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Photoelectrochemical Imaging Using Carbon Dots (CDs) Derived from Chitosan †

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Abstract: Carbon dots (CDs) derived from chitosan via a solvothermal method were covalently linked to an indium tin oxide (ITO) surface and showed a direct photoelectrochemical response. We attribute the photocurrent of the ITO-silane-CD surface to a photogenerated electron-transfer process by CDs under illumination. The ITO-silane-CD surface was successfully used for ac-photocurrent imaging. This opens up new applications for CDs as biocompatible and light-addressable electrochemical sensors in bioimaging applications.

Keywords: carbon dots; photoelectrochemistry; ac-photocurrent image; LAPS; LAE

1. Introduction

Carbon dots (CDs) with nanostructures have generated excitement as a semiconductor-like and metal-free photocatalysts [1]. CDs have been widely applied to enhance photocatalytic activities of heterostructured photocatalysts in photoelectric conversion [2], pollutant photodegradation [3], water splitting [4], CO_2 conversion [5] and organic synthesis [6]. CDs played important roles in photoreactions by light absorption, electron-hole pair generation, photoexcited charge separation and migration, which showed both electron donor and acceptor abilities under illumination. However, the photoinduced electron transfer process of CDs is still unclear. Self-assembled monolayers of conventional quantum dots have been used in light-addressable electrodes for electrochemical sensing [7]. Compared to conventional quantum dots, CDs are cheap, non-poisonous and biocompatible, which are ideal for bioimaging. Herein, we report the photoelectrochemical behaviour of CDs prepared by simple bottom-up solvothermal approach from chitosan and their use in electrochemical imaging sensors.

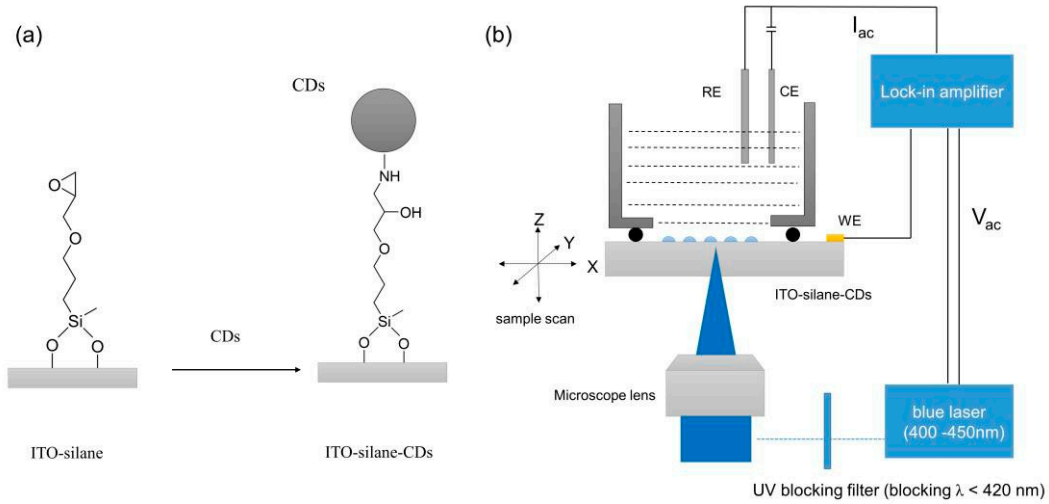
2. Materials and Methods

2.1. The Preparation of CDs

CDs were prepared by a one-step solvothermal carbonization of chitosan dispersed in ethanol (4% *w*/*v*) at 200 °C for 12 h. The dark brown liquid phase obtained was centrifuged at 20,000 rpm for 10 min to separate the liquid containing fluorescent CDs from the solid black carbonaceous precipitate. The liquid phase containing CDs was then filtered using standard syringe filters.

2.2. The Preparation of ITO-Silane-CD Surfaces

The indium tin oxide (ITO) coated glass (50 Ω/sq, Diamond Coatings Limited, UK) was cut into 1 cm × 1 cm pieces. They were cleaned by ultrasonication for 15 min with acetone, isopropanol and ultrapure water. After drying with nitrogen, the ITO substrates were immersed in a solution of 1:1:5 (*v*/*v*) H_2O_2 (30%)/NH_4OH (30%)/H_2O for 1 h, washed with ultrapure water and dried with nitrogen. Then, ITO substrates were immersed in a 1% 3-glycidoxypropyldimethoxymethylsilane ethanol solution for 20 min. After drying, they were placed in an oven at 110 °C for 1 h, washed with ethanol thoroughly and dried with nitrogen. The ITO-silane surfaces were incubated with the CD ethanol solution overnight at room temperature (Scheme 1a). Finally, the ITO-silane-CD surfaces were washed with ultrapure water. After drying, the ITO-silane-CD surface was kept at room temperature before use [8].



Scheme 1. (**a**) Scheme of CDs binding onto ITO via silane reaction; (**b**) Scheme of the ac-photocurrent image setup by scanning a focused, modulated laser beam across the ITO-silane-CD surface.

2.3. Photocurrent Measurements

Linear sweep voltammetry (LSV) was carried out in 10 mM pH 7.4 phosphate buffer with 0.1 M KCl using an Autolab PGSTAT30/FRA2 (Windsor Scientific Ltd., UK) in a custom made electrochemical cell consisting of a platinum electrode and an Ag/AgCl electrode as the counter and reference electrodes, respectively. The scan rate was 5 mV/s. An adjustable diode laser (wavelength 400–450 nm, max 500 mW) with a UV filter that blocked light of wavelengths lower than 420 nm was used as the chopped back side illumination source. The irradiance was measured as 10 mW/cm^2 with a calibrated power meter.

2.4. AC Photocurrent Imaging

As shown in Scheme 1b, a focused diode laser (400–450 nm) with a UV filter that blocked the light of wavelengths lower than 420 nm was used for charge carrier generation. The modulation frequency was 10 Hz. The position of the sample holder was adjusted by an M-VP-25XL XYZ positioning system with a 50 nm motion sensitivity on all axes (Newport, UK). AC photocurrents were measured in pH 7.4 PBS buffer solution by an EG&G 7260 lock-in amplifier using a platinum electrode and an Ag/AgCl electrode as the counter and reference electrodes, respectively.

3. Results and Discussion

CDs were prepared by a one-step solvothermal carbonization of chitosan dispersed in ethanol (4% *w*/*v*), which showed spherical morphologies and an average diameter of around 4 nm in a transmission electron microscopy (TEM) image. To investigate the photoelectric conversion behaviour, CDs were covalently linked to an indium tin oxide (ITO) surface through a

3-glycidoxypropyldimethoxymethylsilane monolayer. X-ray photoelectron spectroscopy (XPS) confirms the linking of silane and CDs by the appearance of a nitrogen peak assigned to the amine in the CDs from chitosan. Photoelectrochemical response measurements of ITO-silane-CDs were carried out by linear sweep voltammetry (LSV) in 10 mM pH 7.4 phosphate buffer with 0.1 M KCl. The results (Figure 1) confirmed the direct photoelectrochemical response of CDs under 420–450 nm laser illumination. The photocurrent generated by CDs and the mechanism have been studied (Figure 2). The photocurrent was attributed to the enhanced electron-transfer process catalyzed by CDs under illumination.

The ITO-silane-CD surface was applied to ac-photocurrent imaging, which measures the local photocurrent by illuminating the substrate with a focused, modulated laser beam. Figure 3a shows circular islands of PMMA with a diameter of 40 μm and 30 μm gaps on an ITO-silane-CD surface obtained by microcontact printing. Figure 3b shows the corresponding ac-photocurrent image measured at a bias voltage of 1.8 V and a modulation frequency of 10 Hz with micron scale lateral resolution. This discovery opens up new applications for CDs as light-addressable electrochemical sensors in bioimaging applications.

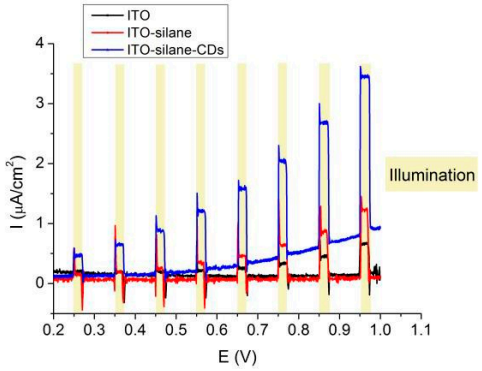


Figure 1. LSV curves of ITO, ITO-silane, and ITO-silane-CDs with chopped illumination (420–450 nm, 10 mW/cm²).

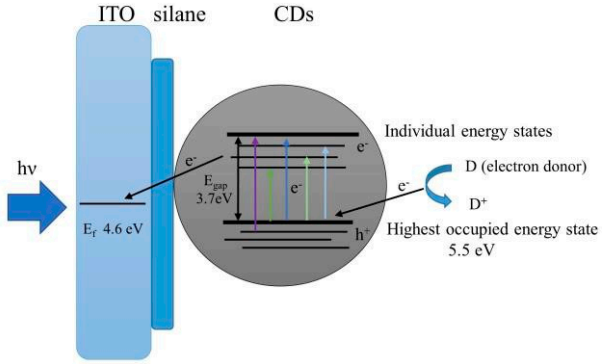
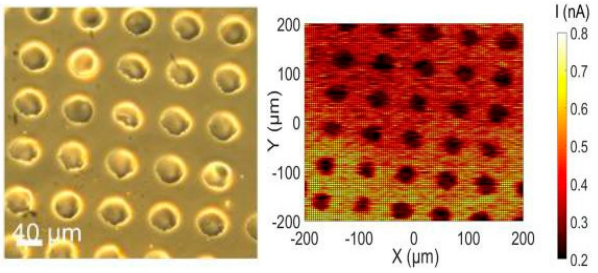


Figure 2. The mechanism of photoelectric conversion of CDs.



(**a**) (**b**)

Figure 3. (**a**) Optical micrograph of a PMMA dot array on ITO-silane-CD surface by microcontact printing; (**b**) Corresponding ac-photocurrent image of (**a**) measured at 1.8 V.

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Author Contributions: D.Z., M.-M.T., and S.K. designed the experiments. N.P. produced the CD samples and performed the characterization of CDs. D.Z. performed the binding of CDs onto the ITO surface, photocurrent measurements and ac-photocurrent imaging. All authors contributed to the interpretation of the results. D.Z. and S.K. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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