Opto-electronic conversion logic behaviour through dynamic modulation of electron/energy transfer states at TiO₂-carbon quantum dot interface

Supplementary information

Experimental details:

Fabrication of CQDs/TNTs system

All chemicals were purchased from Sigma-Aldrich. In our experiments, CQDs (1-4 nm) were synthesized by a one-step alkali-assisted electrochemical approach developed by our research group,¹⁵ and TNTs were fabricated by anodization of Ti foils.²⁴ The CQDs/TNTs nanocomposite with the physical adsorption interface was prepared using a simple wet impregnation method, followed by vacuum annealing treatment at 300 °C to yield the chemical interface between CQDs and TNTs.

In a typical experiment, the electrolyte of the electrochemical process was prepared by mixing 100 mL of ethanol / H_2O (volume ratio = 99.5: 0.5) with a suitable amount (0.2~ 0.4 g) of NaOH. Using graphite rod (diameter about 0.5 cm) as both anode and cathode, we succeeded in synthesizing CQDs with a current intensity in the range of 10-200 mA/cm². The raw CQDs solution was treated by adding a suitable amount of MgSO₄ (5~7 wt% to CQDs solution, stirred for 20 min and then stored for 24h) to remove the salts and water. Afterwards, the purified CQDs solution was separated by silica-gel column chromatography with a mixture of petroleum ether and diethyl ether as the developing solvent. To confirm CQDs (within 5 nm, see Figure S1) carrying positive charges, we conducted an electrodeposition experiment. CQDs electrolyte was prepared by dissolving CQDs in 85 ml ethanol and 5 ml deionized water. The electrode position was performed with a standard two-electrode system, consisting of a graphite flake as the counter electrode and indium tin oxide (ITO)-coated conducting glass plates as the working electrode. CQDs were deposited onto the ITO surface at – 10.0 V (vs. graphite) for 1h. The surface of ITO glass varied from transparent to brown, then to black at prolonged time, as shown in Figure S2.

Characterization of the synthesized materials

The size and morphology of the samples were examined with a Philips XL30 FEG scanning electron microscope (SEM) at an accelerating voltage of 20 KV. X-ray diffraction (XRD) patterns, obtained on a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using Cu K α radiation at a scan rate (2 θ) of 0.05°s⁻¹, were used to characterize the sample crystalline phases. The accelerating voltage and applied current were 40 kV and 80 mA, respectively. The Raman spectra were obtained with a Renishaw Raman system model 1000 spectrometer with a 20 mW air-cooled argon ion laser (514.5 nm) as the exciting source (the laser power at the sample position was typically 400 μ W with an average spot size of 1 μ m in diameter). The photoluminescence (PL) spectra were obtained at room temperature employing a Horiba JOBIN YVON Luminescence spectrometer FluoroMax-4. UV-visible diffuse reflectance spectra were obtained on a UV-visible spectrophotometer (Lambda 750) equipped with an integrating sphere assembly. Fine BaSO₄ powders were used as a reflectance standard.

Photoelectrochemical and Electrochemical Measurements

Photoelectrochemical measurements were carried out using a conventional three-electrode, single-compartment glass cell fitted with a synthesized quartz window. The CQDs/TNTs electrode was employed as the working electrode, and a saturated Ag/AgCl electrode and a platinum electrode served as the reference and counter electrode, respectively. The electrolytic cell was filled with 0.1 M Na₂SO₄. Photocurrent density versus time curves were measured under simulated sunlight irradiation ($I_0 = 33 \text{ mW cm}^{-2}$). The IPCE were measured at different wavelength with a monochromatic light. For the pulse-bias tuning photoelectrochemical measurements, after the physical

deposition of CQDs on the TNTs, we used the weak bias, such as -3 V to 2 V, to treat the CQDs/TNTs electrode. For example, a nucleation pulse (E = - 2 V or -1 V etc., against Ag/AgCl) was applied for 10 s in the Na₂SO₄ electrolyte, and then the IPCE of the resulting CQDs/TNTs electrode under 0 V vs. Ag/AgCl were measured. Afterwards, different opto-electric conversion states were obtained. The electrochemical impedance spectroscopy measurements were performed using an IM6 electrochemical workstation in the frequency range from 1 Hz to 100 MHz.

Computation method

The atomistic TiO_2 -CQD- TiO_2 junction model was composed of three parts as illustrated in Figure S4: the left TiO_2 electrode region, the central CQD scattering region, and the right TiO_2 electrode region. A 7-ring C24H12 nanographene CQD was used in the simulation and placed parallel to the (100) surface of the TiO_2 electrodes. The distance between the nanographene and the surface atom layer of each electrode is L=dz+a, with a being the lattice constant of anatase TiO_2 crystal in the [100] direction. The transport simulation was carried out with the help of the Atomistix Toolkit.²⁵ The whole system was described by density functional theory (DFT) with the standard nonlocal norm-conserving pseudopotential and the one-dimensional quantum conductance G versus dz was evaluated by the non-equilibrium Green's function (NEGF) technique. The wave functions were expanded on a numerical basis set of

double- ζ plus polarization (DZP) for all atoms. The local density approximation with Perdew-Zunger (LDA.PZ) parametrization of the exchange-correlation functional was employed in the calculation. Convergence was achieved by using a Monck Horst-Pack mesh grid with (1, 1, 500) k-points in the 3D Brillouin zone of the TiO₂ and a cutoff energy of 150 Ry.



Figure S1 TEM images of CQDs.



Figure S2 Photo image of CQDs electrodeposition on ITO glass.



Figure S3 (a) IPCE spectra and (b) Photocurrent density versus time curves of CQDs / TNTs (formation of chemical bonding interface in CQDs/TNTs) measured in 0.1 M Na₂SO₄ solution under simulated sunlight irradiation ($I_0 = 33 \text{ mW cm}^{-2}$).



Figure S4 The atomistic TiO_2 -CQD-TiO_2 junction model: the left is TiO_2 electrode region, the central CQD scattering region, and the right TiO_2 electrode region.



Figure S5 The result indicates that, with the shortening of the distance between the CQD and TiO_2 surface, the conductance or charge transfer rate increases quickly.



Figure S6 IPCE spectra of pure TNTs under different bias potential treatment from -2 V to 2V.



Figure S7 the enlarged part of the decay curves for Figure 3d.