Electronic Supplementary Material (ESI) for Materials Horizons.
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Supporting Information for

Photoelectrochemical response of carbon dots (CDs) derived from chitosan and their use in electrochemical imaging

Experimental Section:

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 hours. The obtained dark brown liquid phase 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.

Highly N doped CDs were prepared by a one-step solvothermal carbonization of chitosan and ethylenediamine dispersed in water at 200 °C for 12 hours, the ratio of chitosan and ethylenediamine was 1:3, as 1.4 g: 0.58 mL in 35mL water.

XRD measurements: The structure of the carbon dots powder was analysed by X-ray diffraction (XRD) using Panalytical Xpert Pro diffractometer with Cu-Kα radiation. The range of XRD scan was between 5º to 70º and in a continuous scan mode at a scan speed of 0.6°/min with a collection width of 0.0167°.

FTIR measurements: Fourier Transform Infrared Spectroscopy (FTIR) measurements were recorded by using a Bruker Tensor 27 instrument equipped with diamond lens Attenuated Total Reflectance (ATR) module in the range from 4000 cm^{-1} to 400 cm^{-1}. Freeze dried carbon dots powder was used to obtain the FTIR spectra.

The binding of CDs onto ITO surface: The indium tin oxide (ITO) coated glass (50 Ω/cm^2, 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 1h, washed with ethanol thoroughly and dried with nitrogen. The ITO-silane surfaces were incubated with the CD ethanol solution overnight at room temperature. 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.

XPS measurements: The XPS was performed using an AXIS Ultra DLD (Kratos Surface Analysis) setup equipped with an 180° hemispherical analyzer, using Al $K_{\alpha 1}$ (1486.74 eV) radiation produced by a monochromatized X-Ray source at operating power of 300 W (15 kV × 20 mA).

AFM measurements: Atomic force microscopy (AFM, Ntegra Prima, NT-MDT Spectrum Instruments) in tapping mode was used to image the ITO-silane and ITO-silane-CD surface.

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 nm - 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 light intensity was measured as 10 mW/cm^2 with a calibrated power meter.

Photoelectron spectroscopy in air (PESA): The ionisation potentials of the CDs were determined by photoelectron spectroscopy in air (PESA) using a Riken Keiki spectrophotometer (Japan) model AC-2. Powders of the CDs were loaded into a powder holder for the measurement. The conditions employed during the measurements were an incident photon energy range from 4.2 to 6.2 eV with a measurement interval of 0.05 eV, an integration time of 10 s and an illumination power of 30 nW. The resolution of the instrument was 10 meV and the incident UV spectrum was calibrated against a standard photodiode.

Microcontact printing (µCP): PDMS stamps were prepared by using a 10:1 ratio (v/w) of PDMS resin and curing agent (184 silicone elastomer, Sylgard). After degassing under vacuum, the PDMS was poured over a prepared silicon master and cured at 50°C overnight. The cured PDMS was peeled off from the master, treated in an oxygen plasma (pressure: 0.8 Torr, generator: 40 kHz/100 W) for 30 s and then cut into 7 mm × 7 mm pieces. The pattern of the PDMS consisted of circular islands with a diameter of 40 µm and 30 µm gaps. The PDMS stamp was dipped in 11% poly(methyl methacrylate) (PMMA) anisole solution. The soaked stamp was dried under nitrogen gas for 40 s and placed onto the ITO-silane-CDs surface for 40 s. After removing the stamp, the PMMA dot array formed on the surface.

Immobilization of yeast cells: Low gelling temperature agarose gel was used to immobilize yeast cells onto the ITO-silane-CD surface. After boiling for 5 min, the 1.5% agarose gel was slowly cooled down to 37 °C, and was then held at 37 °C in a compact dry bath and a block heater (Thermo Scientific). Yeast was washed five times in ultrapure water by centrifuging (1800 rpm, 5 min). The agarose gel was mixed with 80 mg/mL (8×10^8 cells/mL) yeast (v/v, 9:1). One drop of the mixture (~ 0.2 µL, 8×10^7 cells/mL) was added onto the ITO-silane-CD surface. The yeast-agarose gel formed after it slowly cooled down to room temperature effectively immobilizing a multilayer of yeast cells on the ITO-silane-CD surface.

AC photocurrent imaging: 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 positon 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.

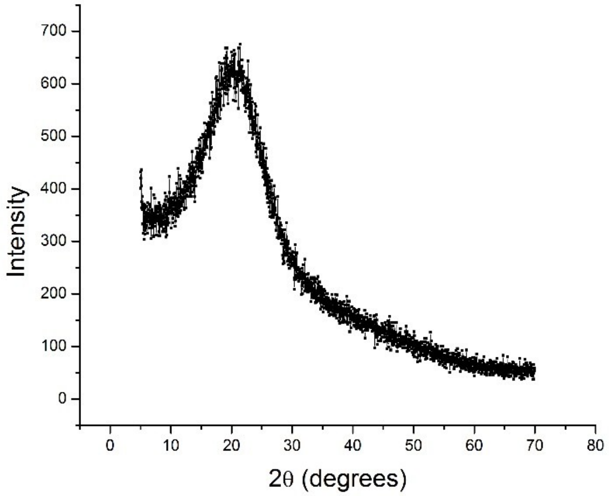

Figure S1. XRD pattern of synthesized CDs in powder form.

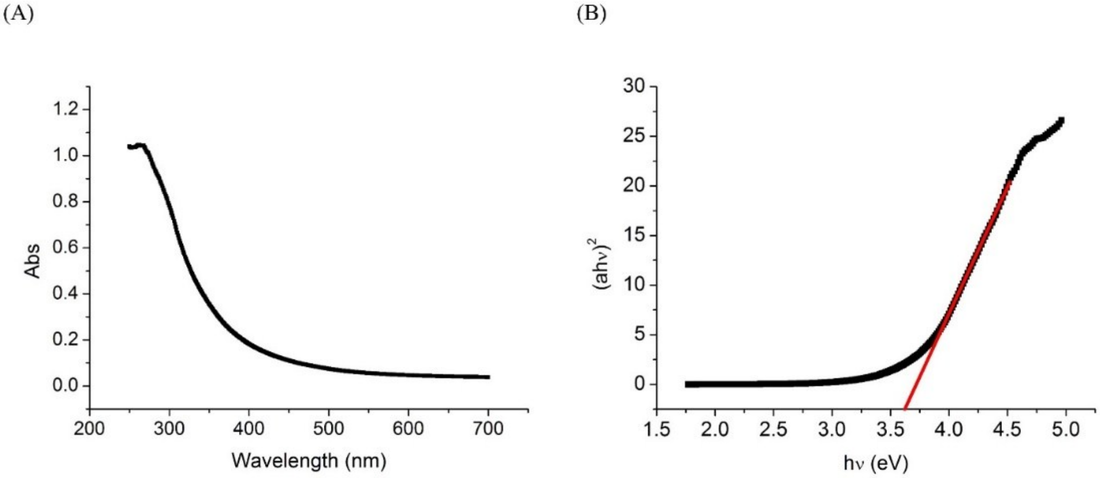

Figure S2. (A) UV/Vis absorption spectrum of the CDs ethanol solution; (B) Tauc plot of the CDs ethanol solution derived from (A).

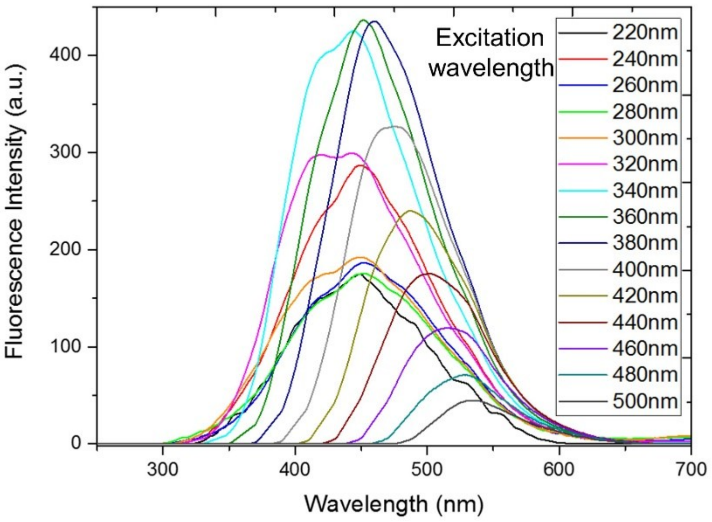

Figure S3. Fluorescence spectra of CDs samples at different excitation wavelengths.

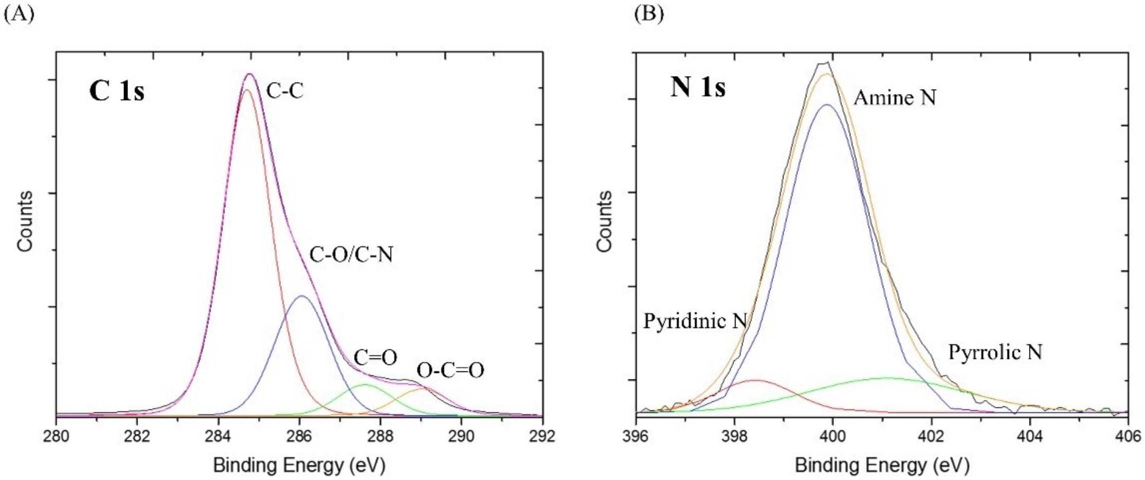

Figure S4. (A) XPS C1s spectrum of the CDs; (B) XPS N 1s spectrum of the CDs.

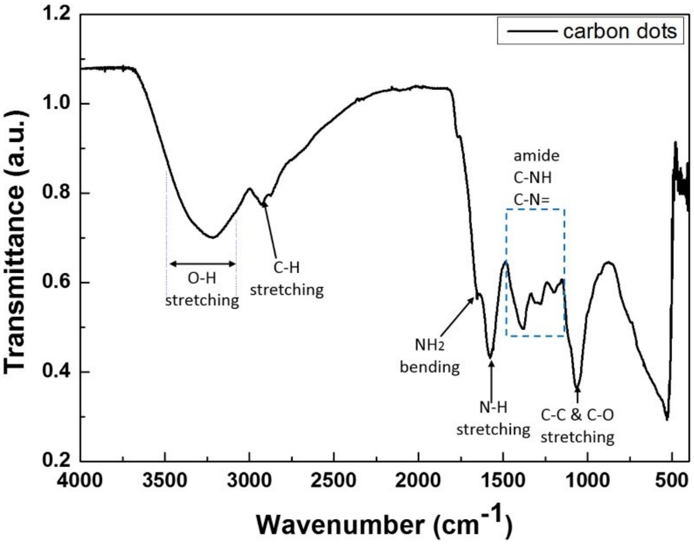

Figure S5. FTIR spectrum of synthesized CDs in powder form.

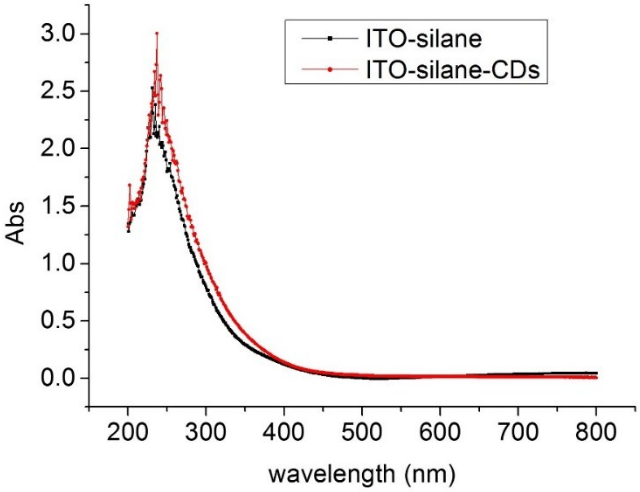

Figure S6. UV/Vis absorption spectra of ITO-silane and ITO-silane-CD surfaces.

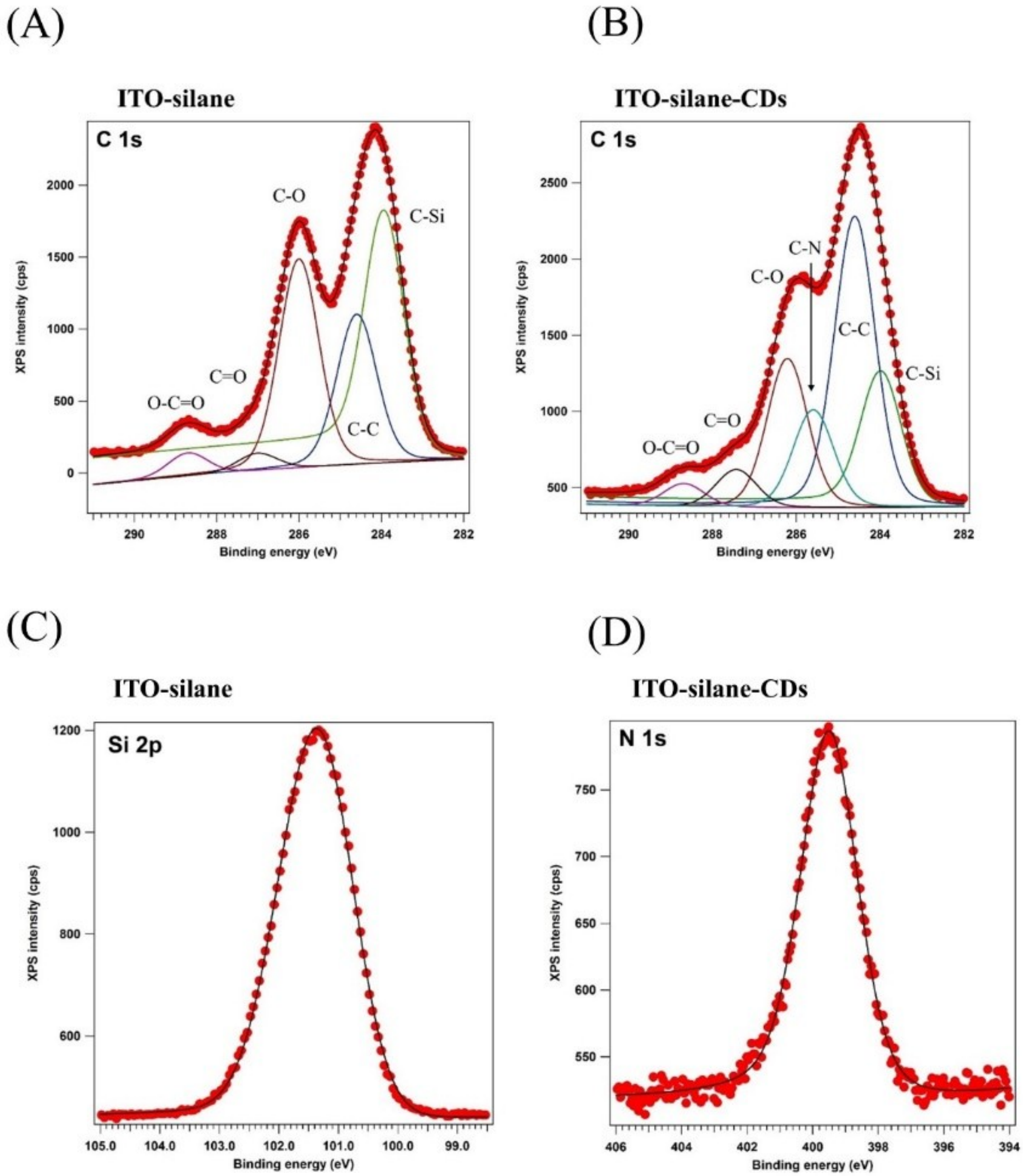

Figure S7. (A) XPS C 1s spectrum of the ITO-silane; (B) XPS C 1s spectrum of the ITO-silane-CDs; (C) XPS Si 2p spectrum of the ITO-silane; (D) XPS N 1s spectrum of the ITO-silane-CDs.

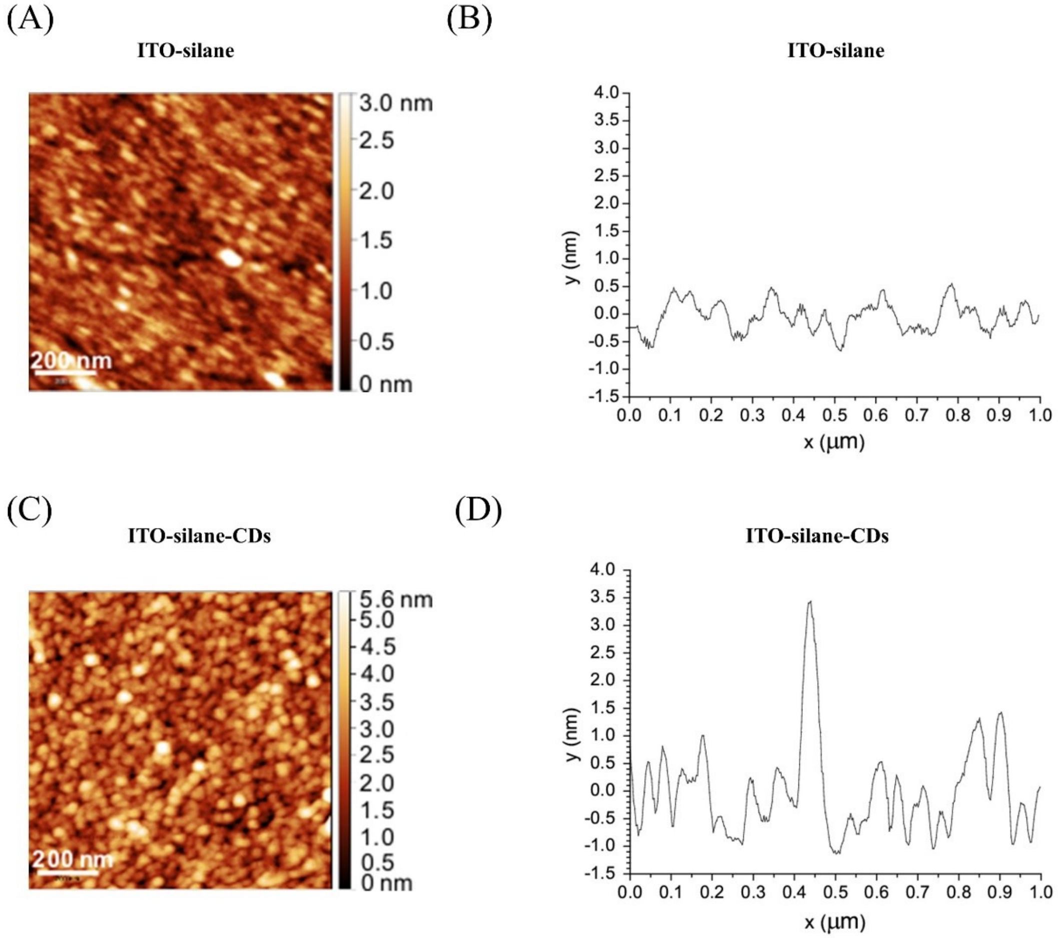

Figure S8. AFM of ITO-silane (A), ITO-silane-CDs (B), and their height distribution (C) (D).

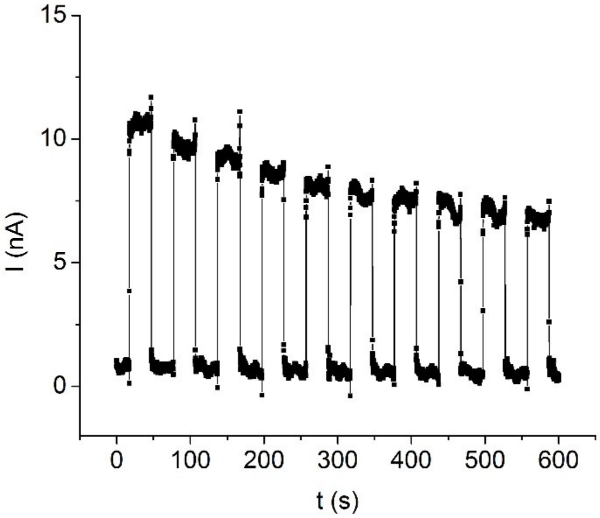

Figure S9. The cycling stability of the photocurrent of the ITO-silane-CD surface at 1.0 V with chopped illumination for 10 minutes.

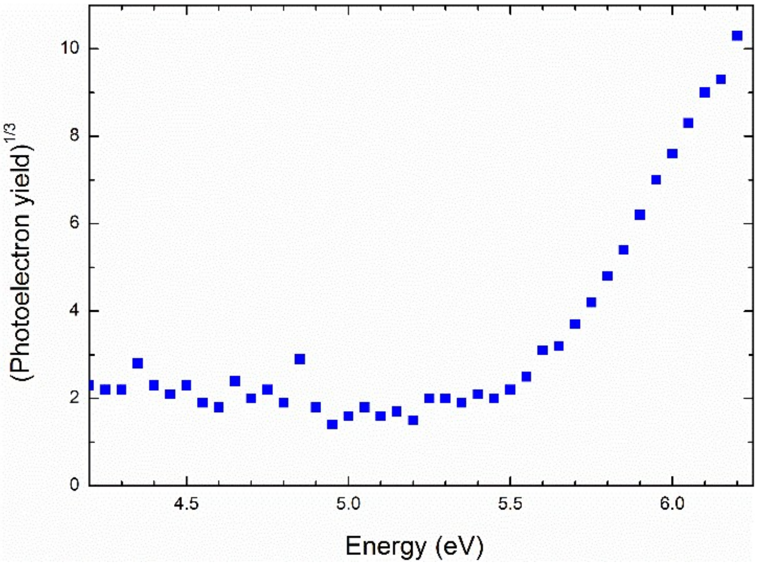

Figure S10. Photoelectron spectroscopy in air (PESA) of the chitosan-derived CDs in powder form.

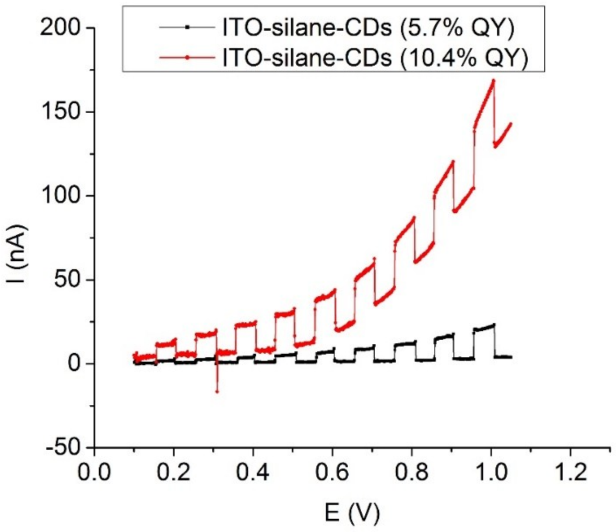

Figure S11. LSV curves of ITO-silane-CDs (5.7% QY) and ITO-silane-CDs (10.4% QY) with chopped illumination (420-450 nm, 10 mW/cm^2).

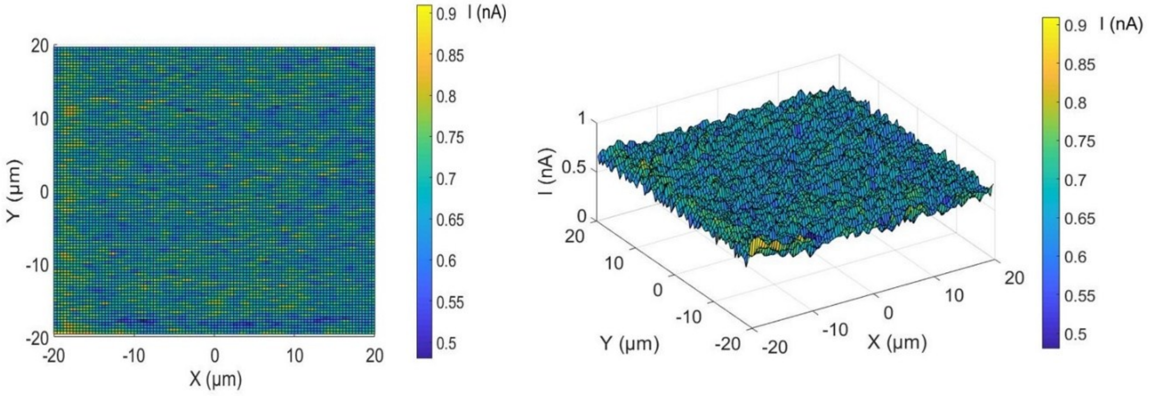

Figure S12. AC-photocurrent image of ITO-silane-CD surface with step size of 0.4 μm at 1.8 V

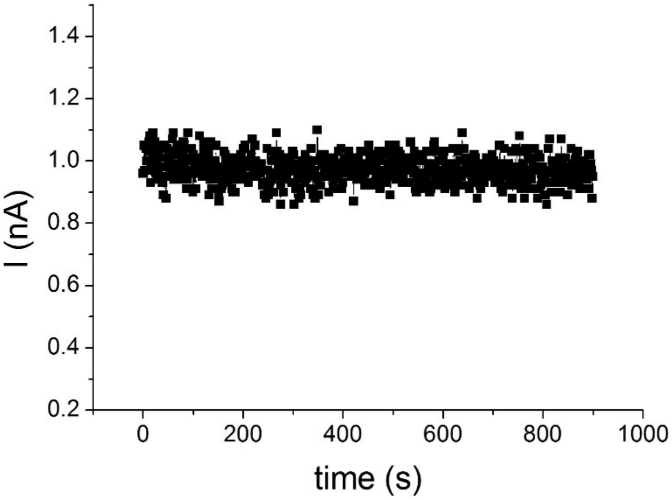

Figure S13. The stability of the ac-photocurrent of an ITO-silane-CD surface at 1.8 V and a modulation of 10 Hz with unfocused 420-450 nm laser illumination.

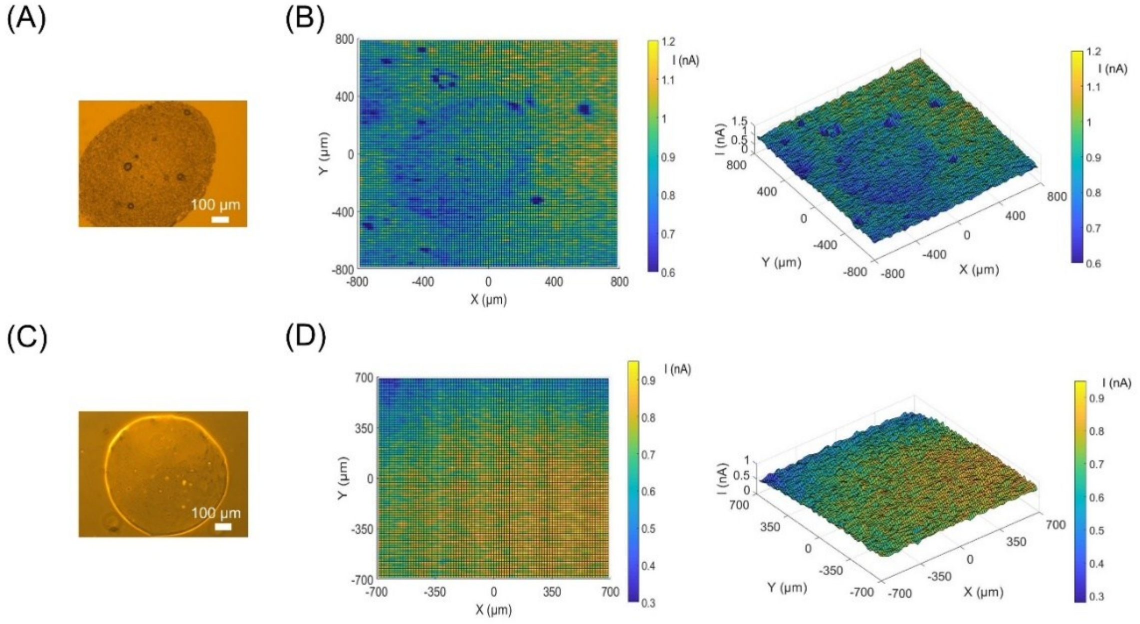

Figure S14. (A) Optical microscope image of yeast-agarose gel on ITO-silane-CD surface; (B) Corresponding ac-photocurrent image of (A) measured at 1.5 V; (C) Optical microscope image of agarose gel on ITO-silane-CD surface; (D) Corresponding ac-photocurrent image of (C) measured at 1.5 V.