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Photocurrent Generation

CdS Nanoparticles/β-Cyclodextrin-Functionalized Electrodes for Enhanced Photoelectrochemistry[**]

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The integration of semiconducting nanoparticles (NPs) with electrodes currently attracts substantial research efforts because of the potential application of the functionalized electrodes in solar cell devices.[1] Various methods for the assembly of 2D and 3D arrays of semiconducting NPs on electrodes have been reported.[2] These include the covalent attachment of chemically modified NPs to surfaces,[3] layer-by-layer deposition of NPs through the use of molecular bridging units or electrostatic interactions,[4] and the aggregation of NPs through complementary supramolecular interactions such as interparticle hydrogen bonds.[5] Complementary biomolecular interactions, such as DNA hybridization, have also been used.[6] A further method to assemble semiconducting NPs on surfaces involves the electropolymerization of NPs capped with electroactive, polymerizable, functional groups.[7] The immobilization of semiconducting NPs on electrodes is a prerequisite for the construction of solar cell devices. The organization of nanoparticle architectures and the assembly of molecular hybrid structures of NPs on electrodes to control electron transfer at the electrode–solution interface are, however, the key elements that can enhance the performance of the resulting solar cells. The photoexcitation of the semiconducting NPs yields electron-hole pairs in both the conduction-band and the valence-band levels. The light-induced formation of the electron-hole pairs is the primary event in photoelectrochemical processes. The ejection of the conduction-band electrons to the electrode, or their transfer to an electron acceptor in solution, and the concomitant reductive scavenging of the valence-band holes, lead to the formation of anodic or cathodic photocurrents, respectively. The efficiency of the conversion of light to electrical energy is, however, limited by the competitive, destructive, electron-hole recombination process. Charge separation of the electron-hole pairs is thus essential for the enhancement of the photocurrent yields. Various methods to facilitate charge separation, and to stabilize the electron-hole pairs against recombination processes, have been developed. These include the construction of NP–NP,[8] NP–carbon nanotube hybrid structures,[9] or the generation of electron relay/NP conjugated systems.[10] For example, charge separation was induced in hybrid semiconducting NP–C_{60} systems by transferring the conduction-band electrons to the relay sites.[11] Also, charge separation proceeded in semiconducting composites, such as CdSe/TiO_2,[12] CdS/SnO_2,[13] or core-shell NPs,[14] by interparticle charge transport. Also, the coupling of semiconducting NPs to electrodes by electron relay bridges[15] or charge-transporting molecular wires[7] resulted in charge separation, and improved the generation of photocurrent. The concentration of the electron acceptor or the electron donor at the surface of the semiconductor NP could provide a general means to assist charge separation by the effective trapping of the conduction-band electrons or the scavenging of the valence-band holes, respectively. Herein, we report a novel "click" chemistry method to assemble CdS NPs on Au electrodes by using saccharides, and particularly β-cyclodextrin (β-CD, **1**), as bridging units. This was achieved by the presence of boronic acid ligands, bound as monolayers to both the electrodes and the NPs, that act as linkage units. We further demonstrate that the β-CD bridging units act as receptor sites that concentrate either an electron donor (I_3^-) or an electron acceptor (*N*,*N'*-dioctyl-4,4'-bipyridinium) at the semiconducting NP surface, which results in significantly enhanced photocurrents. We also demonstrate that the encapsulation or the displacement of the electron donor into, or from, the β-CD units allows the switching of the photocurrents between anodic or cathodic directions, respectively.

Cyclodextrins are cyclic oligosaccharides consisting of glucose units linked by 1,4-glycosidic bonds.[16] The cyclic structure includes a hydrophobic receptor cavity, which provides a means for the association of the cyclodextrin with hydrophobic organic substrates.[17] Numerous studies have utilized the binding properties of cyclodextrins to develop materials for chromatography,[18] slow-release systems,[19] enzyme-mimetic systems,[20] and others.[21] The present study extends the use of cyclodextrins to the development of solar cells.

The association of boronic acid ligands to vicinal dihydroxy-substituted substrates to form boronate esters is well established.[22] Recent reports have described the formation of boronate complexes for the assembly of monolayers on electrode surfaces.[23] The preparation of the Au electrode functionalized with the β-CD/CdS NPs is depicted in Scheme 1 A. An electrode modified with phenylboronic acid was prepared by immersing an Au-coated slide in mercaptophenylboronic acid. A β-CD was then linked to the boronic acid ligand. The CdS NPs were functionalized and stabilized by a capping layer that contained 2-mercaptoethanesulfonic acid and the phenylboronic acid ligands. The CdS NPs functionalized with boronic acid were then ligated to the free vicinal hydroxy functions associated with the β-CD.

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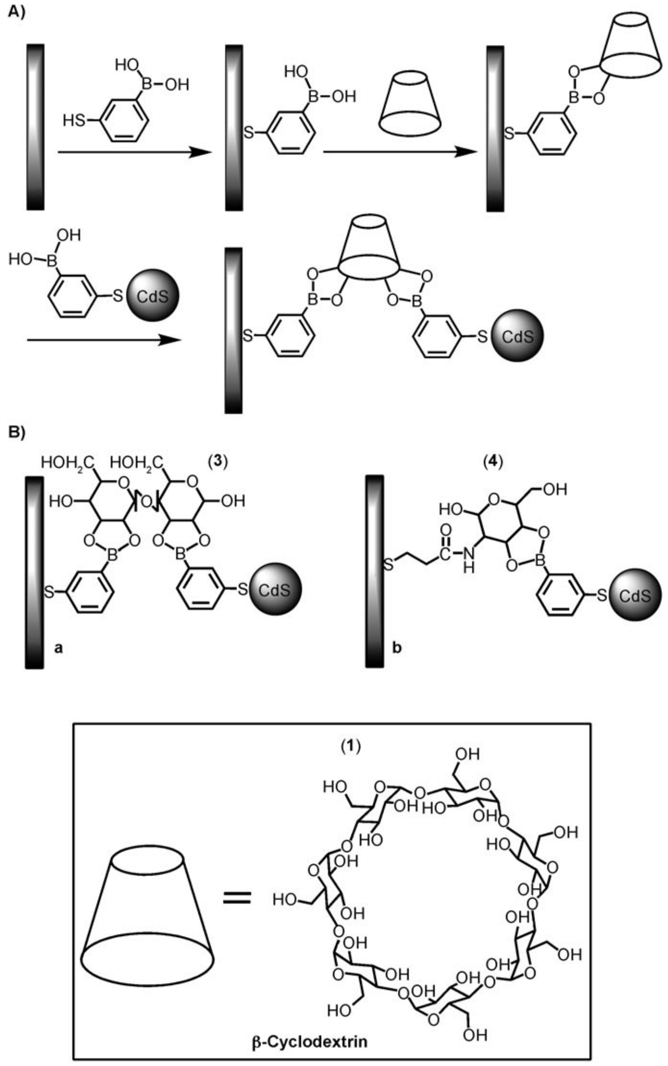


Scheme 1. A) Assembly of the β-CD/CdS NP electrode. B) The configuration of: a) The lactose-bridged/CdS NP electrode. b) The aminoglucose-bridged/CdS NP electrode.

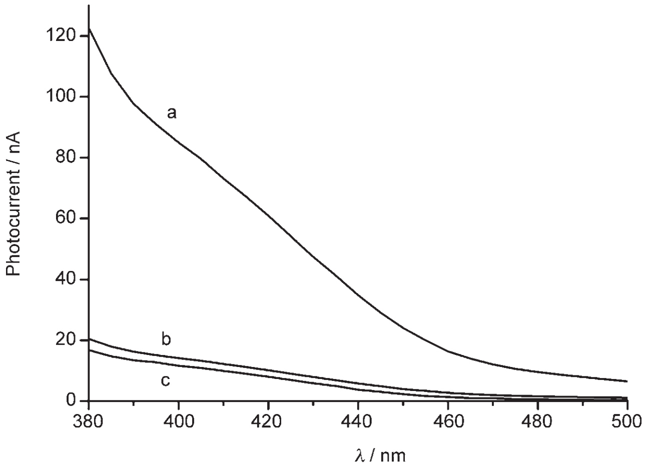
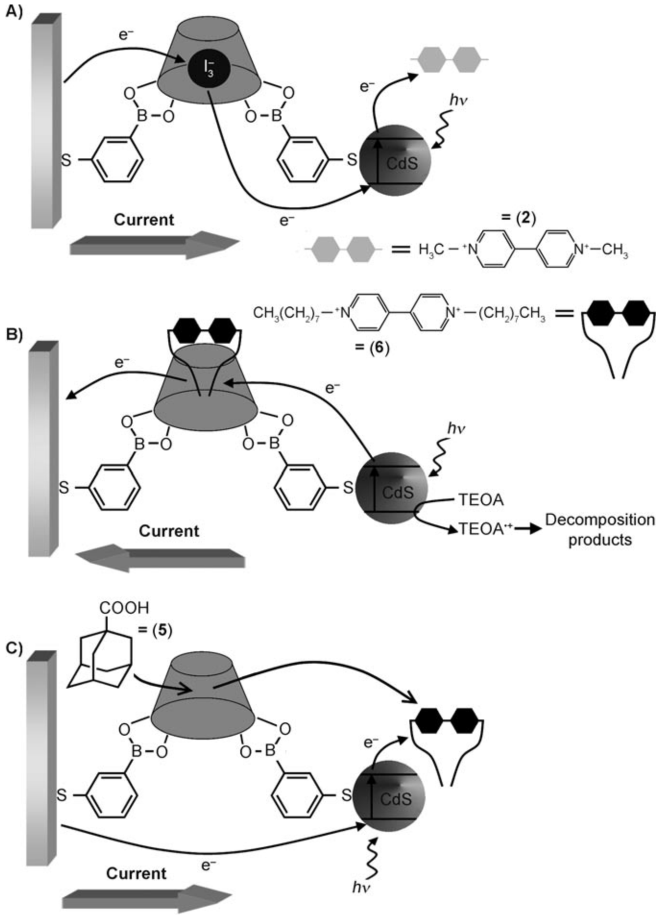


Figure 1. Photocurrent action spectra generated by different CdS NP systems in the presence of I_3^- (5 mM) and MV^{2+} (2 mM): a) CdS NPs linked to the Au electrode by β-CD. CdS NPs linked to electrodes functionalized with b) an aminoglucose and c) a lactose monolayer, respectively. All measurements were performed under Ar in an aqueous phosphate buffer solution (0.1 M, pH 7.4).

Microgravimetric quartz crystal microbalance (QCM) measurements indicated that the surface coverage of the CdS NPs corresponded to 8.3×10^{-13} mole particles per cm^2 (approximately 30% of a randomly densely packed NP monolayer). The electron donor I_3^- binds to β-CD ($K_a = 6.5\times10^2\,\mathrm{M}^{-1}$),[24] and, thus, its concentration in the β-CD cavity could lead to the effective reduction of the photogenerated valence-band holes.

Accordingly, we examined the photocurrent generated by the β-CD/CdS NPs electrode in the presence of *N*,*N*′-dimethyl-4,4′-bipyridinium (methyl viologen, MV^{2+}, **2**), as an electron acceptor, and I_3^- as an electron donor. Figure 1, curve (a) shows the photocurrent action spectrum generated by the electrode modified with CdS NPs. The photocurrent action spectrum follows the absorbance characteristics of the CdS NPs. The net light intensity absorbed by the CdS NPs could be elucidated by the immobilization of the β-CD/CdS NP system on a semitransparent Au electrode, from which the quantum yield of the photocurrent generated at 400 nm was estimated to be 2.4%. Several control experiments indicated that all of the components are essential to generate the photocurrent: no photocurrent was produced in the absence of I_3^- or MV^{2+}. Furthermore, the effect of concentrating I_3^- ions at the semiconducting NPs by means of the β-CD receptor was confirmed by modifying the Au electrode with CdS NPs that were linked to the electrode by lactose (**3**) or aminoglucose (**4**) bridges (Scheme 1B, routes (a) and (b), respectively). These saccharides do not bind I_3^- ions, and, thus, the electron donor is not concentrated at the NPs. Figure 1 (curves (b) and (c)) shows the photocurrent action spectra in the presence of MV^{2+}/I_3^-. The surface coverage of the CdS NPs in these systems is comparable to that observed for the β-CD/CdS NPs system. The resulting photocurrent in these reference systems is, however, approximately six times lower than that of the β-CD/CdS NPs system. Moreover, the directon of the photocurrent generated by the β-CD/CdS NPs was found to be cathodic. The mechanism for the formation of photocurrent involves the primary photoinduced generation of the electron-hole pair in the semiconductor. The ejection of the conduction-band electrons into the MV^{2+} ions that are in solution, and the concomitant transfer of electrons from I_3^- ions to the valence-band holes, completes the electron-transfer process, and results in the passage of current through the external circuit, Scheme 2A.

The role of β-CD in the concentration of I_3^- ions at the surface of the CdS NPs for the generation of enhanced photocurrent was further supported by inhibiting the association of I_3^- ions to the β-CD receptor. Adamantane carboxylic acid (**5**) binds more strongly ($K_a = 4.3\times10^4\,\mathrm{M}^{-1}$) than I_3^- ions to β-CD.[25] Accordingly, the photocurrent action spectra of the β-CD/CdS NP system were examined in the presence of various concentrations of adamantane carboxylic acid (Figure 2). As the concentration of **5** increased, the intensity of the photocurrent was found to decrease. This is consistent with the fact that **5** competes with I_3^- ions for the β-CD



Scheme 2. A) Generation of cathodic photocurrent by the β-CD/CdS NP/MV^{2+}/I_3^- system. B) Generation of anodic photocurrent by the β-CD/CdS NP/octyl viologen/TEOA system. C) Generation of cathodic photocurrent by the β-CD/CdS NPs/octyl viologen system in the presence of adamantane carboxylic acid as an inhibitor and TEO (2 mM) as sacrificial electron donor.

receptor sites. Thus, as the concentration of the receptor-bound I_3^- ions decreased, the photocurrents became smaller.

The selective association of a host compound with the β-CD receptor sites enabled us to design alternative systems where the electron acceptor (rather than the electron donor) is encapsulated in the receptor sites. In this configuration, the effective trapping of the conduction-band electrons proceeds by the concentration of the electron acceptor at the semiconductor surface (Scheme 2B). This configuration is not only anticipated to enhance the photocurrent by the effective trapping of the conduction-band electrons, but it can also be used to switch the photocurrent to an anodic direction.

While MV^{2+} (**2**) ions lack affinity for β-CD, *N,N′*-dioctyl-4,4′-bipyridinium ions (OV^{2+}, **6**) binds to β-CD, ($K_a = 5.6 \times 10^3\,\text{M}^{-1}$),[26] because of the hydrophobic chains tethered to the bipyridinium salt. Accordingly, the photocurrents generated by the β-CD/CdS NP electrode in the presence of OV^{2+} and triethanolamine (TEOA), as a sacrificial electron donor, were examined. Figure 3A, curve (a), shows the photocurrent action spectra generated by the β-CD/CdS-modified electrode in the presence of OV^{2+}/TEOA. The photocurrent spectrum overlaps that of the CdS NPs. Control experiments

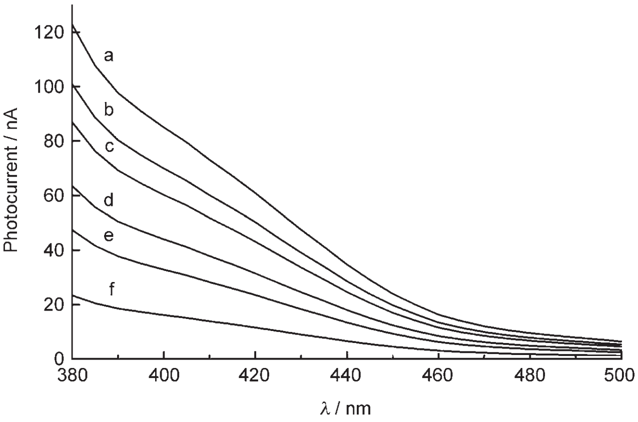


Figure 2. Photocurrent action spectra generated by the β-CD-bridged, CdS NP electrode using I_3^- (5 mM) and MV^{2+} (2 mM) as an electron donor and an electron acceptor, respectively, in the presence of various concentrations of adamantane carboxylic acid: a) 0; b) 5; c) 7.5; d) 10; e) 20; f) 50 mM. All measurements were performed under Ar in an aqueous phosphate buffer solution (0.1 M, pH 7.4).

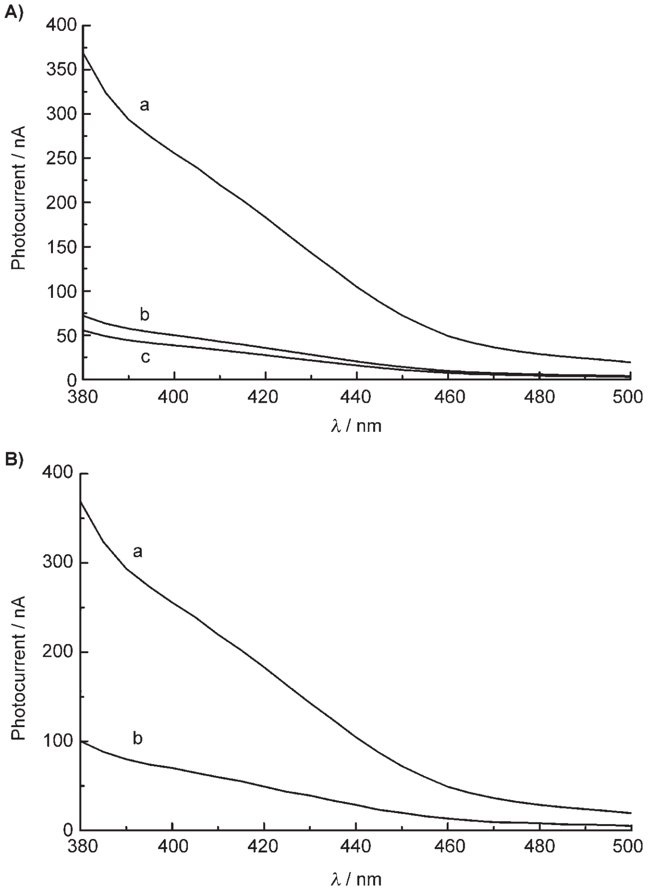


Figure 3. A) Photocurrent action spectra corresponding to: a) The β-CD/CdS NP electrode in the presence of octyl viologen (2 mM) and triethanolamine (20 mM), b) the aminoglucose- or c) lactose-bridged CdS NP electrodes in the presence of octyl viologen (2 mM) and triethanolamine (20 mM); B) Photocurrent action spectra of the β-CD/CdS NP electrode in the presence of octyl viologen (2 mM) and triethanolamine (20 mM): a) in the absence of the adamantane carboxylic acid inhibitor, b) in the presence of adamantane carboxylic acid (5×10^{-6} M). All measurements were performed under Ar in an aqueous phosphate buffer solution (pH 7.4).

show that the aminoglucose-functionalized CdS NP electrode, curve (b) or the lactose-modified CdS NP electrode, curve (c), result in a photocurrent that is approximately six times lower than that obtained using β-CD. The direction of the photocurrent was found to be anodic, that is, the conduction-band electrons are ejected to the electrode (Scheme 2B).

The high photocurrent intensities in the presence of the β-CD/CdS NP monolayer are attributed to the concentration of the electron acceptor **6** in the β-CD cavities, which results in the effective trapping of the conduction-band electrons by the OV^{2+} units. This leads to effective charge separation and facilitates the efficient reduction of the valence-band holes by TEOA, and the concomitant transfer of the OV^{2+}-trapped electrons to the electrode.

The quantum yield for the light-to-current conversion was estimated to be 4.5% (which corresponds to an IPCE (incident photon to current efficiency) of approximately 2.7%). Further support for the suggested mechanism for the enhanced yields of the photocurrent in the presence of the β-CD/CdS NP layer was obtained by competitive inhibition experiments (Scheme 2C). The photocurrent action spectra generated by the β-CD/CdS NP electrode in the presence of OV^{2+} are depicted in Figure 3B, curve (a), and upon addition of **5** (5×10^{-6} M), curve (b). The decline in the photocurrent is consistent with the fact that the binding of **5** to the β-CD units eliminates the OV^{2+} from the receptor sites.

In conclusion, the present study has introduced a new functionalized semiconductor nanoarchitecture on electrodes for the generation of enhanced photocurrent. The nanostructured electrode consists of CdS NPs linked to the surface by means of β-CD bridging units. The β-CD receptors provide cavities for either the encapsulation of an electron donor (I_3^-) or the binding of an electron acceptor (OV^{2+}). The concentration of the electron donor or acceptor at the surface of the semiconductor NPs results in the effective reduction of the photogenerated valence-band holes, or the efficient trapping of the conduction-band electrons, respectively. The scavenging of the valence-band holes, or the trapping of the conduction-band electrons, lead to charge separation and to substantially improved photocurrents. The electron-transfer units (electron donor or electron acceptor) encapsulated in the β-CD sites control the direction of the resulting photocurrents. Although the quantum yields of the systems are still far from practical utility in the fabrication of solar cells, the concept of concentrating the electron donor or acceptor at the semiconductor surface is, however, a direction to pursue. Similar deposition of the acceptor units on porous semiconductors could substantially improve the performance of the systems.

Experimental Section

Preparation of CdS NPs: These were prepared as reported previously,[7] by using a reverse micellar solution. An average particle size of 8.0 ± 0.5 nm was estimated by TEM.

Electrode modification: Clean Au electrodes were modified with 3-mercaptophenylboronic acid (5 mM) in ethanol for a period of 3 h. The modified electrodes were immersed for 2 h in a phosphate buffer solution (0.1 M, pH 7.4) containing β-CD (10 mM) to covalently bind the β-CD to the boronic acid monolayer (alternatively, lactose (10 mM) was used for the preparation of lactose-bridged CdS NPs). The resulting electrodes were treated with the CdS NPs functionalized with boronic acid for 2 h. For the preparation of aminoglucose-bridged CdS electrodes, Au electrodes were placed in an aqueous solution containing 3-mercaptopropionic acid (10 mM) for 3 h. The electrodes were then treated with HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer (0.01 M, pH 7.4) containing 3-aminophenylboronic acid (5 mM) solution for 2.5 h, then a phosphate buffer (0.1 M, pH 7.4) containing aminoglucose (10 mM) for 2 h, and were finally modified with the CdS NPs functionalized with the phenylboronic acid for 2 h.

Instrumentation: Photocurrents were measured using a home-built photoelectrochemical system described previously.[7] The photogenerated currents were measured between the CdS-NP-functionalized Au working electrode and a carbon rod ($d = 5$ mm) counter electrode. Quartz crystal microbalance (QCM) measurements were performed on a home-built instrument linked to a frequency analyzer (Fluke) with Au-quartz crystals (AT-cut 10 MHz). The geometrical area of the Au electrode was (0.2 ± 0.05 cm^2).

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