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Photoelectrochemistry of Pure and Core/Sheath Nanowire Arrays of Cu_2S Directly Grown on Copper Electrodes

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Photoelectrochemistry (PEC) of straight and isolated Cu_2S nanowires arrayed on a copper foil is studied. A cathodic photocurrent is observed, which increases with the increasing negative bias of the film electrode, conforming to the p-type semiconducting nature of Cu_2S. PEC studies on the core/sheath nanowires of Cu_2S (Cu_2S nanowires coated with other nanoparticles such as CdS, polypyrrole, and Au) have revealed distinctly different characteristics. Cu_2S/CdS nanowires exhibit a slightly higher photocurrent response due to the charge transfer between the p-type Cu_2S core and n-type CdS sheath, whereas the photocurrent response obtained for Cu_2S/PPy nanowires is generally an order of magnitude smaller than that for pure Cu_2S nanowires under the same bias voltage. For Cu_2S/Au nanowires, however, Au nanoparticles can readily accept the photogenerated electrons from the conduction band of Cu_2S; this redirects the electron transfer pathway and results in the anodic photocurrent response. On the basis of these findings, different photocurrent generation mechanisms are proposed.

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The favorable material characteristics of Cu_2S makes it suitable for large-scale photovoltaic (PV) applications, particularly in combination with CdS or $Zn_xCd_{1-x}S$.[1] p-n Heterojunctions based on Cu_2S/CdS thin film solar cell show peculiarities, including the crossover of the I-V characteristic in the dark and under illumination, and the light bias effect.[1-3] Theoretical analyses have revealed that the Cu_2S/CdS and Cu_2S/ZnCdS thin film PV systems are capable of achieving practical conversion efficiencies of 11 and 14-15%, respectively.[1] A thin film solar cell based on a single-component $Cu_{1.8}S$ was developed by constructing nanoporous heterojunctions of $TiO_2/Cu_{1.8}S$, showing an open-circuit voltage (OCV) of about 200 mV and a short-circuit current of 30 $\mu A/cm^2$ at 2.8 kW/m^2.[4] For dye-sensitized solid-state PV cells based on TiO_2/dye/CuI thin films, a power conversion efficiency of 2.8% was recently reported.[5] On the other hand, photoelectrochemical (PEC) cells based on nanocrystalline materials have emerged in recent years as a new generation of PV devices and offer the prospect of enhanced efficiency and cheap fabrication together with other attractive features such as flexibility.[6-9] PEC properties of nanoparticles or quantum dots of SnO_2,[10] TiO_2,[11-12] ZnO,[13] $CuO(Cu_2O)$,[14] CdS,[15-17] ZnS,[18] CdSe[19] have been reported.

Nanowires and nanotubes may become important building blocks for nanoscale optoelectronics because they can function as miniaturized devices as well as electrical interconnects.[20] Nanodevices such as field-effect transistors,[21] single-electron transistors,[22] metal-semiconductor juctions,[23] and interwire crossed junctions[24] have been demonstrated. However, less attention has been paid to the PEC properties of nanowires despite the exciting prospects. PEC of oriented nanorod thin films of hematite (α-Fe_2O_3) including dye sensitization was reported by Hagfeldt *et al.* revealing the considerable enhancement of the photoconversion efficiency compared to that based on the hematite nanoparticles.[25] A more recent study based on the photoresponses toward the water-splitting reaction of the thin film and nanowire electrodes of n-type TiO_2 indicated that a more than twofold increase in maximum photoconversion efficiency was observed when a single-layer thin film of n-TiO_2 was replaced by nanowires.[26]

Here, we report the PEC study of straight and isolated Cu_2S nanowires arrayed on copper foils, prepared by using a gas-solid reaction under ambient conditions. By using a nanostructured thin film based on perpendicularly oriented Cu_2S nanowires, one hopes to reduce the recombination losses at grain boundaries between the nanoparticles and thus enhance the power conversion efficiency.[25,26] Several core/sheath nanowire systems have also been studied and compared. By examining the effects of the nanowire coating, bias voltage, and electrolyte solution, we have proposed plausible photocurrent generation mechanisms, which are also presented.

Experimental

Materials.—The preparation of straight and isolated Cu_2S nanowires arrayed on copper foils by using a gas-solid reaction under ambient conditions was reported previously.[27] Briefly, cleaned copper foils (0.5×0.5 cm) were placed in a homemade reactor. The reactor was first pumped to vacuum, then a gas flow was directed to the reactor which consists of a mixture of oxygen (99.8%) and hydrogen sulfide (99.8%, Aldrich) at a given molar ratio and the total pressure in the reactor was kept at ~1.05-1.08 atm. After 10 h reaction, the copper surface became black and fluffy, indicating the formation of dense Cu_2S nanowire arrays. Nanoparticles (NP) were coated onto the Cu_2S nanowires to form Cu_2S/NP core/sheath nanowires (NP = CdS,[b] polypyrrole (PPy),[c,28] Au[d,29]). KCl (RDH AG), Na_2SO_3 (sodium sulfite, RDH AG), and $Na_2C_2H_4O_6\cdot 2H_2O$ (sodium tartrate dibasic dihydrate, Fisher) were used as received.

PEC measurements.—The PEC measurements were carried out with a model 600 electrochemical analyzer from CH Instruments, Inc., U.S. A 500 W mercury-xenon lamp (Hamamatsu, Japan) was used as the light source. The beam intensity of the light was calibrated with a power meter (Newport Co., U.S.), but no corrections were made for the reflections. The collimated white light beam passed through an FS-3 filter (od = 0.05, Newport Co., U.S.), which was used to eliminate light with $\lambda < 330$ nm. The irradiation passed through a homemade water filter before entering the PEC cell to minimize thermal effects by removing IR lights. The electrochemical cell was under a flowing nitrogen atmosphere (but without bubbling) to eliminate the influence of oxygen. Before measurements, the electrolyte solution was bubbled with N_2 (purity $> 99.9\%$) for ~30 min. A three-electrode configuration was used for the quartz cell. The Cu_2S (Cu_2S/NP) nanowires on Cu foil were used as the working electrode. Typically, The thickness and length of the Cu_2S nanowires are 60-100 nm and several micrometers, respectively, and the outer sheath layers are around 20-50 nm thick for the core/sheath nanowires, as described above and else-

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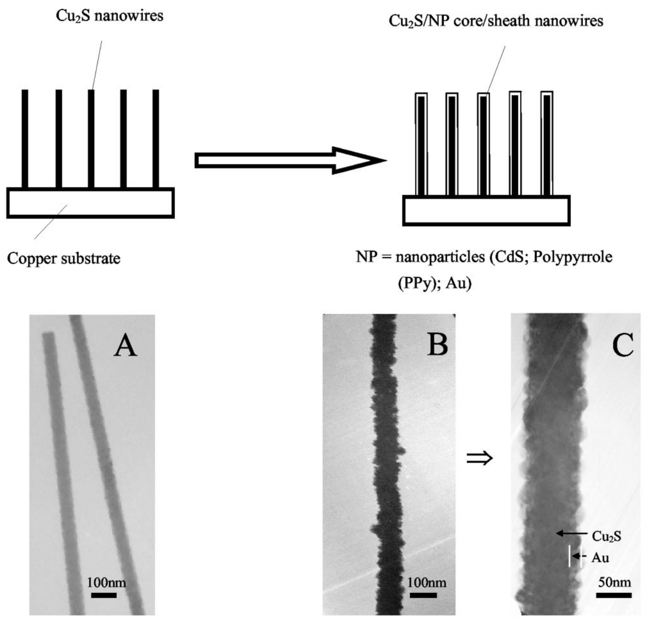

Figure 1. Top: schematic illustration showing the preparation of the Cu$_2$S/NP core/sheath nanowires. (A) Representative TEM image of Cu$_2$S nanowires; (B) TEM image of a Cu$_2$S/Au core/sheath nanowire; (C) magnified TEM image of a Cu$_2$S/Au core/sheath nanowire.

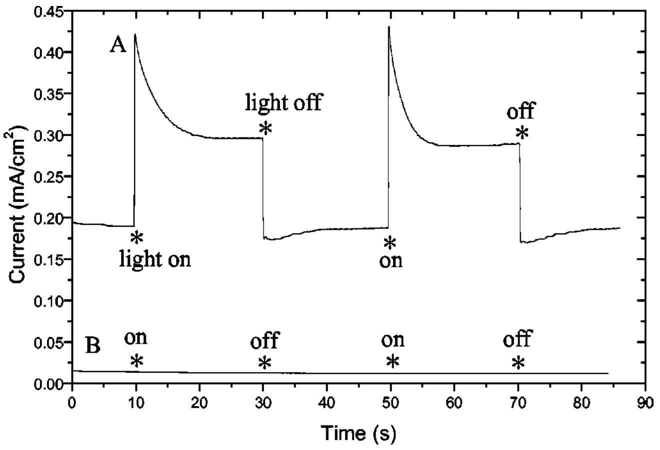

Figure 2. Representative photocurrent traces *vs.* time obtained from a Cu$_2$S nanowire film on Cu electrode (A) and pure Cu foil (B). [−0.50 V bias voltage; 0.1 M KCl electrolyte solution (pH 7); light intensity = 38.0 mW cm^{-2}]. The asterisks indicate the light on-off cycles.

where.[27-29,b,c,d] The counter electrode was a Pt wire, and the reference electrode was Ag/AgCl. The electrolytes were aqueous solutions of KCl (pH 6.5), Na_2SO_3 (pH 9), and $Na_2C_2H_4O_6 \cdot 2H_2O$ (sodium tartrate dibasic dehydrate, pH 7) with concentrations of 0.1, 1.0, and 0.5 mol dm^{-3} (M), respectively. Due to the opaqueness of the substrate (Cu foil), the nanowire working electrode was always illuminated through the electrolyte/electrode interface (EE).[30] More than six nanowire samples were measured under each experimental condition to ensure the reproducibility of the photocurrent data.

Results and Discussion

Nanowire structures.—Figure 1 illustrates the typical transmission electron microscopy (TEM) images of Cu$_2$S and Cu$_2$S/NP core/sheath nanowires (here NP = Au is shown as an example). The latter was converted from the former as shown in the figure. It has been established that the straight and isolated Cu$_2$S nanowires are uniformly arrayed on copper foils,[27-29,b,c,d] we expect that this facilitates the efficient charge carrier transport among the nanowires with the abated charge recombination losses in the film. Furthermore, by uniformly coating of NP as the outer sheaths, charge transfer is expected to occur between the core of Cu$_2$S and the sheath of NP, which may subsequently tune the PEC performance of the nanowires.

Photoelectric response of Cu$_2$S nanowires on Cu electrodes.—Shown in Fig. 2 is a typical photocurrent response curve for Cu$_2$S nanowires (A) on Cu electrode at a bias voltage of −0.50 V and the white light beam irradiation intensity of 38.0 mW cm^{-2} and that for pure Cu substrate (B) as a reference.[e] Clearly, the observed cathodic photocurrent response, which is absent for the pure Cu substrate, is from the photoactive Cu$_2$S nanowires. Under the relatively low irradiation intensity condition we used, the net steady-state cathodic photocurrent was calculated to be ~0.11 mA/cm^2 with little attenuation for the two successive cycles (curve A). Although the PEC data for Cu$_2$S nanoparticles is not available presently, this photocurrent response is estimated to be comparable to those of TiO$_2$,[11] CdS nanoparticles,[15-17] and TiO$_2$/Cu$_{1.8}$S heterojunctions[4] by considering the different irradiation conditions. Such a high photocurrent response is understandable, because the uniformly arrayed nanowire nature of Cu$_2$S, as demonstrated elsewhere,[27-29,b,c,d] may facilitate the efficient charge-carrier transport among the nanowires with the abated charge recombination losses in the film.[25,26] However, the dark current due mainly to electrochemical reactions prior to the light illumination has the same magnitude as the photocurrent in this case. First, this is because the Cu substrate is actually electroactive in an aqueous solution [*e.g.*, $2H_2O + Cu \rightarrow H_2\uparrow + 2OH^- + Cu^{2+} \rightarrow H_2\uparrow + Cu(OH)_2\downarrow$] according to the cyclic voltammetry (CV) analysis (not shown). This can also be confirmed by noticing that the dark current of the pure Cu foil (curve B) is much higher than that with other inert substrates such as indium tin oxide (ITO) which was used in our other work.[30] Moreover, the dark current for the Cu$_2$S nanowire film (see curve A) appears to be much higher than that of pure Cu electrode, suggesting the partial reduction of Cu$_2$S under the dark condition. Because the absorption spectrum of Cu$_2$S nanowires has not been determined yet due to the opaqueness of Cu substrate, the incident photon-to-current conversion efficiency (IPCE) could not be calculated at

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[b] The pretreated Cu$_2$S nanowires were fixed on a glass capillary and immersed into 40 mL CdCl$_2$ aqueous solution with a concentration of 1×10^{-2} M. After 6 h, 10 mL hydrogen sulfide gas was injected into the solution slowly using a syringe. After coating for 2 h, the samples were collected and washed three times with deionized water and dried in air.

[c] 0.1 mL pyrrole was first dissolved in 40 mL chloroform. Then the Cu$_2$S nanowire arrays were immersed in the solution and stirred for 2 h. Afterward, the Cu$_2$S nanowires was raised and positioned right on the surface of the chloroform solution without magnetic stirring. 20 mL of a $(NH_4)_2S_2O_8$ aqueous solution (0.1 M) was then added slowly to the chloroform solution. A thin white film was formed at the interface within half an hour, which turned to gray/black within another half an hour. By then the film nearly covered the whole interface. The film became increasingly black with increasing polymerization time.[28]

[d] First the Au-coating solution was prepared by dissolving 0.395 g $HAuCl_4 \cdot 3H_2O$ in 10 mL deionzed water. The solution was then diluted to different concentrations and an appropriate amount of a NaOH solution (1 M) was added to adjust the pH value of the solution. The pretreated Cu$_2$S nanowires were fixed on a glass capillary and immersed into the coating solution. After coating for 1 h, the nanowires were collected and washed three times with deionized water following with absolute alcohol.[29]

[e] Prior to the photoelectrochemical measurement, the pure Cu foil was first treated by 6.0 M HCl for 10 min to remove the oxide layer, and then cleaned for ~5 min in an ultrasonic bath of absolute ethanol.

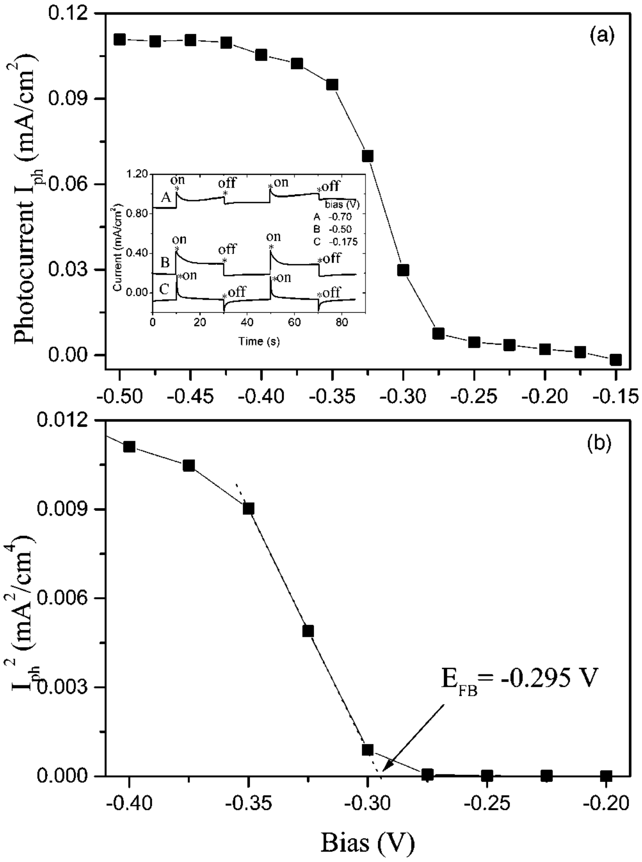

Figure 3. (a) Photocurrent (I_{ph}) as a function of the bias voltage for a Cu_2S nanowire film on Cu electrode (0.1 M KCl electrolyte solution (pH 7); light intensity = 38.0 mW cm^{-2}. Inset: representative photocurrent traces under different bias voltage. (b) I_{ph}^2 as a function of the bias voltage derived from a.

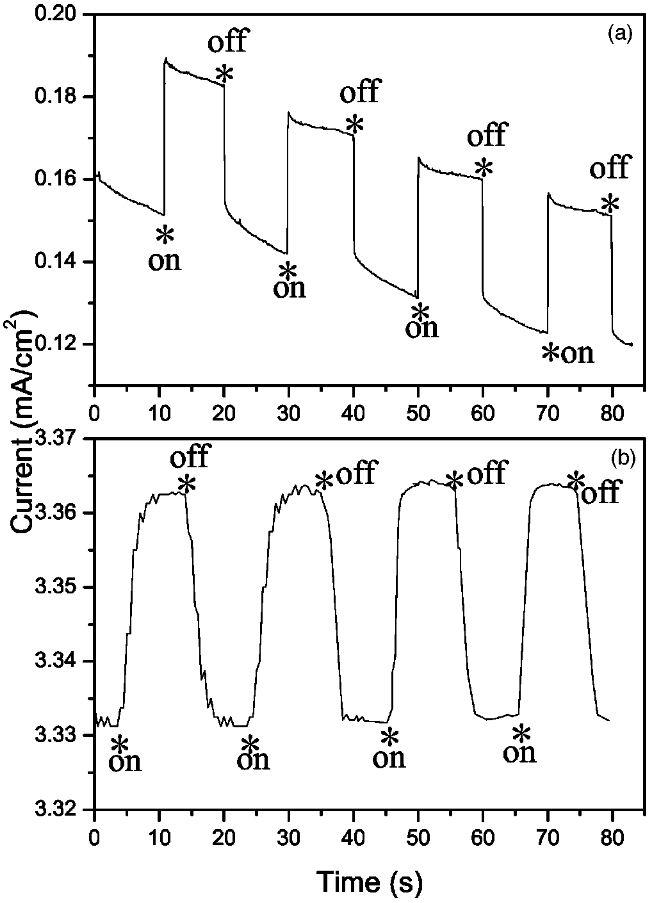

Figure 4. Representative photocurrent trace *vs.* time obtained with a Cu_2S nanowire film on Cu electrode in different electrolyte solutions of Na_2SO_3 (1.0 M; pH 12) (a) and $Na_2C_2H_4O_6$ (0.5 M; pH 14) (b). (−0.50 V bias voltage; light intensity = 38.0 mW cm^{-2}). The arrows indicate the light on-off cycles.

present. Nevertheless, the present study demonstrates the potential use of Cu_2S nanowires for facilitating the photoelectric conversion.

An interesting feature of the observed cathodic photocurrent trace shown as A of Fig. 2 is the photocurrent overshooting upon light illumination. This becomes more evident when the bias voltages are more positive (see also the inset of Fig. 3). One would expect the overshooting to be suppressed completely by applying further higher negative bias. However, due to the higher dark current under the very high negative one, we are unable to detect photocurrents with bias more negative than −0.70 V. As reported by Hickey *et al.* based on the PEC studies of CdS nanoparticle modified tin oxide electrodes in an aqueous 1.0 M Na_2SO_3 electrolyte,[16] a similar phenomena was observed, in which an anodic photocurrent transient was obtained with different shapes under different applied potentials. This was explained by the back electron transfer process competing with hole scavenging by the solution species at relatively negative potentials.[16] Bakkers *et al.* also reported the photocurrent transients of different shapes obtained in an aqueous 1.0 M KCl electrolyte.[17] We believe that a similar photocurrent generation mechanism is operative in the case of Cu_2S nanowires, which is discussed in detail below.

Effect of bias voltage.—The steady-state cathodic photocurrent (I_{ph}) as a function of bias voltage (V_{bias}) from −0.50 to −0.15 V (*vs.* Ag/AgCl) of the Cu_2S nanowires is shown in Fig. 3a. The cathodic photocurrent increases with the increasing negative bias of the nanowire film electrode, exhibiting a sharp increase for the portion from −0.275 to −0.35 V, then starts to level off at −0.40 V. The fact that the cathodic photocurrent increases with the increasing negative bias of the film electrode indicates the electrons flow from the Cu electrode through the nanowire film to the electrolyte, which is consistent with the p-type semiconducting nature of Cu_2S.[1] Furthermore, shown in Fig. 3b is the dependence of I_{ph}^2 on the bias voltage for the Cu_2S nanowire film electrode, from which the flatband potential (E_{FB}) is determined (−0.295 V) by extrapolating the linear region of the curve of I_{ph}^2-V to zero bias voltage.[30-32] Here E_{FB} is the upper limit of a blocking potential region for p-type semiconductor where the electrode response is dominated by the space-charge region layer.

Effect of electrolyte solution.—The effect of the electrolyte solution on the photocurrent response for the better known n-type CdS has been revealed based on the PEC studies of the nanoparticles or quantum dots.[15-17] For example, aqueous Na_2SO_3 solution could suppress the photodissolution of CdS,[15,33] while tartrate and triethanolamine are well-known stabilizing agents for CdS.[17,34] In both cases, the electrolyte plays the role as the hole scavenger.[15-17,33,34] An immediate interest thus arises to investigate whether such a modulation effect of the electrolyte solution would exist in the present Cu_2S nanowire system especially for the transient-state photocurrent overshooting stated above. We then replaced the electrolyte with sodium sulfite (Na_2SO_3, 1.0 M, pH 12)[f] and sodium tartrate ($Na_2C_2H_4O_6$, 0.5 M, pH 14)[f] for comparison. When Na_2SO_3 is used as the electrolyte solution (Fig. 4a), the photocurrent over-

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[f] The pH of Na_2SO_3 and $Na_2C_2H_4O_6$ electrolyte solutions were adjusted by using 1.0 M NaOH.

Table I. Characteristic of the PEC cells based on Cu_2S and Cu_2S/NP nanowire films on Cu electrodes under different conditions.

Nanowire film	Photocurrent I_{ph}[a] (mA/cm^2)	E_{FB}[d] (V *vs.* Ag/AgCl)	Correlation coefficient R[d,e]	Electrolyte solution
Cu_2S	0.11[b]	−0.295	0.981	0.1 M KCl (pH 7)
Cu_2S/CdS	0.14[b]	−0.258	0.993	0.1 M KCl (pH 7)
Cu_2S/PPy	0.0033[b]	−0.363	0.976	0.5 M $Na_2C_2H_4O_6$ (pH 14)
Cu_2S/Au	−0.091[c]	−0.278	0.962	0.5 M $Na_2C_2H_4O_6$ (pH 14)

[a] Under white light illumination (intensity = 38.0 mW cm^{-2}); bias voltage = −0.50 V. I_{ph} is the mean value based on three reproducible measurements.
[b] Cathodic photocurrent.
[c] Negative value denotes anodic photocurrent.
[d] Obtained by linear fit analysis which is based on the corresponding data points in the linear region.
[e] Parameter for linear fit analysis.

shooting observed for the case of KCl being the electrolyte generally appears to be diminished and a more stable cathodic photocurrent is obtained. However, the dark current of the same magnitudes as for the former case is unstable over time, indicating that some additional electrochemical reactions occur under dark condition. In this case, the cathodic photocurrent obtained under the same conditions is smaller than that when KCl was used (see Fig. 2). This result indicates that Na_2SO_3 is not as effective for promoting the photocurrent response of Cu_2S as for CdS although the transient-state photocurrent overshooting is suppressed. On the other hand, as shown in Fig. 4b, the use of sodium tartrate ($Na_2C_2H_4O_6$) as the electrolyte solution seems to diminish the transient-state photocurrent overshooting too, confirming its similar stabilizing effect on the photocurrent response of Cu_2S.[17,34] Nevertheless, the dark current is an order of magnitude higher, indicating again the increasing electrochemical reactions in the dark. The photocurrent response obtained in this case is comparable to the case when Na_2SO_3 was used but smaller than that when KCl was used. Moreover, the observed photocurrent response appears to be slower upon applying/removing light illumination in this case. Normally it takes 3-4 s for the photocurrent to reach the saturation value, suggesting that the electron transfer from the Cu electrode to the nanowires and then to the electrolyte is slower. These results reveal that the additions of Na_2SO_3 and $Na_2C_2H_4O_6$ diminish the cathodic photocurrent response instead, presumably because such hole scavengers could suppress the charge carrier separation process as hole is the major carrier for p-type Cu_2S.

Photoelectric response of core/sheath nanowires.—The success in preparing Cu_2S/NP (NP = CdS, PPy, Au) core/sheath nanowires[b-d,28,29] enables us to extend the PEC investigation to these nanocomposites with the possibility of charge transfer between the nanowire core and the outer nanoparticle sheath. Upon coating with the CdS sheath,[b] no difference on the shape of cathodic photocurrent trace under the same measurement condition (0.1 M KCl) was detected, while the photocurrent response appears to be slightly higher as evidenced by the I_{ph}-V curve shown in Fig. 5. This is understandable because the charge transfer between the p-type Cu_2S core and n-type CdS sheath is expected to occur in the Cu_2S/CdS p-n heterojunction nanowire, resulting in enhanced energy conversion efficiency.[1-3] Moreover, E_{FB} appears to shift positively by ~40 mV (see inset), confirming the charge transfer from Cu_2S to CdS (see Table I).[11,35] By optimizing the relative thickness of the core and sheath layers, a higher enhancement of the efficiency is expected.

A conducting polymer, polypyrrole (PPy), is also coated as the sheath layer onto the Cu_2S nanowire core.[28,c] PEC studies of PPy in both aqueous and nonaqueous solutions had revealed its p-type semiconductor properties.[36] Figure 6 demonstrates the I^2_{ph}-V curve for the Cu_2S/PPy core/sheath nanowire film measured in 0.5 M $Na_2C_2H_4O_6$ (pH 14) together with the cathodic photocurrent trace (inset). The measured photocurrent under the same bias voltage is generally an order of magnitude smaller than that for pure Cu_2S nanowire film (see Fig. 4b), presumably due to the misalignment of the band levels and/or the poor adhesion of the PPy sheath layer. Similar to the case for pure Cu_2S film, no obvious photocurrent overshooting is detected. However, the slow response for the photocurrent response for pure Cu_2S by using $Na_2C_2H_4O_6$ as electrolyte (see Fig. 4b) is not observed here (see inset), indicating that electron transfer is faster in this case. In addition, contrary to the case of Cu_2S/CdS nanowire, E_{FB} experiences a negative shift of ~70 mV (see Table I), indicating that the charge distribution between Cu_2S and PPy is quite different from the former case. In fact, the obtained E_{FB} is also more positive than that determined for pure PPy film (−0.474 V *vs.* Ag/AgCl),[36] suggesting the possible charge transfer from PPy to Cu_2S.

Recently, Kamat *et al.* showed that metal nanoparticles or islands deposited on semiconductor surfaces play an important role in catalyzing interfacial charge-transfer.[11,35,37] Particularly, PEC performance of nanostructured TiO_2 films was improved by adsorption of Au nanoparticles based on the charge distribution between photoexcited n-type TiO_2 and Au nanoparticles.[37] Moreover, PEC of Au nanoparticle arrays are also reported by Lahav *et al.*[38] It thus appears interesting to investigate whether the PEC properties of Cu_2S core could be modulated by the Au sheath for Cu_2S/Au nanowires.[29,d] Upon coating Au nanoparticle layer, as shown in Fig. 7a, the photocurrent becomes anodic instead of cathodic which is generally observed for the above cases, suggesting a significant change for the electron-transfer process in this case. The anodic photocurrent is stable and no obvious photocurrent overshooting is detected, indicating that the photocurrent originates from the electron transfer from the electrolyte to the Cu electrode through the nanowire film, which is mediated by Au nanoparticles layer. Furthermore, the photocurrent decreases with the decreasing negative bias voltage of the film electrode in the range of −0.65 to −0.20 V (Fig. 7b). This unusual dependence is quite surprising because it is the characteristic of a cathodic photocurrent instead and contradictory to the anodic nature of the photocurrent observed here. For example, the anodic photocurrent for n-type semiconductors such as TiO_2 and CdS normally exhibit an increase of anodic photocurrent upon decreasing negative bias voltage.[11,12,15-17,37] One plausible interpretation is that although the electron transfer from the Au to the Cu electrode becomes hindered upon applying more negative bias voltage, the competing back electron transfer from Au to the surface states (SS) of Cu_2S (cathodic) would be even more abated (see also Scheme Ib), and the net result then is the increase of the anodic photocurrent. If the bias voltage is too negative (say, <-0.65 V), however, the electron transfer from Au to the Cu electrode is much hindered and thus

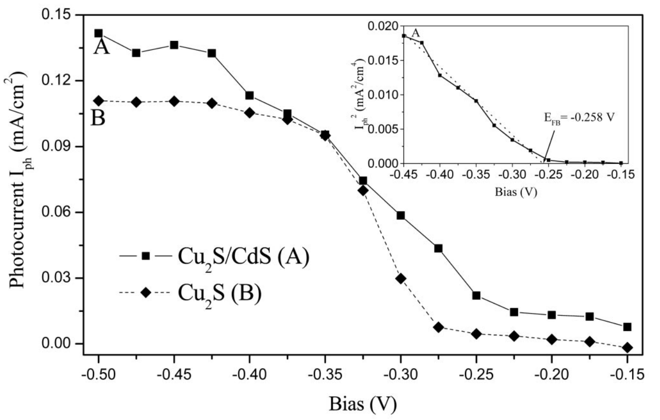


Figure 5. Photocurrent (I_{ph}) as a function of the bias voltage for a Cu_2S/CdS (A) and pure Cu_2S (B) nanowire films on Cu electrodes. (0.1 M KCl electrolyte solution (pH 7); light intensity = 38.0 mW cm^{-2}). Note that curve B is copied from Fig. 3a for comparison. Inset: I_{ph}^2 as a function of the bias voltage derived from curve A.

the anodic photocurrent begins to decrease. In fact, as determined from the I_{ph}^2-V curve (inset of Fig. 7b), the charge transfer from Cu_2S to Au is deduced by the positive shift of E_{FB} (see Table I).

Photocurrent generation mechanism.—The results presented above show that different photocurrent generation mechanisms may operate in the different nanowire films. According to the PEC theories, the photoexcitation of semiconductor upon light illumination generates charge carriers, which are separated at the electrode/electrolyte interface and then transferred between the surface of the electrode and the underlying substrate.[11,15-17,37] Proposed in Scheme I is the possible mechanism for the electron-transfer processes occurring for different nanowire films. As shown in Scheme Ia, photoexcitation of Cu_2S [$(Cu_2S)^*$] results in an electron in the conduction band (CB) transferring to the electron acceptor H_2O in the electrolyte. Subsequently, the Cu_2S molecule is replenished by an electron transferred from the Cu electrode, completing the external circuit with the generation of cathodic photocurrent. The plausible half reactions are proposed as follows

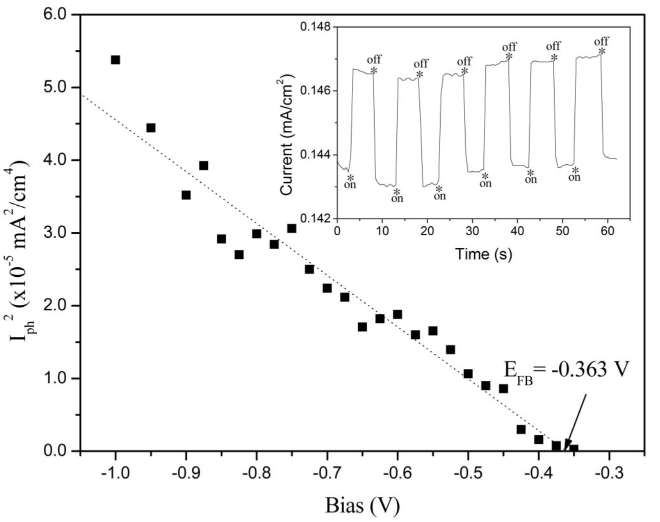


Figure 6. I_{ph}^2 as a function of the bias voltage for a Cu_2S/PPy nanowire films on Cu electrode. [0.5 M $Na_2C_2H_4O_6$ electrolyte solution (pH 14); light intensity = 38.0 mW cm^{-2}.] Inset: representative photocurrent traces obtained at −0.50 V bias voltage.

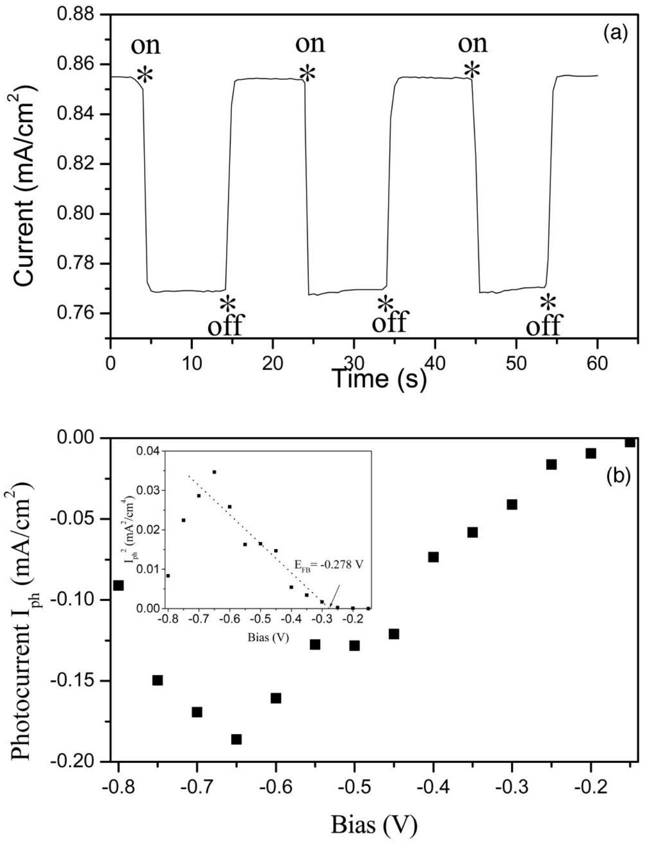


Figure 7. (a) Representative photocurrent traces for a Cu_2S/Au nanowire films on Cu electrode. [−0.50 V bias voltage; 0.5 M $Na_2C_2H_4O_6$ electrolyte solution (pH 14); light intensity = 38.0 mW cm^{-2}.] (b) Anodic photocurrent (I_{ph}) as a function of the bias voltage. [0.5 M $Na_2C_2H_4O_6$ electrolyte solution (pH 14); light intensity = 38.0 mW cm^{-2}]. Inset: I_{ph}^2 as a function of the bias voltage derived from b.

Oxidation of $(Cu_2S)^*$

$$Cu^{2+} + CuS + 2e \rightarrow Cu_2S \qquad [1]$$

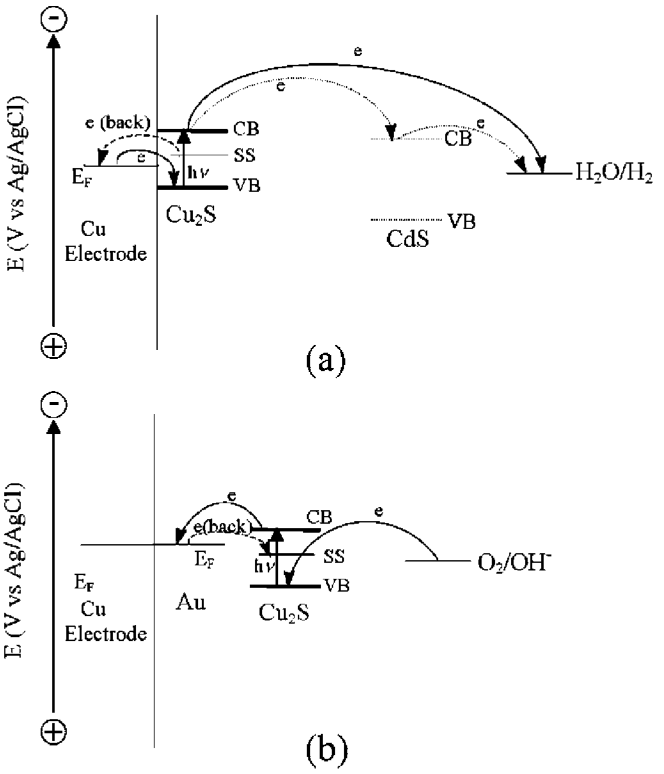
Reduction of H_2O

$$2H_2O + 2e \rightarrow H_2\uparrow + 2\ OH^- \qquad [2]$$

The overall reaction can then be described as

$$\begin{aligned}(Cu_2S)^* + 2H_2O &\rightarrow Cu^{2+} + CuS\uparrow + H_2\downarrow + 2\ OH^- \\ &\rightarrow Cu(OH)_2\uparrow + CuS\uparrow + H_2\downarrow \qquad [3]\end{aligned}$$

To account for the photocurrent overshooting observed in the case when KCl was used as the electrolyte, one expects to consider the existence of the SS, which had been proposed to interpret the anodic photocurrent transient for CdS nanoparticles.[15,16] In this case, the e(back) may compete with the electron transfer from CB of Cu_2S to the electrolyte, resulting in the occurrence of the transient photocurrent (see Scheme Ia).



Schematic representation of the electron transfer processes for the photocurrent generation. (a) Cu_2S (solid lines) or Cu_2S/CdS core/sheath (dotted lines) nanowires. The dashed line denotes e(back), which exists only when KCl is used as electrolyte. (b) Cu_2S/Au core/sheath nanowires. The dashed line denotes e(back), which competes with the anodic photocurrent generation process. (E_F: Fermi level; CB: conduction band; VB: valence band; SS: surface states.)

In the existence of the CdS sheath layer, because the bandgap of CdS is much larger than that of Cu_2S by neglecting the slight deviations at nanosize[2] and the thickness of CdS is smaller in the Cu_2S/CdS nanowires, it is expected that only Cu_2S is primarily excited. After photoexcitation of Cu_2S, the electron transfer process from Cu_2S to the electrolyte may be mediated via the conduction band of CdS owing to the characteristic of p-n heterojunction (the dotted lines in Scheme Ia), contributing to the enhanced photocurrent response for Cu_2S/CdS nanowires. On the other hand, for the Cu_2S/PPy nanowires, PPy may just play the role of an electron transport layer instead of mediator like CdS due to the possible reasons stated above.

After Au nanoparticles were deposited on the Cu_2S nanowires, however, such an interfacial charge-transfer process may experience a distinct change.[11,35,37] Here Au nanoparticles can readily accept the photogenerated electron from the CB of Cu_2S, and thus redirect the electron transfer pathway, resulting in the anodic photocurrent response. In fact, besides the coating on the top of the Cu_2S core layer, Au sheath layers may also coat the surfaces of the individual Cu_2S nanowire (see Fig. 1c), this would accomplish the electron transfer from Au to the Cu electrode (see Scheme Ib). The possible reactions involved could be stated as below

Oxidation of OH^-

$$O_2 + 2H_2O + 4e \rightarrow 4\ OH^- \qquad [4]$$

Reduction of $(Cu_2S)^*$

$$(Cu_2S)^* + 2e \rightarrow 2Cu\uparrow + S^{2-} \qquad [5]$$

$$2(Cu_2S)^* + 4\ OH^- \rightarrow 4Cu\uparrow + 2S^{2-} + O_2\downarrow + 2H_2O \qquad [6]$$

Conclusions

We have demonstrated the PEC of straight and isolated Cu_2S nanowires arrayed on copper foils. The observed cathodic photocurrent increases with the increasing negative bias of the film electrode, indicating that the electrons flow from the Cu electrode through the nanowire film to the electrolyte, which is consistent with the p-type semiconducting nature of Cu_2S. An interesting photocurrent overshooting upon light illumination on and off is detected when KCl was used as the electrolyte, which is believed to originate from back electron transfer competing with the electron transfer from CB of $(Cu_2S)^*$ to the electrolyte. This feature is not observed when Na_2SO_3 or $Na_2C_2H_4O_6$ are used as electrolytes. PEC studies on the core/sheath nanowires of Cu_2S/NP (NP = CdS, PPy, Au) indicate different charge-transfer pathways between the Cu_2S core and the nanoparticle sheath. Cu_2S/CdS nanowires exhibit a slightly higher photocurrent response due to charge transfer between the p-type Cu_2S core and n-type CdS sheath in the p-n heterojunction. The photocurrent response obtained for Cu_2S/PPy nanowires is generally an order of magnitude smaller than that for pure Cu_2S nanowires under the same bias voltage, presumably due to the misalignment of the energy bands and/or the poor adhesion of the PPy sheath layer. For Cu_2S/Au nanowires, the photocurrent response is completely reversed to anodic because Au nanoparticles can readily accept the photogenerated electrons from the CB of Cu_2S and thus redirect the electron transfer pathway. By transferring the nanowire films onto transparent conducting substrates such as tin oxide or indium tin oxide, the absorption spectrum of Cu_2S nanowires could be obtained and the IPCE may be determined. Further optimization of the present PEC cell may be accomplished by using different substrates, optimizing the relative thickness of the sheath layer and the Cu_2S core, and utilizing dye sensitization.

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