Letter

Photoelectrochemical performance of NiO-coated ZnO–CdS core-shell photoanode

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Abstract

A nano-structured core-shell ZnO–CdS photoanode device with a mesoporous NiO co-catalyst layer was fabricated using solution-processing methods. The growth of the sparse ZnO nanorod film with a thickness of ca. 930 nm was achieved by optimizing parameters such as the thickness of the ZnO seed layer, choice of Zn precursor salt and the salt concentration. CdS was then coated by a combination of spin coating and spin SILAR (Successive Ionic Layer Adsorption and Reaction) methods to completely fill the interspace of ZnO nano-rods. The uniform CdS surface facilitated the growth of a continuous mesoporous NiO layer. Upon illumination of 100 mW cm$^{-2}$ AM 1.5 G radiation the device exhibits stable photocurrents of 2.15 mA cm$^{-2}$ at 1.23 V and 0.92 mA cm$^{-2}$ at 0.00 V versus RHE, which are significantly higher as compared to the bare ZnO–CdS device. The excellent performance of the device can be ascribed to the higher visible region absorption by CdS, and effective separation of the photogenerated charge carriers due to the suitable band alignment and nanostructuring. Additionally, the mesoporous NiO overlayer offered a larger contact area with the electrolyte and promoted the kinetics enabling higher and stable photocurrent even till the 35th min. of testing.

Keywords: photoanode, cadmium sulphide, nanostructure

(Supplementary material for this article is available online)

1. Introduction

The development of technology to store and dispatch solar energy as per our requirements is one of the most imperative steps towards sustainability [1–4]. Solar driven electrolysis of water to produce H$_2$ is being widely investigated as a solar to chemical fuel conversion, and hence, a solar energy storage method [5, 6]. Since the claim of cleavage of water at a TiO$_2$-electrolyte interface by Honda and Fujishima in [7], a lot of attention has been given to semiconductor based PEC water splitting [8–12]. Increasing the efficiency of the photoelectrodes, improving the stability against corrosion, use of nanostructuring for better charge transfer, and cost reduction by the exploration of new and earth abundant material combinations for absorbers and catalysts are the challenges dominating research in this field [13–15].

CdS ($E_g = 2.4$ eV) has garnered interest as a photoanode material due mainly to the suitably aligned band position with the water splitting potentials [16–18]. However, two caveats to the use of this material arise from (i) the susceptibility to photocorrosion and (ii) low minority carrier diffusion length of lesser than 0.5 μm [19, 20]. There have been many
efforts to address these shortcomings by using surface protection against photo-corrosion and nano-heterostructuring using charge carrier selective semiconductor layers to inhibit recombination [21, 22].

Transition metal oxides, owing to their suitable electronic properties, their ease of synthesis, and resistance to corrosion have been used to protect the nanostructured photoanodes based on CdS [23–28]. Among these, solution-processed ZnO ($E_g = 3.2$ eV) nanorods forming a Type-II semiconductor heterojunction with CdS have been extensively investigated as a bottom layer in nanostructured CdS photoanode devices [29–33]. However, as mentioned earlier, the surface of CdS readily undergoes photo-corrosion in aqueous environments due to the preferential oxidation of $S^2^–$ by the photogenerated holes as opposed to oxidation of water [34]. NiO is a wide bandgap $p$-type material that is a known co-catalyst for water oxidation and is also resistive to photo-corrosion [35–37]. The suitable band alignment of NiO and ZnO with CdS has motivated the investigation of the same as components of a nano-heterostructure [8, 38].

There have been recent reports of nanostructured CdS photoanodes with stable performance [39, 40]. Strategies such as improving visible light absorption and facile transfer of the photogenerated holes to the solution via nanostructuring can be adopted to improve performance from CdS based photoanodes. Here, we discuss the synthesis optimisation and testing of a solution processed ZnO–CdS core-shell heterostructure covered on the surface by a mesoporous NiO film (schematic in figure S12, electronic supplementary information (ESI) (stacks.iop.org/JPhysD/50/10LT01/mmedia)), showing high and stable PEC performance.

2. Experimental

The detailed synthesis procedure and characterization details of the photoanode device fabrication are provided in the ESI. Briefly, a ZnO nanorod film of thickness ca. 930 nm was grown using the hydrothermal method over a sputtered ZnO seed layer on FTO-coated glass [31]. The nanorod film was then coated with CdS using a combination of spin coating based methods adapted from literature, to form a ZnO–CdS core-shell structure with an extremely uniform surface morphology [33, 39]. A well established chemical bath deposition (CBD) method was used to grow a mesoporous NiO ($m$-NiO) layer over the prepared ZnO–CdS core-shell structure [41].

3. Results and discussion

Figure 1 shows the SEM cross-section images of the ZnO nanorod film [figure 1(a)] and the NiO–CdS–ZnO photoanode device [figure 1(b)]. The optimized growth parameters of the sputtered ZnO seed layer and duration of hydrothermal growth yielded a sparse nanorod film as can be seen in figure 1(a). Also, the orientation of the nanorods being slightly displaced from vertical allows for a reduced density of ZnO and larger extent of porosity. This allows a larger density of CdS in the nanostructure, enabling greater light absorption in the visible spectrum thereby yielding larger photocurrent. The detailed discussion of the ZnO nanorod film optimisation can be found in the ESI.

In order to sufficiently cover the sparser ZnO nanorod film, we modified the CdS coating procedure from earlier reports. Specifically, spin SILAR in addition to spin coating was employed to get a coating with a uniform surface morphology thereby allowing for the contiguous deposition of the next layer in the heterostructure. The optimized ZnO–CdS core-shell structure is shown in figures S9(b) and (d). Firstly, we note that the thickness of the composite film is limited by the length of the nanorods. Secondly, the part of the film towards the top looks denser than that at the bottom. Our hypothesis is that this larger density top section is the result of the spin SILAR regime after the spin coating. Importantly, we observe that the CdS has completely filled the ZnO nanorod structure and has formed a compact film with a continuous and uniform surface. In contrast, the heterostructure obtained by just spin coating insufficiently covers the ZnO nanorod structure as seen in figures S9(a) and (c) and a large fraction of the ZnO nanorods still remain exposed due to partial CdS coating. The CdS film obtained under the optimized conditions allowed for a more continuous deposition of the $m$-NiO as compared to that obtained on a purely spin coated CdS film. Further discussion on the structural and PEC performance superiority of the $m$-NiO coated photoanode synthesised using the spin coating + spin SILAR CdS coat can be found in the ESI.
We used NiO as the top layer as it has been demonstrated that NiO offers effective surface passivation and also improves photo-generated charge carrier separation due to its hole selective nature [36, 39]. Also, recently Feng et al established that facile infiltration of the electrolyte into a mesoporous structured photoanode significantly enhances hole transfer to the solution, thereby facilitating higher charge separation efficiency [42]. Figure 1(b) is an SEM cross-section image of one such m-NiO film grown via CBD atop the ZnO–CdS structure. We have used CBD synthesised m-NiO at the electrode–electrolyte interface for surface passivation of a photoanode film for the first time to the best of our knowledge. The same CBD procedure was also used to grow NiO on FTO-coated glass for the purpose of analysis. It is seen from figure S8 (ESI) that the base of the NiO film is uniformly spanning the available substrate area, even though the surface of the NiO film is flake-like. This greatly reduces the ZnO–CdS core–shell film contact area with the electrolyte, thereby successfully passivating the same from degradation. The deposition of this mesoporous protective layer was key to achieving the large photocurrent from the device as it provides a larger electrode–electrolyte surface area for enhanced interfacial charge transfer in addition to surface passivation.

Figure 2 shows the diffraction patterns of the various successive layers in the course of the heterostructure synthesis on FTO-glass substrate. The analysis was carried out in grazing incidence mode (at $\theta \approx 0.5^\circ$) so that the crystal structure of each successively deposited layer could be investigated, due to the low penetration depth of the x-rays. A randomly oriented polycrystalline ZnO film (JCPDS 003-0891) with high crystallinity was obtained in our deposition conditions. The peaks corresponding to the CdS layer being broad, are however distinctly visible and well matched with the standard JCPDS file (002-0454). The broad peaks perhaps arise either due to the low crystallinity of the material or the presence of smaller grains occupying the interspaces between the ZnO nanorods resulting in the ZnO–CdS core–shell structure. Similar broad peaks for the NiO layer were also obtained, grown in (003), (012) and (104) orientation (JCPDS 022-1189). The broad peaks of lower intensity can be attributed to the flaky structure of the m-NiO layer as seen from the FE-SEM analysis.

To investigate the photoelectrochemical (PEC) behavior of the heterostructured device, with and without NiO layer, chronoamperometry ($j$ versus $t$) and linear sweep voltammetry ($j$ versus $V$) experiments were carried out with the device under chopping mode (1 Sun AM 1.5G illumination/Dark) and continuous illumination (only chronoamperometry with 1 Sun AM 1.5G illumination) as shown in figure 3. An aqueous solution comprising of 0.25 M Na$_2$S and 0.35 M Na$_2$SO$_3$, pH $\approx 12.5$ was taken as a hole scavenging electrolyte and the experiments were carried out using three electrode system. To test CdS based photoanodes, hole scavengers in the solution are required to inhibit the oxidation of S$^{2-}$ present in the CdS lattice [18].

Considering figure 3(a), the photocurrent obtained in the first pulse ($t = 0$ min) for the bare ZnO–CdS core–shell photoanodes is $j_b(1.23 \text{ V}) = 0.93 \text{ mA} \cdot \text{cm}^{-2}$ and $j_b(0.00 \text{ V}) = 0.21 \text{ mA} \cdot \text{cm}^{-2}$; i.e. $j_b(1.23 \text{ V})/j_b(0.00 \text{ V}) = 4.42$. This is indicative of faradaic oxidative processes at the working electrode that have an onset potential below the potential at which the device is tested. E.g. dissolution of CdS, oxidation of the hole scavenging species; increasing the overpotential leads to increased rate of reaction. The dissolution of the CdS itself via the reaction: CdS $+ 2\text{H}^+ \rightarrow \text{Cd}^{2+} + \text{S}$. This is achieved by efficient oxidative processes at the working electrode, leaving us with the thermodynamically preferred oxidation of S$^{2-}$ and SO$_3^{2-}$ in the solution at the CdS-electrolyte interface [18]. Oxidation of the hole scavengers in the solution is hence the major contributor to the anodic performance of the photoanode.

We also observe a decay in the photocurrent on continued testing at both the potentials. The current after 14 cycles of light chopping ($t = 14 \text{ min}$) testing is found to decay to $j_{14}^{0}(1.23 \text{ V}) = 0.68 \text{ mA} \cdot \text{cm}^{-2}$ ($j_{\text{dec}}(1.23 \text{ V}) = 26.8\%$) and $j_{14}^{0}(0.00 \text{ V}) = 0.18 \text{ mA} \cdot \text{cm}^{-2}$ ($j_{\text{dec}}(0.00 \text{ V}) = 14.2\%$) (Note: $j_{\text{dec}}(V) = (j_b(V) - j_{14}(V))/j_b(V) \times 100$). The reduction in the current obtained at the two potentials as well as the reduced $j_{14}^{0}(1.23 \text{ V})/j_{14}^{0}(0.00 \text{ V}) = 3.77$ can be attributed to the more rapid film degradation at the higher potential, leading to reduced active area of the electrode as well as light absorption cross-section. However, the usage of the hole scavenging species eliminates the possibility of CdS photocorrosion [18]. Presence of few micro-gaps or pinholes in the CdS coverage of the ZnO nanorod film could leave a small fraction of the ZnO nanorod tips to be exposed to the electrolyte. This electrolyte-ZnO contact results in ZnO nanorod degradation via the well-reported non-faradaic alkaline dissolution of ZnO [43]. Reduction in the length of the ZnO nanorods results in...
the loss of support for the CdS crystals adherent to them, causing the CdS crystals to also leach into the solution thereby reducing the quantity of the primary light absorber on the photoanode film. We propose that the decay in photocurrent could be attributed to the loss of CdS by this mechanism.

Light chopping chronoamperometry data for the \( m \)-NiO coated ZnO–CdS core-shell device is presented in figure 3(b). The photocurrent obtained in the first pulse \((t = 0 \text{ min})\) is \(j \) (1.23 V) = 2.18 mA cm\(^{-2}\) and \(j \) (0.00 V) = 0.94 mA cm\(^{-2}\). Similar to the case of the device with no \( m \)-NiO layer, here too, we observe an increase in current at 1.23 V. However, the \(j \) (1.23 V)/\(j \) (0.00 V) value is only 2.31, lower than that observed for the bare ZnO–CdS device. As mentioned earlier, the photogenerated holes oxidise the reduced species \(\text{S}_2^2\) and \(\text{SO}_3^{2-}\) in the solution. As the oxidation processes have different rate of reaction dependence with the anodic polarization, this leads to different changes in observed current upon changing the anodic polarization. Clearly noticeable in figure 3(b) is the enhanced current and improved stability of the photoanode at both, the unbiased and anodic polarisation conditions compared to that of the bare device. Our hypothesis is that the \( m \)-NiO layer effects this improvement by firstly increasing the electrode–electrolyte interface area and secondly inhibiting the dissolution of the film into the solution.

Further evidence towards establishing our hypothesis can be inferred from studying the subsequent cycles in the chopped chronoamperometry data of the protected device. The current after 14 cycles \((t = 14 \text{ min})\) of testing is found to decay to \(j \) (1.23 V) = 2.07 mA cm\(^{-2}\) (\(j_{\text{dec}}\) (1.23 V) = 4.5%) and \(j \) (0.00 V) = 0.92 mA cm\(^{-2}\) (\(j_{\text{dec}}\) (0.00 V) = 2.1%). The percentage decrease in current is about a factor of 6 lower than in the unprotected device, even though the actual current values are higher. Also, the value of \(j \) (1.23 V)/\(j \) (0.00 V) is close to \(j \) (1.23 V)/\(j \) (0.00 V) = 2.31 indicating inhibition of film degradation to a large extent. The highly reduced photocurrent decay in the device with the \( m \)-NiO layer compared to the bare device is due to the large reduction in the pathways through which electrolyte-ZnO contact is established leading to the reduction in leaching of CdS via the mechanism proposed earlier.

To show that the device with the \( m \)-NiO layer is indeed stable, we performed extended chronoamperometry (35 min) under continuous light illumination. The results of the test done at both 0.00 V and 1.23 V versus RHE is shown in figure 3(c). We can clearly see that the performance in both cases exhibits remarkable stability, yielding photocurrent densities of 2.15 mA cm\(^{-2}\) at 1.23 V versus RHE and 0.92 mA cm\(^{-2}\) at 0.00 V versus RHE consistently for up to 35 min of activity.

A study of the linear sweep voltammetry (LSV) of the layered photoanode at various synthesis stages is shown in figure 3(d). We can see that the ZnO nanorod film yielded negligible photoresponse throughout the entire range, reaching a maximum of 0.03 mA cm\(^{-2}\) under illumination.
at 1.23 V versus RHE. Hence we may infer that the ZnO nanorods themselves do not contribute significantly to the observed anodic photocurrent. This also supports the fact that the decay in bare ZnO–CdS film photocurrent is due to CdS loss, albeit caused by alkaline ZnO dissolution. The increased visible spectrum absorption due to the CdS coating is evident from the comparison between the ZnO–CdS core-shell film and the bare ZnO nanorod film photoresponse curves. Comparing the low voltage (at 0.18 V versus RHE) photoresponse of the bare (0.54 mA cm$^{-2}$) and m-NiO covered (1.39 mA cm$^{-2}$) devices shows the improvement on account of the m-NiO film. Also, the saturation currents of 2.05 mA cm$^{-2}$ and 1.12 mA cm$^{-2}$ at 1.12 V versus RHE of the covered and bare ZnO–CdS core-shell photoanodes respectively demonstrate the same. The photocurrent of 0.92 mA cm$^{-2}$ even at 0.00 V versus RHE of the m-NiO covered ZnO–CdS core-shell is indicative of its excellent photocurrent onset potential. Further, the $j(1.12 V)/j(0.00 V)$ for the bare device is 6.2 and protected devices decreases to 2.2, which is consistent with the corresponding reductions in the $j_0(1.23 V)/j_0(0.00 V)$ and $j_{aq}(1.23 V)/j_{aq}(0.00 V)$ ratios from the bare to the covered device as discussed in the chronocamperometry studies.

Presence of a nanostructured surface morphology has been known to enhance absorption through confinement resulting from multiple light diffusion [42, 44]. Here we discuss a similar role played by the m-NiO film on the surface. The absorption spectra at different synthesis stages of the device have been studied and shown in figure 4. We can see that the absorption edge of the ZnO nanorod film is at 387 nm and that of the ZnO–CdS core-shell film is at 523 nm. These correspond to bandgaps of 3.20 eV and 2.37 eV respectively. Interestingly, the absorption edge at 552 nm in the case of the m-NiO covered ZnO–CdS core-shell film seems to have shift compared to the bare film. It is evident that the presence of the m-NiO film on the surface has indeed increased the absorption in the higher frequency range of the visible spectrum. This may be ascribed to the light confinement via multiple diffraction due to the m-NiO surface, as opposed to the reflection off the uniform surface of the bare ZnO–CdS core-shell film surface.

Figure 4. Absorbance spectra of the m-NiO coated ZnO–CdS core-shell photoanode (blue), bare ZnO–CdS core-shell photoanode (red) and ZnO nanorods (black).

4. Conclusions

In summary, we have successfully fabricated a core-shell ZnO–CdS heterostructure with a uniform and continuous over-layer of mesoporous NiO (m-NiO) via solution processing methods. The device shows enhanced and stable photo-electrochemical (PEC) performance. This has been attributed to (a) the sparser arrangement of the ZnO nanorods that allows for more loading of CdS in the device structure, (b) the mesoporous structure of NiO that facilitates rapid charge transfer to the solution on account of the increased electrode–electrolyte interface area, (c) enhanced absorption due to light confinement at the nanostructured m-NiO surface, and (d) inhibition of degradation via film dissolution effected by the m-NiO layer. We believe that obtaining the optimal density of nanorods in the bottom layer and employing stable oxide materials as the top protective layer are effective strategies to further enhance the performance of heterostructured thin film PEC devices.

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