoms [40]. For the $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ sample the I_D/I_G ratio is estimated as 1.14.

Fig. 2. (a) N_2 adsorption-desorption isotherm (the inset: the BJH pore-size distribution) and (b) Raman spectrum of $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ nanocomposite

FE-SEM micrographs of $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ nanocomposites in different magnifications are shown in Fig. 3(a-c). The surface morphology of Mo-doped ZnV_2O_6 and the pure sample have almost identical features [23], as both have flower-like structures with mean particle diameters of about 250 nm. We believe that the adsorbed SDBS surfactant around the $\text{ZnV}_2\text{O}_6\text{:Mo}$ crystals results in a hierarchical flower-like framework through a self-assembly process [41]. Such a structure is expected to expand the electrode-electrolyte interfacial area decreasing charge carrier travel distances and charge recombination rate upon illumination in the solar water splitting reactions [42]. In addition, the vanadate microspheres are homogeneously anchored on the rGO sheets. The carbon-based sheets display a two-dimensional network with chiffon-like ripples and

wrinkles resulting from the deformation and distortion of graphite sheets during the oxidation process [43]. The EDS spectrum displayed in Fig. 3d reveals the presence of elemental Zn, V, O, Mo and C in the composites, thus confirming that the Mo-doping and rGO are effectively incorporated in ZnV_2O_6 to obtain the composite.

Fig. 3. (a-c) FE-SEM images in different magnifications (d) EDS spectrum of $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ nanocomposite

Mott-Schottky (M-S) analysis can be used to estimate the flat band potential and doping density of semiconductor photoelectrodes. However, the doping density cannot be reliably obtained through the M-S slope due to the frequency dependence and unknown specific surface area of the films. In addition, the potential drop is not usually uniform across this kind of heterogeneous films and therefore surface states can also contribute to the capacitive properties [44,45]. Nevertheless, the positive slopes of linear regression ($1/C^2$ vs V) in Fig. 4(a) qualitatively

confirm the *n*-type character for all ZnV_2O_6 -based semiconductors. Among three samples, the pure ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ photoelectrodes possess the lowest and highest charge carrier concentrations, respectively. The Mo-dopant acts as an electron donor in the ZnV_2O_6 lattice promoting charge carrier concentration and decreasing the resistance. Furthermore, the M-S plots illustrate x intercepts in the range of 0.48-0.55 V vs RHE corresponding to the flat band potential. In the presence of Mo or rGO, a negative shift of the flat band potential occurs due to the increase in the Fermi level of ZnV_2O_6 which leads to a higher degree of band bending and a large space charge layer potential. Thus, a large driving force for the generated electron-hole pairs in $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ is expected to separate in the space charge region, which is favorable for PEC performance. According to the estimated band gap and Fermi level (flat band potential), a schematic band diagram for ZnV_2O_6 photoanode is portrayed in Fig. 4b. The conduction band energy is often assumed to be more negative by about 0.1 eV than the Fermi level for *n*-type semiconductors [46,47]. The conduction band (CB) and valence band (VB) positions suggest that photogenerated holes in ZnV_2O_6 can thermodynamically perform water oxidation, while H_2 can be generated with the additional photovoltage provided by a photocathode in the tandem PEC.

Fig. 4. (a) M-S plots of the ZnV_2O_6 -based photoanodes at 1 kHz using 0.1 M sodium borate buffer as electrolyte (pH= 9.2) and 0.1 M Na_2SO_3 as hole scavenger and (b) approximate band positions diagram of ZnV_2O_6 film

To further assess the efficiency of the prepared photoanodes for PEC water oxidation, we acquired LSV measurements under simulated solar illumination (AM 1.5G). Figure 5a displays the chopped LSVs for pristine ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$ films in 0.1 M sodium borate buffer solution (pH 9.2). The anodic photocurrents (current density increases with increasing anodic bias) in both samples confirm the *n*-type character of the ZnV_2O_6 -based electrodes. In addition, the photocurrent responses at low applied bias exhibit onset potentials near 0.6 V vs RHE (inset of Figure 5a), which are consistent with the flatband potential estimated from M-S results. Although the photocurrent of $\text{ZnV}_2\text{O}_6\text{:Mo}$ film is generally higher than pure ZnV_2O_6 , the current densities for both samples are rather low ($<0.3 \text{ mA/cm}^2$) at the onset of dark water oxidation (1.23 V vs RHE) due to slow kinetics at the semiconductor surface [48]. To explore this hypothesis, 0.1 M Na_2SO_3 was added as a sacrificial hole scavenger into the electrolyte. According to Fig. 5b, a considerable increase (about twice) in photocurrent is observed for both electrodes compared with borate alone. These observations confirm that water oxidation at the surface of ZnV_2O_6 -based electrodes is kinetically limited and a significant fraction of charge carriers are lost to recombination before surface reactions take place. Considering the band gap of 2.5, the maximum theoretical photocurrent density for ZnV_2O_6 can be calculated about 7 mA/cm^2 when all solar photons are assumed to be captured and converted to photocurrent [49]. Moreover, we performed chronoamperometric (I-t curve) analysis to investigate the instant photocurrent response behavior of pristine ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$. Figure 5c displays

photocurrent measurements obtained under on-off switching 455 nm light irradiation at anodic bias 1.23 V versus RHE. When the light is switched on, a steep increase of transient photocurrent is observed for both samples and when it is switched off, the current density decreases immediately. This typical response, known as “spike and overshoot” photocurrent transient, is generally caused by an accumulation of holes in the semiconductor space charge layer under prolonged illumination and the recombination of bulk electrons with these holes [50]. In the steady state, the rate of hole arrival can be assumed to be equal to the rate of hole transfer towards the electrolyte (water oxidation reaction) and the rate of electron-hole surface recombination. Therefore, the instantaneous photocurrent (J_{ini}) under irradiation represents a charging or displacement current due to the initial movement of photo-generated holes towards the surface. The relatively high incident photon flux $10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ led to more accurate monitoring of the decay dynamics of photogenerated holes especially in measurement of J_{ini} [51]. On the contrary, the steady state photocurrent (J_{ss}) stands for the flux of holes transferred successfully to the electrolyte and participating in the water oxidation reaction. Consequently, the ratio of J_{ss} and J_{ini} can be considered as a measure of the hole transfer efficiency for photoanodes [52]. The hole transfer efficiency for the pure and Mo-doped ZnV_2O_6 electrodes were estimated as 0.16 and 0.25, respectively. These values are comparative with those reported for $\text{BiVO}_4:0.05\text{Mo}$ [35] and $\text{Fe}_2\text{O}_3:0.1\text{Sn}$ [53] which are 0.45 and 0.25, respectively. After steady state conditions and when the light is switched off, a negative transient occurs which can be assigned to the recombination of the bulk electrons with the accumulated holes in the space charge layer resulting in a back flow of electrons into the photoanodes (overshoot stage). The decrease in overshoot peak after n -type doping can be related to two effects, narrowing the space

charge width due to the increased donor concentration and/or elimination of surface trapping states [35].

Fig. 5. (a) Chopped LSV scans in the absence of hole scavenger (inset: onset potential), (b) J - V curves in different electrolytes and (c) photocurrent transients for ZnV_2O_6 and $\text{ZnV}_2\text{O}_6:\text{Mo}$ photoanodes without hole scavenger at 1.23 V vs RHE under 455 nm light irradiation

To clarify the origin of the different photoelectrochemical performance of the Mo-doped photoanode, the partial density of states (PDOS) and the total electronic density of states (TDOS)

projected onto Zn, V, O and Mo atoms were computed using DFT calculations. Figure 6 and 7 compare PDOS and TDOS of ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$ semiconductors along high symmetry directions in the Brillouin zone, where the Fermi level (E_F) was referenced at 0 eV. There is no noticeable change in the shape of the VB and CB for both structures where they mainly consist of oxygen $2p$ orbitals and vanadium $3d$ states, respectively. Because the V $3d$ states are split into the crystal-field levels “ e ” and “ t_2 ”, the CB is divided into two parts for both structures. The $4d$ states of Mo are partially delocalized in $\text{ZnV}_2\text{O}_6\text{:Mo}$ contributing to the formation of impurity energy levels which are constituted by the interplay with adjacent oxygen anions. Since the band gap remains nearly unchanged (2.31 and 2.33 eV), the difference in the photophysical properties between ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$ can arise from these interactions leading to changes in the width of VB. This suggests that the hole mobility and subsequently the hole transfer efficiency may be affected by the Mo-doping which enhances separation of the photogenerated charge carriers [54]. *Ab initio* calculations based on DFT with local or gradient-corrected exchange-correlation potentials are known to underestimate the band gap values [55]. Nevertheless, atomic Mo has one more valence electron compared to atomic V and this type of impurity likely act as a shallow donor which donates electrons to the ZnV_2O_6 lattice. As illustrated in Fig. 7e, the Fermi level is located inside the CB implying partial filling of the V $3d$ states (orbital energy levels Mo $4d \approx \text{V } 3d$) [56]. It is expected that the excess electron is delocalized over the V ions while filling the bottom of the CB. In these conditions, polaron formation can cause a lattice distortion around the reduced V^{4+} ion leading to migrate the excess electron from the V^{4+} site to a neighboring V^{5+} (or Mo^{6+}) site. The polaron transport usually follows a thermally activated hopping mechanism resulting in an improvement of charge carrier mobility and subsequently the photoelectrochemical performance.

Fig. 6. (a-c) PDOS on Zn, V and O atoms and (d) TDOS for ZnV_2O_6 structure

Fig. 7. (a-d) PDOS on Zn, V, O and Mo atoms and (e) TDOS for (f) DFT-optimized unit cell of $\text{ZnV}_2\text{O}_6\text{:Mo}$

The current-voltage function under AM 1.5G illumination was also performed to understand the role of rGO in the $\text{ZnV}_2\text{O}_6\text{:Mo}$ photoanode. The LSV scans for $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ film during light ON-OFF cycles in the absence and presence of hole scavenger in the electrolyte are shown in Fig. 8a. The photocurrent density generated in $\text{ZnV}_2\text{O}_6\text{:Mo}$ increases significantly from 0.49 mA/cm^2 to 2.07 mA/cm^2 at 1.23 V vs RHE after rGO treatment. This value for $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ without hole scavenger was obtained 1.62 mA/cm^2 at 1.23 V vs RHE. We previously discussed the role of rGO as a solid-state electron mediator leading to efficient charge separation and prolonged recombination time of electron-hole pairs in ZnV_2O_6 [23]. Therefore, it seems that Mo-doping mainly contributes to an increase in donor density and improvement of hole transport in the bulk, whereas graphene modification accelerates the electron transfer particularly at the surface. Accordingly, combining the two strategies can synergistically enhance the PEC performance. Overall, the magnitude of the photocurrent density after molybdenum doping and rGO decoration is nearly five times higher than that of pure ZnV_2O_6 . EIS measurements were also carried out to study the intrinsic electronic properties and charge transfer kinetics at the photoanode/electrolyte interface. Figure 8b presents typical Nyquist plots of ZnV_2O_6 , $\text{ZnV}_2\text{O}_6\text{:Mo}$ and $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ photoanodes under simulated solar illumination at an electrode potential of 1.45 V vs RHE. Since the carrier densities are rather significant in the doped photoanodes, the capacitance of the space charge region (C_{sc}) is expected to be the same order of magnitude as the Helmholtz capacitance (C_{ct}). Therefore, we chose a circuit model consisting of five elements to fit the impedance data as shown in the inset of Fig. 8b; R_s is the series resistance including the FTO resistance, the resistance related to the ionic conductivity in the electrolyte and the external contact resistance (e.g. wire connections). R_{sc} and R_{ct} are the

internal bulk charge transport resistance and the charge transfer resistance, respectively. In addition, C_{sc} represents charge diffusion in the space charge layer, whereas C_{ct} is attributed to the capacitance of the double layer at the semiconductor/electrolyte interface. The fitting curves (solid line) are in good agreement with the experimental results (symbols) confirming that the proposed equivalent circuit is quite reliable. The fitted values of R_{sc} are 621.4, 201.8 and 99.7 Ω/cm^2 for ZnV_2O_6 , $\text{ZnV}_2\text{O}_6:\text{Mo}$ and $\text{ZnV}_2\text{O}_6:\text{Mo}/\text{rGO}$ respectively, while the obtained values for R_{ct} are 2311.8, 997.2 and 405.9 Ω/cm^2 . The decrease in both resistances is in agreement with the observed increase in photocurrents and although the charge transfer determined for ZnV_2O_6 was kinetically poor, both molybdenum doping and rGO decoration dramatically reduced the resistances. The results suggest that Mo-doping is more beneficial for charge transfer in the bulk of the material, while rGO nanosheets are enabling improved charge transfer particularly across the semiconductor-electrolyte interface. Thus the synergistic effect of the modifications resulted in the lowest resistances for the $\text{ZnV}_2\text{O}_6:\text{Mo}/\text{rGO}$ electrode, indicating longer charge carrier lifetimes and reduced photogenerated electron-hole recombination. Consequently, more holes from the VB can reach the semiconductor-electrolyte interface to drive water oxidation reactions in agreement with LSV results.

Fig. 8. (a) Chopped LSV scans for $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ in the absence and presence of hole scavenger (Na_2SO_3) in electrolyte and (b) EIS Nyquist plots of ZnV_2O_6 , $\text{ZnV}_2\text{O}_6\text{:Mo}$ and $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ under illumination at 1.45 V vs RHE (inset: proposed equivalent circuit)

Finally, the incident photon-to-current conversion efficiencies (IPCEs) were determined at 1.23 V vs RHE under monochromatic light illumination to investigate the relationship between photoelectrochemical activity and wavelength (Fig. 9). The photoresponse was observed from 350 to 520 nm for all samples, as expected from the UV-Vis absorbance spectra. In comparison to pristine ZnV_2O_6 , Mo-doped photoanode shows higher IPCE values over the entire spectral range. Moreover, the IPCE value of $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ was up to 17% at 370 nm which is almost 4.5 and 3.6 times as high as that of the pure ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$ electrodes, respectively. In general, these data are in good agreement with the J - V scans and verify again the synergistic effect between ion doping and graphene decoration.

Fig. 9. IPCE plots for ZnV_2O_6 , $\text{ZnV}_2\text{O}_6\text{:Mo}$ and $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ films performed at 1.23 V vs. RHE using 0.1 M sodium borate buffer as electrolyte (pH= 9.2) and 0.1 M Na_2SO_3 as hole scavenger (bars represent standard deviation)

Based on the obtained results, the plausible mechanism of charge transfer during PEC water splitting using the $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ photoanode is proposed in Fig. 10. When the $\text{ZnV}_2\text{O}_6\text{:Mo}$ and rGO composite forms initially, free electrons are transferred from the rGO to the interface states due to the higher Fermi level of rGO, until reaching equilibrium. The composite material can be excited under illumination and generates the electron-hole pairs. Subsequently, the Fermi level in $\text{ZnV}_2\text{O}_6\text{:Mo}$ rises and the photogenerated electrons can be transferred to rGO. The Schottky barrier formed in rGO and the metal oxide would effectively hinder the electrons' backward transfer from rGO to $\text{ZnV}_2\text{O}_6\text{:Mo}$, which leads to a decrease of the electron-hole recombination rate [57]. The rGO nanosheets as the electron acceptor and mediator can effectively collect the electrons from $\text{ZnV}_2\text{O}_6\text{:Mo}$, then quickly transfer to the counter electrode (Pt) via an external bias voltage to drive the hydrogen generation reaction. In addition, the donor level formed by Mo-doping can remove the hole traps in the undoped ZnV_2O_6 and promote the separation of the photogenerated charge carriers. On the other hand, the photogenerated holes in the valence band transfer to the interface of photoanode and electrolyte where they promote water oxidation.

Fig. 10. Schematic representation for charge transfer process along ZnV₂O₆:Mo/rGO photoanode for PEC water splitting reactions

4. Conclusions and Perspectives

We describe the fabrication of a photoanode based on ZnV₂O₆:Mo/rGO which exhibits promising performance in solar water splitting tandem cells. Pristine ZnV₂O₆, Mo-doped ZnV₂O₆ and ZnV₂O₆:Mo/rGO nanocomposites were synthesized via a one-step hydrothermal route and coated on FTO-based electrodes. ZnV₂O₆ is introduced as a promising *n*-type semiconductor with a band gap near 2.5 eV and a valence band position which can thermodynamically perform water oxidation reactions. DFT calculations revealed that the hole mobility is affected by Mo-doping which enhances the separation of photogenerated charge carriers in the bulk. In addition, EIS measurements demonstrated that rGO decoration can effectively accelerate slow kinetics for water oxidation at the semiconductor surface. The discussed charge transfer process will aid the design and fabrication of thin film photoelectrodes. The composite of ZnV₂O₆:Mo/rGO photoanode exhibited the highest photocurrent density of 2.07 mA/cm² at 1.23 V vs RHE and IPCE of 17% at 370 nm. In conclusion, this study sheds light on the unique features of this semiconductor and motivate further exploration of other visible-light-active metal oxide candidates for PEC water splitting reactions.

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Figure Captions

Fig. 1. (a) XRD patterns and (b) UV-Vis absorbance spectra of ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$ (inset: the corresponding Tauc plots)

Fig. 2. (a) N_2 adsorption-desorption isotherm (the inset: the BJH pore-size distribution) and (b) Raman spectrum of $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ nanocomposite

Fig. 3. (a-c) FE-SEM images in different magnifications (d) EDS spectrum of $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ nanocomposite

Fig. 4. (a) M-S plots of the ZnV_2O_6 -based photoanodes at 1 kHz using 0.1 M sodium borate buffer as electrolyte (pH= 9.2) and 0.1 M Na_2SO_3 as hole scavenger and (b) approximate band positions diagram of ZnV_2O_6 film

Fig. 5. (a) Chopped LSV scans in the absence of hole scavenger (inset: onset potential), (b) J-V curves in different electrolytes and (c) photocurrent transients for ZnV_2O_6 and $\text{ZnV}_2\text{O}_6\text{:Mo}$ photoanodes without hole scavenger at 1.23 V vs RHE under 455 nm light irradiation

Fig. 6. (a-c) PDOS on Zn, V and O atoms and (d) TDOS for ZnV_2O_6 structure

Fig. 7. (a-d) PDOS on Zn, V, O and Mo atoms and (e) TDOS for f) DFT-optimized unit cell of $\text{ZnV}_2\text{O}_6\text{:Mo}$

Fig. 8. (a) Chopped LSV scans for $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ in the absence and presence of hole scavenger (Na_2SO_3) in electrolyte and (b) EIS Nyquist plots of ZnV_2O_6 , $\text{ZnV}_2\text{O}_6\text{:Mo}$ and $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ under illumination at 1.45 V vs RHE (inset: proposed equivalent circuit)

Fig. 9. IPCE plots for ZnV_2O_6 , $\text{ZnV}_2\text{O}_6\text{:Mo}$ and $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ films performed at 1.23 V vs. RHE using 0.1 M sodium borate buffer as electrolyte (pH= 9.2) and 0.1 M Na_2SO_3 as hole scavenger (bars represent standard deviation)

Fig. 10. Schematic representation for charge transfer process along $\text{ZnV}_2\text{O}_6\text{:Mo/rGO}$ photoanode for PEC water splitting reactions

Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical Abstract