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## Small Molecular Amine Mediated Synthesis of Hydrophilic CdS Nanorods and their Photoelectrochemical Water Splitting Performance<sup>†</sup>

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Photoelectrochemical (PEC) water splitting is a promising route for solar energy harvesting and storage, but it has been highly limited by the performance of the semiconductor photoelectrodes. Herein, we report a small molecular amine-mediated solvothermal method for synthesizing CdS nanorods. The obtained CdS nanorods are hydrophilic and can be easily dispersed in water. Furthermore, the small molecular amine, activating element sulfur and mediating the growth of CdS, plays a role similar to that of long-chain surfactant moleculars in "non-aqueous" system. Thus, the obtained CdS nanorods show uniform shape with monodispersed size, the length of which can be tuned by sulfur dosage. In addition, the CdS nanorods show broader light absorption than that of CdS nanoparticles. Their photoelectrochemical water splitting performances were then tested. Under light irradiation of  $\lambda > 200$  nm, the photocurrent density of CdS nanorods at -0.2 V bias potential (vs. Ag/AgCl) is 25 times of that obtained with CdS nanoparticles. The present finding demonstrates that small amine molecules would be efficient mediator for synthesis of hydrophilic sulfides with high quality. The simple synthesis method and the good photoelectrochemical properties illustrate the hydrophilic CdS nanorods as a potential candidate for photoelectrochemical applications.

#### Introduction

Inspired by nature, Fujishima and Honda creatively demonstrated photoelectrochemical (PEC) water splitting route, in which water is split into H<sub>2</sub> and O<sub>2</sub>.<sup>1</sup> If coupled with a tandem cell,<sup>2, 3</sup> the only inputs are water and sunlight. This process offers an appealing prospect to harvest solar energy and store it in chemical form. The whole process involves only the absolutely, environmentally benign reactions without delivering any polluted by-products and the free, unlimited supply of solar energy and water. Thus, after the first demonstration, abundant materials have been investigated as the photoelectrode for this process including TiO2,<sup>4, 5</sup> ZnO,<sup>6, 7</sup> Fe<sub>2</sub>O3.<sup>8, 9</sup> Although these pioneering researches on this topic, the reported water splitting efficiency still remains far away from being viable for practical applications.<sup>10, 11</sup> It is believed that developing effective nanostructured electrode materials would address this issue from the aspects of wide-range light absorption, reduction of charge transfer kinetic limitation, and increase of the thermodynamic driving force via quantum size effect.<sup>12</sup>

CdS is considered to be a promising material used in the field of solar energy storage.<sup>13-15</sup> Its valence and conduction band positions are suitably aligned with water decomposition

potentials, thermodynamically favorable for both water oxidation and reduction.<sup>16</sup> During the past decades, much attention has been devoted into the synthesis of CdS nanomaterials. Their application in photocatalysis splitting of water was also demonstrated.<sup>17-26</sup> It was found that nanostructured CdS show good H<sub>2</sub> production capacity compared to that of bulk CdS.<sup>21, 22</sup> The crystal phase, size, and morphology of the CdS nanocrystals have great effects on the photocatalytic H<sub>2</sub>-production activity.<sup>23-25</sup> Recently, Liu *et al* has demonstrated that CdS nanocross with 64 % of hexagonal phase exhibited a much higher H<sub>2</sub>-production rate than CdS nanoparticles.<sup>25</sup> Zhang *et al* shows that CdS nanosheets are also efficient visible-light-driven water splitting photocatalysts for hydrogen evolution.<sup>27</sup>

High quality CdS nanocrystals with uniform size and shape are usually prepared in non-aqueous system.<sup>28-30</sup> The classical route is the so-called "hot-injection" method, in which sulfur dissolved in the long-chain organic amine/phosphine is injected into the solution of Cd salts at high temperature, inducing the formation of CdS nanomaterials.<sup>31, 32</sup> The obtained CdS products by this method often have high quality with excellent size monodispersity and shape uniformity.<sup>33</sup> The long-chain organic amine/phosphine is usually selected because they

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can activate element sulfur. They not only gives excellent protection for the CdS nanocrystals from oxidation, aggregation, but also endows them a good dispersion in non-polar solvent such as CHCl<sub>3</sub>, hexane. However, when used in aqueous system, the obtained hydrophobic CdS materials capped with longchain amine/phosphine shows the disadvantages. The longchain organic molecules prevent their contact with water or other reactive molecules in aqueous solution. Thus, they cannot be easily dispersed in aqueous solution system. In addition, the long chain molecules would also inhibit the carriers transport during photo-electrical process.

Short-chain small molecular amines can dissolve well in water and have been employed as solvent for the synthesis of CdS. For example, with thiourea as sulfur source, Yang *et al.* reported a solvothermal synthesis of CdS nanorods using *n*-butylamine as solvent.<sup>34</sup> Jang *et al.* also synthesized one-dimensional CdS nanowires with thiourea in ethylenediamine solvent.<sup>35</sup> In these cases, active thiourea was used as sulfur source; and thus higher reaction rates were possibly involved in the generation of CdS.

Herein, we developed a small molecular amine mediated synthesis of hydrophilic CdS nanorods with element sulfur as sulfur source, in which *n*-butylamine is selected as the activation agent for element sulfur. The activation process of sulfur by the amine was proposed. Possibly because the activation process mediates the reaction kinetics, the obtained hydrophilic CdS products have good size monodispersity and shape uniformity. It was found that the ratio of sulfur to CdCl<sub>2</sub> plays a key role for the formation of nanorods. The PEC water splitting properties of the synthesized CdS were then tested. Among our tested CdS products, the best PEC property is obtained with CdS nanorods.

#### **Experimental Section**

#### Materials

The chemical reagents employed in this research are A. R. grade and were purchased from Sinopharm Chemical Reagent Co. China. Tri-n-octylphosphine (TOP) with a purity of >98% and 1-octadecylene with a purity of >99% were purchased from Alfa Aesar. They were used without further purification. The used substrates were fluorine-doped SnO<sub>2</sub> (FTO) coated glass purchased from Wuhan lattice solar energy technology Co., LTD.

#### Synthesis of CdS products

In a typical procedure, 190 mg of S (6 mmol) was firstly dissolved in 4 mL of *n*-butylamine. Note that sulfur powder can be easily dissolved in *n*-butylamine forming a uniform brown solution (Fig. 1a). After that, 0.46 g of  $CdCl_2 \cdot 2.5H_2O$  (2 mmol) was added in. With strongly stirring, the mixed solution was transferred into a 30 mL of Teflon cup and heated in a sealed autoclave at 100 °C for 12 h. After cooling to room temperature, the precipitate was washed with ethanol and water for several times and dried under vacuum at 45 °C for further analysis. The

sample was denoted as CdS-190. With other conditions constant, a series of contrast samples were prepared by changing the used sulfur amount to be 150 mg (4.7 mmol), 130 mg (4 mmol), 60 mg (1.9 mmol), and 16 mg (0.05 mmol). The samples were denoted as CdS-150, CdS-130, CdS-60, CdS-16, respectively.

#### **Contrast experiments**

For comparison, hydrophobic CdS nanocrystals capped with long chain dodecylamine or tri-n-octylphosphine (TOP) were also prepared. With dodecylamine as solvent, dodecylamine capped CdS nanorods was obtained under conditions similar to that of CdS-190. For synthesis of TOP capped CdS, 190 mg of S was firstly dissolved in 3.5 mL of 1-octadecylene and 0.5 mL of TOP, in which 0.46 g of CdCl<sub>2</sub>·2.5H<sub>2</sub>O was added in. The mixed solution was transferred into a 30 mL of Teflon cup and heated in a sealed autoclave at 100 °C for 12 h. The obtained CdS precipitate was then washed with ethanol and hexane for several times and dried under vacuum at 45 °C for further test. Both of the two CdS products are hydrophobic owing to the long chain dodecylamine or TOP capped on them.

#### Characterizations

Powder X-ray diffraction (PXRD) patterns were recorded on an X-ray diffractometer (Bruker D8 Advance diffractometer) with Cu K $\alpha$  radiation. The scanning electron microscopy (SEM) observation was carried out on a Hitachi S-4800 field emission scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observation was performed by using a JEM-2100 (JEOL) microscope with an acceleration voltage of 200 kV. Optical diffuse reflectance spectra were measured at room temperature with a UV-2450 UV-vis spectrophotometer. BaSO<sub>4</sub> powder was used as a standard (100% reflectance).

#### Photoelectrochemical measurement

For PEC measurements, the obtained CdS products were coated onto FTO substrates forming thin films. A certain amount of the obtained CdS product was firstly dispersed in ethanol forming a paste, which was then carefully coated on the FTO substrate with an area of about  $1 \times 1$  cm<sup>2</sup>. After dried in vacuum at 45 °C for 30 min, a yellow thin film was formed on the substrate (Fig. 1b). Note no any additives were added in the fabrication of the CdS photoelectrodes.

The PEC tests were carried out in a conventional threeelectrode, single-compartment quartz cell filled with 0.5 M  $Na_2SO_4$  electrolyte. The working electrodes are CdS thin films. The platinum wire electrode and the Ag/AgCl electrode are used as counter electrode and reference electrode, respectively. The illumination source is a 300 W Xe lamp (PLS-SXE300 (UV), Perfect light Technology Co., Ltd. Beijing). The distance of illumination source and the CdS photoelectrode was fixed to be 20 cm. For testing the photoresponse behavior of light with different wavelength region, an optical filter was used. The PEC tests were performed on a CHI 760D electrochemical analyzer (ChenHua Instruments, Shanghai, China). The

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potential was swept from -0.7 to +1.0 V (vs. Ag/AgCl) with a sweep rate of 10 mV/s.



Fig. 1 (a) The solution of sulfur dissolved in *n*-butylamine. (b) The prepared CdS thin film photoelectrodes.

#### **Results and discussion**

#### Synthesis and characterization of CdS products

The CdS products were synthesized by an amine-mediated solvothermal reaction. The common cadmium salt,  $CdCl_2 \cdot 2.5H_2O$ , was selected as the cadmium source, while sulfur powder was used as sulfur source. The main difference from the previous report for CdS quantum dots by "hot-injection" route is that organic amine with shorter carbon chain, *n*-butylamine, is employed as the only involved solvent and mediator for the synthesis of CdS. Importantly, *n*-butylamine also plays an activation role for element sulfur. No other additive or surfactant was used in the synthesis.

The crystal phase of the synthesized sample was firstly determined by PXRD. Fig. 2 shows the PXRD pattern of the saffron yellow product obtained with sulfur dosage of 190 mg. All the diffraction peaks can be well indexed to the hexagonal phase CdS (a = b = 4.141 Å, c = 6.720 Å, JCPDS No. 41-1049). No other diffraction peaks were detected, suggesting the high purity. The strong peaks at 24.9, 26.6, and 28.2° are attributed to the (100), (002), and (101) crystal planes, respectively. Interestingly, the peak corresponding to the (002) crystal plane is relatively narrow and sharp when compared to other peaks



Fig. 2 PXRD pattern of the CdS-190 product obtained with sulfur dosage of 190 mg. The standard pattern with JCPDS No. 41-1049 is also shown for comparison.

such as (100), (101) peaks, which reveals the relatively bigger crystal size along the [002] direction.<sup>36</sup>

The morphology of the as-obtained CdS product was then observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The representative SEM images shown in Fig. 3 demonstrate that the product is composed of uniform rod-like structures. As shown by the statistical analysis, the CdS nanorods exhibit narrow size distribution with diameter of 12-18 nm and an average value of 14.7 nm (Fig. SI-1a, see Supplementary Information). The average length of the nanorods is about 130 nm. It seems that some of them show multi-pod branch-like structures. This structure feature makes the corresponding thin film have amounts of stacking pores. Fig. 3c shows the corresponding TEM image, which gives the same result of SEM observation. The HRTEM image (Fig. 3d) shows clear lattice fringes with a spacing of 0.350 nm, which can be indexed to the (100) plane of hexagonal CdS.



Fig. 3 (a, b) SEM, (c) TEM, (d) HRTEM images of the CdS-190 product.

It should be noted that the sulfur dosage highly influences the final morphology of CdS. Keeping other conditions constant, gradually decreasing the sulfur dosage, the morphology of CdS evolved correspondingly. If 130 mg of sulfur is used, shorter CdS nanorods with length of 22 nm and diameter of 9 nm are obtained (Fig. 4e, f, Fig. SI-1b, see Supplementary Information). The multipod-like structure is also observed, similar to that prepared with 190 mg of sulfur. The corresponding HRTEM image shows the growth of CdS nanorods is along the [001] direction (Fig. 4f). It should be noted that in the range of 130-190 mg of sulfur dosage, the length of CdS nanorods can be tuned, respectively. More sulfur is used, longer nanorods are obtained. For example, with 150 mg of sulfur (sample CdS-150), CdS nanorods with length of 40 nm are obtained (Fig. SI-2, see Supplementary Information).

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Fig. 4 TEM and HRTEM images of the CdS products obtained with different amounts of sulfur powder. (a, b) CdS-16, (c, d) CdS-60, (e, f) CdS-130.

Further decreasing the used sulfur to 60 mg, particle-like CdS product with diameter of 15 nm is obtained (Fig. 4c, d). The detected lattice spacing of 0.317 nm can be attributed to the (101) plane of hexagonal CdS. While, if only 30 mg or 16 mg of sulfur is used in the reaction, the final product is nanosheetlike units (Fig. 4a, b). From the curled part, the thickness of the nanosheets was determined to be about 3 nm. The layer-like stacking of the nanosheets is also observed (as noted in Fig. 4a). The corresponding PXRD spectrum shows complex pattern, but no agreement with the standard pattern of CdS (Fig. 5c). This is in contrast to those obtained with sulfur dosage higher than 60 mg, which demonstrate PXRD patterns corresponding to hexagonal CdS (Fig. 5). According to the literature report, the complex PXRD pattern of the nanosheets may be indexed into inorganic-organic hybrid materials, probably, CdS(butylamine)<sub>x</sub>.<sup>37</sup> This contrast experiments reveal that the final shape of CdS is sulfur-amount dependent. CdS nanorods were formed with relatively high ratio of S to Cd.

In previous report, P. Ramamurthy *et al* prepared CdS nanocrystals with the reaction of  $Cd(TOA)_2$  and  $Na_2S$ .<sup>38</sup> In that case,  $Cd(TOA)_2$  is in the organic phase, while  $Na_2S$  is in the aqueous phase. It was found that the shape of obtained CdS can be manipulated by the adding rate of  $Na_2S$  aqueous solution. CdS nanorods were formed with quick adding rate. In fact, quick adding of sulfur precursor endows a relatively higher

ratio of sulfur to Cd species in the reaction stage. Thus, our result is actually consistent with these report cases.<sup>38-40</sup>

Owing to only small molecular amine used in the reaction system, the obtained CdS products can be easily dispersed in polar solvent such as water, ethanol, and so on. It was reported that the dispersion of polyethyleneimine-capped CdS nanowires is pH-dependent.<sup>41</sup> We then tested absorption spectrum of CdS-190 dispersion with different pH values to investigate the influence of pH value on their dispersion (Fig. SI-3, see Supplementary Information). As expected, the pH value of the aqueous solution indeed affects the dispersion. In basic or neutral solution, a higher absorption was observed, suggesting that the CdS nanocrystals can be well dispersed, which is in contrast to the situation in acidic solution. This pH-dependent solubility behaviour is contrary to that of polyethyleneiminecapped CdS nanowires.41 Polyethyleneimine has branched structure with multiple -NH2 group in the chain. Besides the -NH<sub>2</sub> group bonding to the surface of CdS, many noncoordinated -NH<sub>2</sub> groups exist on them. With lower pH values, the non-coordinated -NH<sub>2</sub> groups can be ionized, forming -NH3<sup>+</sup> group and inducing their well dispersion in acidic solution. In our case, small molecular monoamine was used. The only -NH<sub>2</sub> group bonds to CdS surface. In acidic solution,  $H^+$  ions would also ionize -NH<sub>2</sub> group. While this would weaken the bonding of -NH<sub>2</sub> group to CdS surface, inducing the easy aggregation of CdS product. Thus, they have relatively good dispersion in basic or neutral solution.



**Fig. 5** PXRD patterns of the CdS products obtained with sulfur dosage of (a) CdS-130 mg, (b) CdS-60 mg, (c) CdS-16 mg. The standard pattern with JCPDS No. 41-1049 is also shown for comparison.

#### **Growth Mechanism**

For the synthesis of high-quality sulfide colloidal nanocrystals, sulfur powder is often selected as sulfur source owing to the low-cost. It is believed that there is an activation process for element sulfur before its reaction with metal species. Usually, phosphine-based compounds and octadecene were used as activation agents for sulfur.<sup>42</sup> In our case, no octadecene or phosphine-based compounds but only small molecular butylamine is provided in the reaction system. Thus, it is proposed that *n*-butylamine activates the element sulfur.

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Previously, Ozin's group has reported a detailed account of NMR analysis of the heated mixture of organic amine and element sulfur.<sup>43</sup> This study shows that element sulfur easily reacts with organic amine.

For studying the possible reaction process, the mixture of butylamine and sulfur were heated in an open system. It was found sulfur powder is easily dissolved in butylamine forming a brown solution (Fig. 1a). The color becomes deep with heating. The generated gas was detected with Pb(Ac)<sub>2</sub> testing paper, which was placed above the mixture. It turns black suggesting the formation of black PbS. The generated gas was also tested with CuSO<sub>4</sub> and Cd(NO<sub>3</sub>)<sub>2</sub>, separately. The former becomes black while the latter becomes yellow, implying the formation of black CuS and yellow CdS. All these suggest the formation of H<sub>2</sub>S gas after the reaction between butylamine and sulfur.

According to the previous reports<sup>44-45</sup> and the observed experiment phenomena, the possible reaction is proposed as follows in Scheme 1a. Noted that sulfur exists as S<sub>8</sub> rings in its standard state. The nucleophilic attack by nitrogen atom from the amine on S<sub>8</sub> causes the ring to open, forming active open chain polysulfide ions in the presence form of <sup>n</sup>-BuNH<sub>3</sub><sup>+</sup> -S<sub>8</sub> NH-<sup>n</sup>Bu. The open polysulfide chain shows weak S-S bonds<sup>43</sup> and will react with excess butylamine with the formation of thiobutylamide. Excess butylamine molecules are also expected to attack thiobutylamide. During the two processes, H<sub>2</sub>S is delivered, which is the active sulfur species, reacting with cadmium salt forming CdS. The corresponding side product would be butylammonium chloride. It seems that the sulfur activation process is an abrupt process, which plays a similar role as the rapid "hot-injection" and thus is responsible for the formation of nanorods with relatively higher uniformity and narrow size distribution.

During the reaction of active sulfur species and cadmium compounds, the relative ratio of them plays critical role for the final morphology. For hexagonal phase CdS, the alternate stacking of S<sup>2-</sup> anions or Cd<sup>2+</sup> cations along its [001] direction makes a strong polar (namely, polar {001} lattice planes), which is believed to be the growth driving force for the onedimensional nanostructure.44-46 With higher concentration of sulfur species in the reaction system (that is, more sulfur is used) the bonding of sulfur species to cadmium site on the (001) planes will induce the quick growth of CdS along this direction forming nanorods. Thus one-dimensional CdS is obtained with higher sulfur concentration. In a certain range, more sulfur is used; CdS nanorods with higher aspect ratio are obtained (Fig. 3, 4e, f, Fig. SI-2, see Supplementary Information). In contrast, when sulfur is relatively deficient in the reaction system, along the [001] direction, most terminated {001} planes would be Cd planes. This induces the enrichment of surfactant molecules (in our case, n-butylamine) on them through its bonding to cadmium sites with nitrogen atoms. Surfactants with high concentration or strong binding action will strongly impede the growth along the [001] direction, and thus giving sheet-like or particle-like nano-units. The large amount of amines on the CdS nanosheets will induce the stacking of them through weak interaction between the alkyls chain, forming inorganic-organic

hybrid materials,  $CdS(butylamine)_x$  (Figure 4a, b). With middle sulfur concentration, the growth rate along different directions would be similar, thus giving nearly spherical particles (Fig. 4c, d).



Scheme 1. (a) The possible activation process of element sulfur. (b) The crystal structure of hexagonal CdS.

In our study, elemental sulfur was used as sulfur source. This is different from that of the reported case for CdS synthesis, in which active sulfur source, thiourea, is used; and CdS nanorods can form with equal amount of sulfur and cadmium.<sup>34</sup> For our element sulfur system, an activation process is made by butylamine before its reaction with cadmium source forming CdS. For active thiourea, no activation process is need. The different sulfur source causes the different growth kinetic behaviour of CdS. In our sulfur-alkylamine solution, elemental sulfur was transformed into the above listed sulfur-containing species. It is believed that only low percent of them react with cadmium salt forming CdS. After reaction, the excess S exists in the sulfur-containing species.

#### **Optical properties of CdS products**

The optical properties of the synthesized CdS products were characterized by UV-vis diffuse reflectance spectra. As shown in Fig. 6a, the UV-vis diffuse reflectance spectra of as-prepared CdS nanorods show obvious absorption edge at 540 nm, which is red-shifted compared to that of CdS nanoparticles. The red-shift of absorption edge will increase its absorption for solar energy, thus would show better photo-electrical related performances. The absorption edge for CdS nanoparticles or CdS(butylamine)<sub>x</sub> locates at about 470 nm. The slight blue-shift of CdS nanoparticles or CdS(butylamine)<sub>x</sub> to short wavelength

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compared with bulk CdS may be attributed to the quantum confinement effect originating from its smaller size.<sup>41</sup>



Fig. 6 Optical properties of the prepared CdS-based products. (a) UV-vis diffuse-reflectance spectra, (b) the corresponding plots of  $(\alpha h v)^2 vs. h v.$ 

From optical absorption experiments, the band gap energy can be estimated by the following formula:  $(\alpha h v)^n = B (hv - E_a)$ , where,  $\alpha$  is the absorption coefficient, hv is the photon energy, B is a constant characteristic of the material,  $E_g$  is the band gap energy, and *n* is either 1/2 for an indirect transition or 2 for a direct transition. CdS is a direct *n*-type semiconductor. Figure 6b shows the  $(\alpha hv)^2$ versus hv curves for the four CdS-based products. Extrapolation of the linear portion of the curve to  $\alpha = 0$  gives the optical band gap value of 2.33 eV for nanorod samples (CdS-190, CdS-130) and 2.65 eV for CdS nanoparticles (CdS-60) or CdS(butylamine)<sub>x</sub> products (CdS-16), indicating a slight band gap narrowing when the morphology changes from nanoparticles to nanorods. Both of the CdS nanorods have relatively bigger sizes. Thus, the obtained optical band gap values for nanorods are similar to that of bulk CdS (2.38-2.42 eV).47 This situation is also consistent with the reported case, in which several kinds of CdS nanorods show similar absorption edge position.35

#### PEC performance of the CdS-based thin films

To study the PEC properties of the CdS products, photoelectrodes were prepared by painting ethanol dispersions of the CdS products on FTO substrates. Due to the stacking of nanorods, the photoelectrode surface shows loose and porous structure (Fig. SI-4, see Supplementary Information). During the test, the side coated with CdS product faces toward the incident light. Fig. 7a shows a set of linear sweep voltammetry curves of bare FTO glass and CdS nanorod electrode in the dark and with simulated solar illumination (with  $\lambda > 200$  nm or  $\lambda > 420$  nm). The dark current density of CdS nanorod electrode is very small, on the order of  $10^{-5}$  to  $10^{-4}$  mA/cm<sup>2</sup>. The bare FTO substrate shows no photoresponse, but giving a weak peak at potential of 0 V (vs Ag/AgCl), which would originate from the redox reaction of SnO<sub>2</sub>. Upon illumination, the CdS nanorod electrode shows pronounced photocurrent, the current density is much higher than that in the dark. Under illumination of light with  $\lambda > 420$  nm, the current density is 5.6  $\mu$ A/cm<sup>2</sup> at potential of -0.2 V (*vs* Ag/AgCl). In contrast, the dark current density is 0.078  $\mu$ A/cm<sup>2</sup> at the same potential. Under illumination of light with  $\lambda > 200$  nm, the current density is 12.6  $\mu$ A/cm<sup>2</sup>. This indicates that both UV and visible light are responsible for the photoelectrical chemical response behavior.



Fig. 7 Current-voltage characteristics measured in Na<sub>2</sub>SO<sub>4</sub> electrolyte for (a) the CdS nanorod-based thin films (CdS-190, shown in Figure 3) under various light illumination or in the dark, and (b) all obtained CdS-based thin films under illumination of light > 200 nm.

From Fig. 7b, the electrodes fabricated from the CdS samples obtained with lower sulfur amount show lower photocurrent. That is, the nanorod samples show stronger photoresponse than the particle sample or CdS(butylamine)<sub>x</sub> products. The photocurrent from CdS nanorods with length of ~130 nm is comparable to the nanorods with length of ~20 nm or ~40 nm (Fig. SI-5, see Supplementary Information). Under light irradiation >200 nm, the photogenerated current density (12.6  $\mu$ A/cm<sup>2</sup>) of CdS nanorods at -0.2 V bias potential (*vs* Ag/AgCl) is 25 times of that obtained with CdS nanoparticles (CdS-60, 0.5  $\mu$ A/cm<sup>2</sup>).



**Fig. 8** (a) The current-voltage characteristics for the CdS thin films under chopped light illumination of  $\lambda > 200$  nm. (b) The band edge potential of CdS against the normal hydrogen electrode (NHE) at pH = 0 and vacuum potential.

For clearly demonstrating the photoresponse behavior, the linear sweep voltammetry curves under chopped irradiation were tested with illumination of  $\lambda > 200$  nm and shown in Fig. 8a. This measurement excludes the possibility of dark reactions occurring in the photoelectrode and provides further evidence for its high photoactivity. The current density is basically consistent with that of unchopped irradiation, indicating the photocurrent densities are stable without photoinduced charging effect. The chopped photocurrent changes with different samples further demonstrate the better PEC properties of CdS nanorod products, which is consistent with the above shown results. According to the water disposing potentials shown in Fig. 8b, the observed photocurrent could be ascribed to the water splitting. The water oxidation photocurrent begins at about -0.5 V versus Ag/AgCl, which is similar to CdSsensitized ZnO photoelectrode.<sup>50</sup> In addition, the characteristic transient current spikes (especially for CdS-130) resulting from the accumulation of photogenerated holes at the semiconductor liquid junction (due to the slow oxygen evolution reaction kinetics near the onset potential) are visible, suggesting that recombination in the bulk (or at grain boundaries) no longer limits charge carrier transport.<sup>51</sup> While only very weak spikes were observed for CdS-190, the slight different photoelectrical chemical behaviour between CdS-130 and CdS-190 would be caused by factors such as the different size, crystallinity.

For comparison, hydrophobic CdS products capped with dodecylamine or TOP were also fabricated as photoelectrodes (Fig. SI-6, see Supplementary Information). The dodecylaminecapped CdS shows similar rod-like structure. The TOP capped CdS is composed of irregular sub-microspheres. Both of the tested hydrophobic CdS products show much lower current density compared to the hydrophilic CdS. The long-chain amine/phosphine molecular would inhibit the carriers transport during the photoelectrochemical process, thus causing lower current density. This result suggests that hydrophilic CdS products are preferred for photoelectrode application.

The better PEC performances of CdS nanorod samples would relate to the following reasons. (1) They have wider range light absorption. As shown in Fig. 6, the CdS nanorods have absorption edge at 540 nm, suggesting the wide absorption for light with wavelength < 540 nm, which is contrast to that of < 470 nm for CdS nanoparticles or CdS(butylamine), products. This is further identified by the test with monochrome light irradiation. The monochrome lights with wavelengths of 500, 600, and 700 nm were used to illuminate the CdS thin film for photoresponse. The CdS nanorod sample shows obvious photoresponse to 500 nm monochrome light irradiation, but almost no response to the light of 600 or 700 nm (Fig. SI-7a, see Supplementary Information). In contrast, the CdS particle product shows no response to all the three tested light (Fig. SI-7b, see Supplementary Information). These results correspond well to their light absorption, showing the absorption-dependent photoresponse. (2) The one-dimensional nanorods provide excellent charge transport channels for easy charge collection by the supporting substrate. (3) The rod-like structures, especially the multi-pod-like structures make the thin film be loose and be porous owing to the irregular stacking, which is favorable for the light harvesting through multiple reflections and scattering. In addition, the loose and porous structure is also advantageous for gas evolution.

#### Conclusions

Organic amine with short carbon chain was selected as the activation agent for element sulfur and as a mediator for the formation of hydrophilic CdS nanocrystals. Uniform CdS nanorods with good monodispersity were obtained through this route. The amount of the used sulfur powder highly influences the morphology of the final CdS products. With lower sulfur dosage, sheet-like CdS(butylamine)x or CdS particles are obtained, while with excess sulfur, uniform nanorods generate. The photoelectrode made from CdS nanorods exhibits efficient photoelectrochemical properties for water splitting. Both of UV and visible light are responsible for the electrochemical response. Under light irradiation of  $\lambda > 200$  nm, the photogenerated current density of CdS nanorods at -0.2 V bias potential (vs. Ag/AgCl) is 25 times of that obtained with CdS nanoparticles. The simple synthesis method and the good photoelectrochemical properties illustrate the hydrophilic CdS nanorods as a potential candidate for photoelectrochemical applications.

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#### Notes and references

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