CdS nanoparticle-modified electrodes for photoelectrochemical studies

Stephanie Drouard, Stephen G. Hickey and D. Jason Riley*

School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS. E-mail: Jason.Riley@bristol.ac.uk

Received (in Exeter, UK) 4th November 1998, Accepted 1st December 1998

A novel method of preparing CdS nanoparticle-modified electrodes is described and a relationship between CdS particle size and the photoelectrochemical properties of such electrodes demonstrated.

Nanocrystalline semiconductors exhibit a wide range of novel chemical and physical properties.[1] Hence research on nanocrystalline semiconductors is developing into a large interdisciplinary field. The properties of nanocrystalline particles differ from those of bulk materials for two reasons. First, the high surface area to volume ratio results in there being almost as many atoms at the surface as in the crystalline lattice. Secondly, the electronic bands are split into discrete energy levels as a result of the three-dimensional confinement of charge carriers. This quantum confinement of charge results in an increase in band gap with decreasing particle size. Indeed determination of the band edge allows the calculation of the particle size.[2] Investigations of how the interesting properties of nanoparticles may be exploited in optoelectronic devices,[3] photovoltaic[4] and clean technology applications[5] are being performed in many laboratories.

CdS is the material of choice when studying quantum confinement effects since methods of controlling the size of CdS nanoparticles are well established.[6–8] The study of charge transfer in nanoparticle systems is an active area of research. Electron exchange in colloidal CdS solutions has been extensively studied using photoelectrochemical[9] and radiolysis techniques.[10] However, if the novel properties of CdS nanoparticles are to be exploited in optoelectronic devices, methods of electrically addressing the particles directly are required. This communication is concerned with the preparation and characterisation of electrodes modified with sub-monolayers of nanoparticles; it is demonstrated that such electrodes allow the optoelectronic properties of the nanoparticles to be probed. In previous studies[11–15] of CdS coated surfaces the nanoparticles have been prepared in inverse micelles and deposited on to gold surfaces using dithiols as molecular anchors. Fourier transform IR spectroscopy,[12] UV–VIS spectroscopy,[13] X-ray photoelectron spectroscopy,[14] scanning tunnelling microscopy[15] and limited electrochemical studies have been performed on such electrodes. In this communication a novel method of preparing CdS nanoparticle modified electrodes is described and initial investigations of the optoelectronic properties of the CdS nanoparticles reported. The method of preparation is considerably simpler than that reported previously and allows deposition of CdS on to optically transparent electrodes; this facilitates studies of the optoelectronic properties of the particles. To illustrate that the CdS nanoparticles at the modified electrode surface may be addressed photoelectrochemically the photocurrent spectra are reported.

The strategy employed in the preparation of the CdS nanoparticle modified electrodes is detailed schematically in Fig. 1. The method is essentially a three-step process. First a tin oxide electrode surface is functionalised[16] using established methods. Then CdS nanoparticles are grown and grafted on to the functional groups.

The tin oxide electrodes were first cleaned in a Piranha bath at 70 °C and then placed in a solution of 3 mol dm^{-3} potassium hydroxide for *ca.* 2 h, in order to activate the surface. The electrode surface was then silanised by immersion in a 1 : 10 (3-mercaptopropyl)trimethoxysilane (MPTMS): methanol solution. The resultant surface possessed pendent thiol groups to which the CdS nanoparticles could be anchored.

The CdS colloidal nanoparticles were prepared in non-aqueous solution using a method first reported by Fischer and Henglein.[7] CdS was formed by bubbling H_2S, (2×10^{-4} mol dm^{-3}), into a 1×10^{-3} mol dm^{-3} $Cd(ClO_4)_2$ THF solution. The resultant colloids were strerically stabilised by addition of hexanethiol to the THF. It has been shown that the CdS nanoparticle size may be controlled by varying the hexanethiol concentration.

Initial attempts to attach the CdS nanoparticles to the functionalised surface involved the immersion of the electrodes in a solution containing CdS nanoparticles. This strategy proved unsuccessful; it has been reported[7] that stabiliser exchange is not possible with colloids prepared by this procedure. Hence, to obtain the CdS nanoparticle electrodes the functionalised tin oxide surfaces were immersed in the THF solution during colloid formation, in order that the surface-colloid bonds are formed as nanoparticle growth proceeds. The size of the particles was controlled by varying the hexane thiol concentration, solutions containing 0.400, 8.57×10^{-3} and 5.275×10^{-3} mol dm^{-3} of the stabiliser were studied. After rigorous washing the photoelectrochemical properties of the electrodes were investigated.

Prior to photoelectrochemical investigations of the modified electrodes the UV–VIS adsorption spectra of the parent

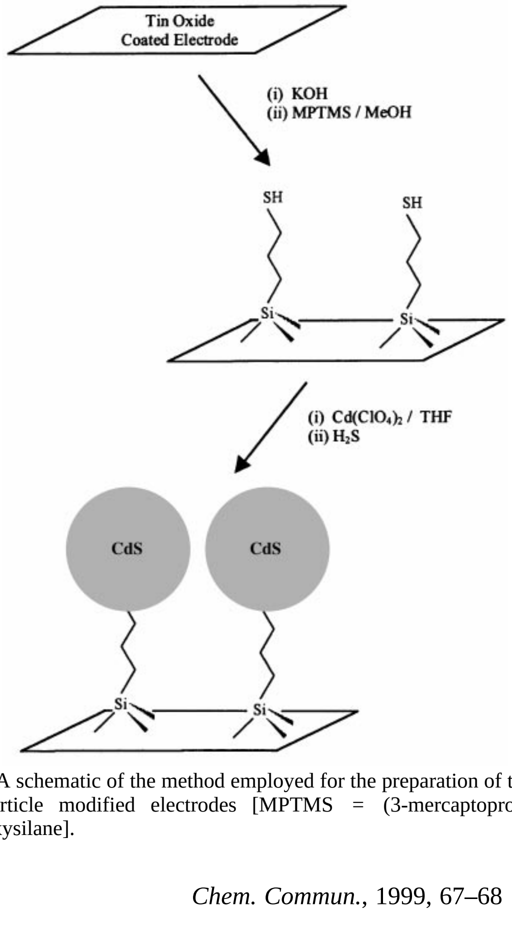

Fig. 1 A schematic of the method employed for the preparation of the CdS nanoparticle modified electrodes [MPTMS = (3-mercaptopropyl)trimethoxysilane].

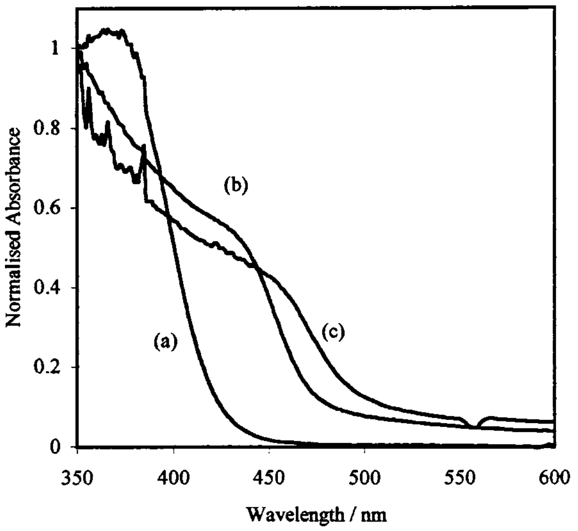

Fig. 2 Normalised UV–VIS absorbance spectra of CdS colloidal suspensions. The suspensions were prepared using varying concentrations of hexanethiol: (a) 0.400, (b) 8.57×10^{-3} and (c) 5.275×10^{-3} mol dm^{-3}.

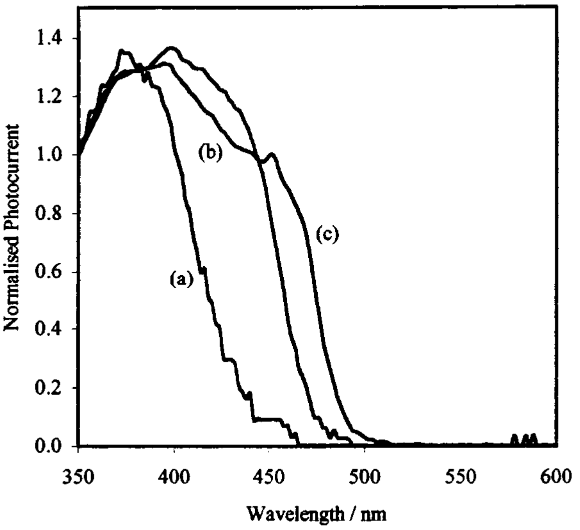

Fig. 3 Normalised photocurrent spectra of CdS nanoparticle modified electrodes. The electrodes were prepared using varying concentrations of hexanethiol: (a) 0.400, (b) 8.57×10^{-3} and (c) 5.275×10^{-3} mol dm^{-3}.

colloidal suspensions were recorded. The spectra for the suspensions prepared using the three different hexanethiol concentrations are shown in Fig. 2. It is apparent that by controlling the stabiliser concentration it is possible to change the band gap of the CdS nanoparticles formed in the solution phase. The sizes of the nanoparticles were determined from band-edge measurements. It was found that hexanethiol concentrations of 0.400, 8.57×10^{-3} and 5.275×10^{-3} mol dm^{-3} result in CdS nanoparticles in the colloidal suspension of 2, 4 and 10 nm diameter, respectively. More detailed studies of the influence of hexanethiol concentration on nanoparticle size in colloidal suspensions have been published.[7]

It was necessary to determine the band gap of the nanoparticles formed at the electrode interface in order to verify that they were of the same size as those formed in the solution phase. Unfortunately it was not possible to record the UV–VIS adsorption spectra for the modified electrodes as the CdS particles were present in sub-monolayer quantities. Hence, the optical properties of the CdS nanoparticles at the modified electrode surfaces were characterised using the more sensitive technique of photocurrent spectroscopy. All electrochemical experiments were performed at 0.2 V *vs.* Ag|AgCl| 3 mol dm^{-3} NaCl in a 1.0 mol dm^{-3} aqueous Na_2SO_3 solution buffered at pH 12. The photocurrent spectra were recorded using chopped monochromatic light and a lock-in amplifier. Photocurrent spectra for modified electrodes prepared using the three different hexanethiol concentrations are shown in Fig. 3. The excellent agreement between the UV–VIS spectra and the photocurrent spectra indicates that the particles deposited on the electrode surfaces were of the same size as those in the parent suspension.

In conclusion, a method of preparing optically transparent electrodes modified with sub-monolayers of CdS nanoparticles has been developed. Further, it has been shown that the size of the CdS nanoparticles on the surface can be controlled by varying the hexanethiol concentration. The photocurrent experiments demonstrate that the physical properties of the CdS nanoparticles at the surface can be addressed using photoelectrochemical techniques. Intensity-modulated photocurrent spectroscopy studies of the effect of quantum confinement on the kinetics of charge transfer from photoexcited CdS nanoparticles are presently in progress.

Notes and references

1 H. Weller, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 41.

2 L. Brus, *J. Phys. Chem.*, 1986, **90**, 2555.

3 A. Loni, A. J. Simons, T. I. Cox, P. D. J. Calcott and L. T. Canham, *Electron. Lett.*, 1995, **31**, 1288.

4 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 739.

5 W. Y. Lin and K. Rajeshwar, *J. Electrochem. Soc.*, 1997, **144**, 2751.

6 A. Chemseddine and H. Weller, *Ber. Bunsenges. Phys. Chem.*, 1993, **97**, 636.

7 C. H. Fischer and A. Henglein, *J. Phys. Chem.*, 1989, **93**, 5578.

8 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.

9 W. J. Albery, P. N. Bartlett and J. D. Porter, *J. Electrochem. Soc.*, 1984, **131**, 2892.

10 S. Baral, A. Fojtik, H. Weller and A. Henglein, *J. Am. Chem. Soc.*, 1986, **108**, 375.

11 V. L. Colvin, A. N. Goldstein and A. P. Alvisatos, *J. Am. Chem. Soc.*, 1992, **114**, 5221.

12 T. Nakanishi, B. Ohtani, K. Uosaki, *J. Phys. Chem. B.*, 1998, **102**, 1571.

13 K. Hu, M. Brust and A. J. Bard, *Chem. Mater.*, 1998, **10**, 1160.

14 T. Nkanishi, B. Ohtani, K. Shimazu and K. Uosaki, *Chem. Phys. Lett.*, 1997, **278**, 233.

15 S. Ogawa, F. F. Fan and A. J. Bard, *J. Phys. Chem.*, 1995, **99**, 11182.

16 K. R. Brown, A. P. Fox and M. J. Natan, *J. Am. Chem. Soc.*, 1996, **118**, 1154.

Communication 8/08572B