

Electronic Supplementary Information

Solvent-Tunable Dipeptide-Based Nanostructures with Enhanced Optical-to-Electrical Transduction

Huimin Xue,^{ab} Xianbao Li,^{ab} Keqing Wang,^{ab} Wei Cui,^a Jie Zhao^a, Jinbo Fei^{*a} and Junbai Li^{*ab}

^a. Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Lab of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: jbli@iccas.ac.cn

^b. University of Chinese Academy of Sciences, Beijing 100049, China.

Experimental Section

Materials

The cationic dipeptide (H-Phe-Phe-NH₂·HCl, CDP) was obtained from Bachem (Bubendorf, Switzerland). 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were purchased from Sigma-Aldrich Company. Genipin was purchased from Wako Pure Chemicals, Japan. Toluene, xylene, ortho-xylene, ethanol and acetone were obtained from the Beijing Chemical Reagents Company (Beijing, China). Deionized water was taken from a Milli-Q plus ultrapure water system (Millipore). All chemicals were used as received unless otherwise stated.

Preparation of nanospheres and nanofibers

1 mL of aqueous solution of genipin (4.5 mM) was added to 10 μ L of CDP/HFIP solution (the initial molar ratio of CDP and genipin is 1:1) and reacted in 50 °C water bath. Two days later, the colorless and transparent solution became a blue suspension. Then, it was washed three times with deionized water by centrifugation and vortexing, and then dried in a vacuum for 2 days. 1 mg CDPG powder was re-dissolved in 200 μ L of HFIP. After that, 400 μ L of different solvents (toluene, ortho-xylene, water, ethanol, acetone) were added respectively at room temperature. Five days later, nanospheres and nanofibers formed and were collected.

Construction of ITO/Nanospheres and ITO/Nanofibers photoanodes

The ITO substrates with 7 mm \times 25 mm rectangular pieces were sonicated in acetone, ethanol and deionized water for 15 min respectively and dried with a stream of N₂. Then 10 μ L of prepared solution of nanospheres and nanofibers were spin-coated on the conductive surfaces of ITO substrates separately to construct the photoanodes with one layer sample. During this process, the spin speed was set to 1000 rpm/s and the time setting was 30 s. Meanwhile, electrodes of 2, 4, 6, 8, 10 layers nanospheres or nanofibers were also constructed by spin-coating corresponding times in the same way. After that, all photoanodes were protected from light in a dry place and held for later photocurrent detection.

Characterization

The scanning electron microscopy (SEM) images of the samples were obtained with a S-4800 (Hitachi, Japan) scanning electron microscope with an accelerating voltage of 10 kV. The transmission electron microscopy (TEM) characterizations were taken with a JEM-1011 (JEOL, Japan). The atomic force microscopy (AFM) images were obtained with FASTSCANBIO (Bruker) equipment. The dynamic light scattering (DLS) measurements were recorded with Zetasizer Nano, Malvern. The optical properties and chemical bonding states of two structures were investigated by the ultraviolet–visible spectroscopy (UV-vis) absorption spectra (Hitachi U-3010) and Fourier transform infrared (FTIR) (Bruker EQUINOX 55/S). The mass spectral data was obtained using an ESI-FTICR-MS instrument. The contact angles of different electrodes were measured with a DS-100 instrument. The photocurrent response tests of the products were carried out by using an electrochemical workstation (CHI 660D).

Photocurrent measurements

The electrochemical characterization system was equipped with electrochemical workstation (CHI 660D) and a 150 W Xe lamp. The power density of the optical path system is 146 mW cm⁻². The photocurrent measurements of different photoanodes were carried out in an electrolyte buffer solutions (pH = 6.5, 20 \times 10⁻³ M MES, 50 \times 10⁻³ M KCl, 5 \times 10⁻³ M MgCl₂ and 3 \times 10⁻³ M CaCl₂) under the same conditions. During this process, the modified ITO samples (ITO/Nanofibers or ITO/Nanospheres) served as the working electrode, while a platinum wire was used as the counter electrode and SCE as the reference electrode. All experimental data was processed by baseline correction.

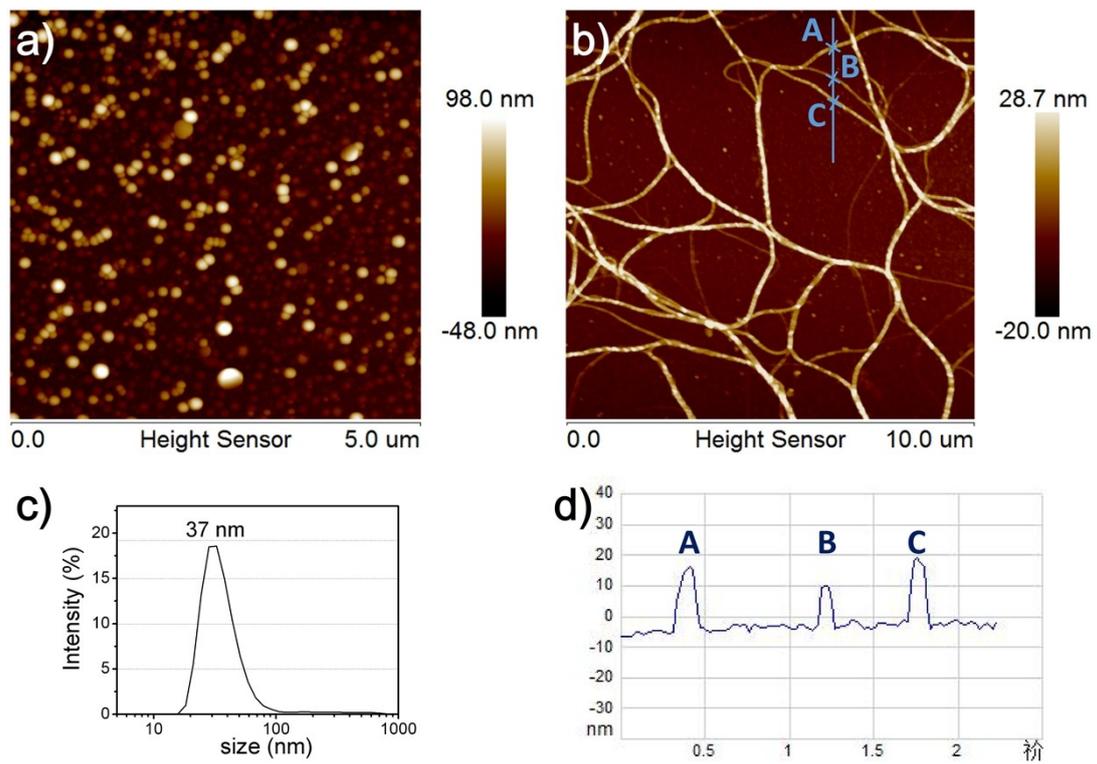


Figure S1. (a, b) AFM images of nanospheres and nanofibers; (c) DLS measurement on the size distributions of nanospheres; (d) the height profiles image corresponded to the marked fibers of A, B and C in Figure S1b.

Table S1 Morphologies of peptide-based assembly in different solvents.

type	solvent	dielectric constant	morphology
Non-aromatic	water	78.4 (25 °C)	nanospheres
	ethanol	24.5 (25 °C)	nanospheres
	acetone	20.7 (25 °C)	nanospheres
Aromatic	benzylalcohol	13.0 (25 °C)	amorphous state
	ortho-xylene	2.6 (25 °C)	nanofibers
	xylene	2.4 (25 °C)	nanofibers
	toluene	2.4 (25 °C)	nanofibers

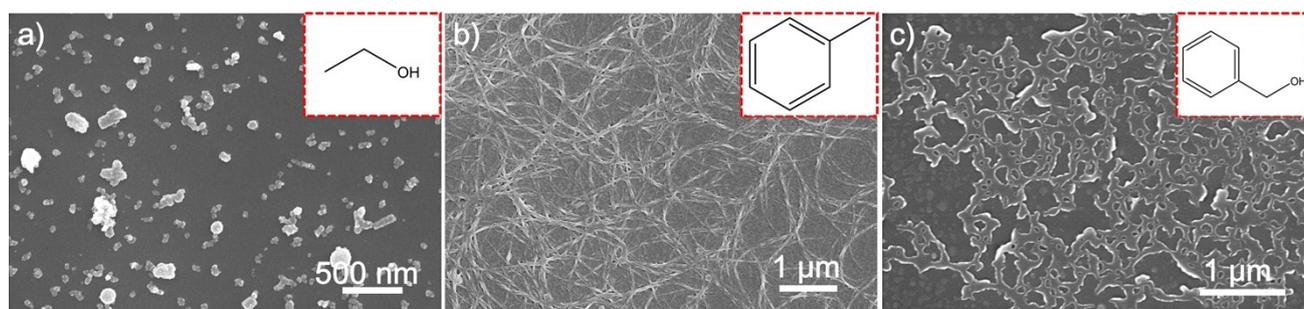


Figure S2. SEM images of sphere-like nanoparticles formed in acetone (a), twisted nanofibers formed in ortho-xylene (b) and undefined nanostructures in benzylethanol (c).

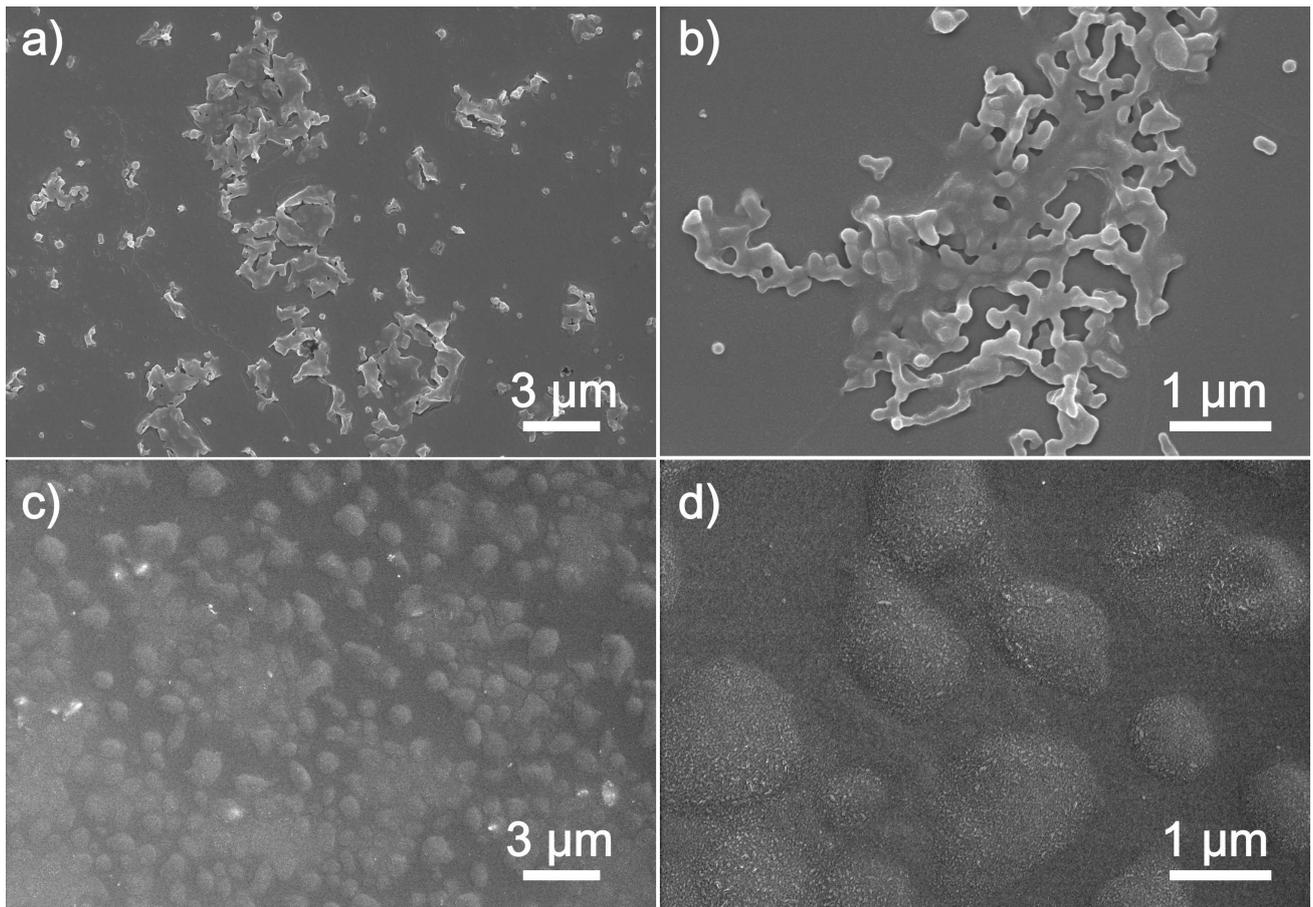


Figure S3. SEM images of CDP monomer assembled in water (a) and xylene (b); SEM images of genipin monomer assembled in water (c) and xylene (d).

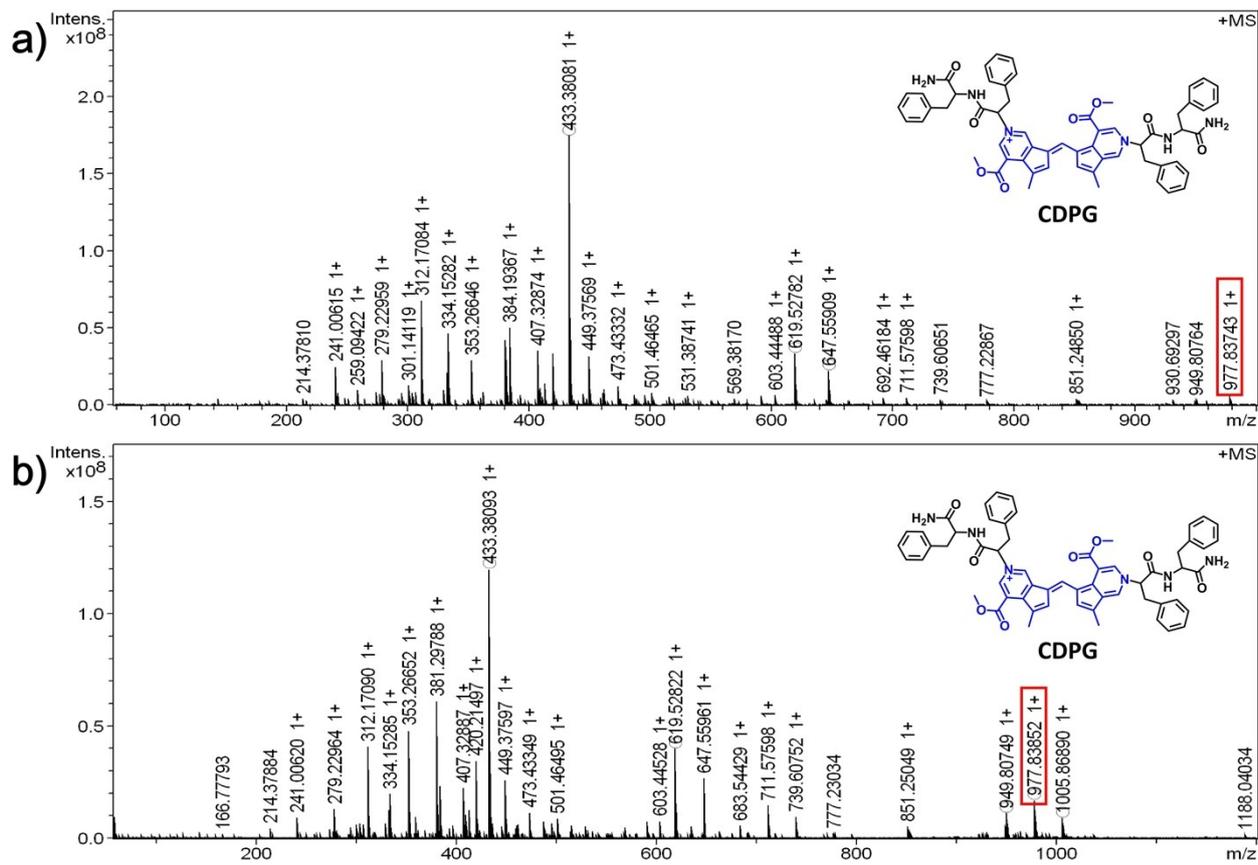


Figure S4. ESI-FTICR MS patterns of nanospheres (a) and nanofibers (b).

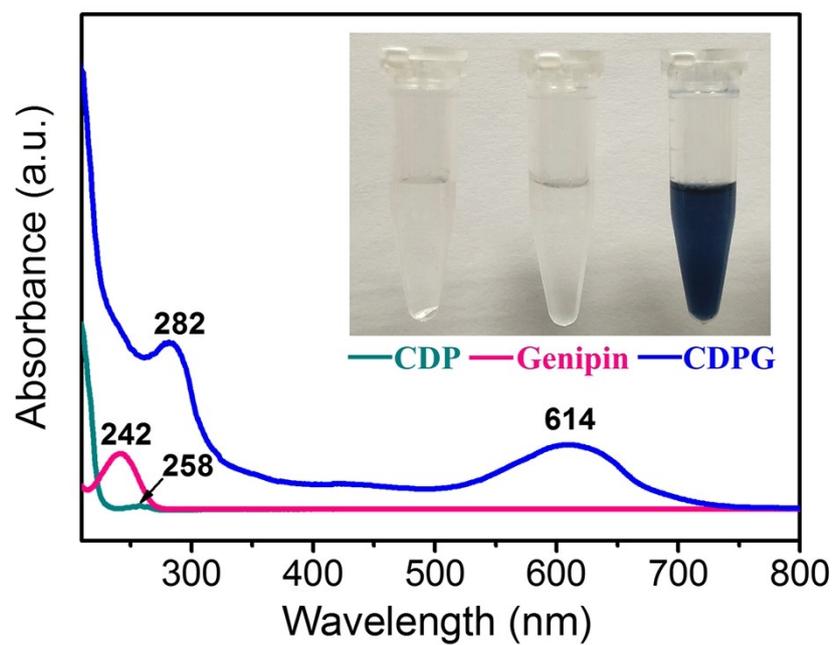


Figure S5. UV-vis spectra and relevant photo images of CDP, genipin and CDPG.

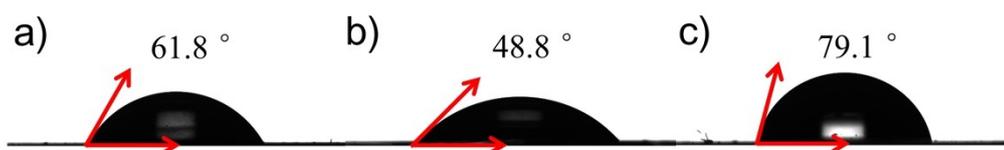


Figure S6. The contact angle measurement of bare ITO (a), ITO/Nanospheres (b) and ITO/Nanofibers (c).

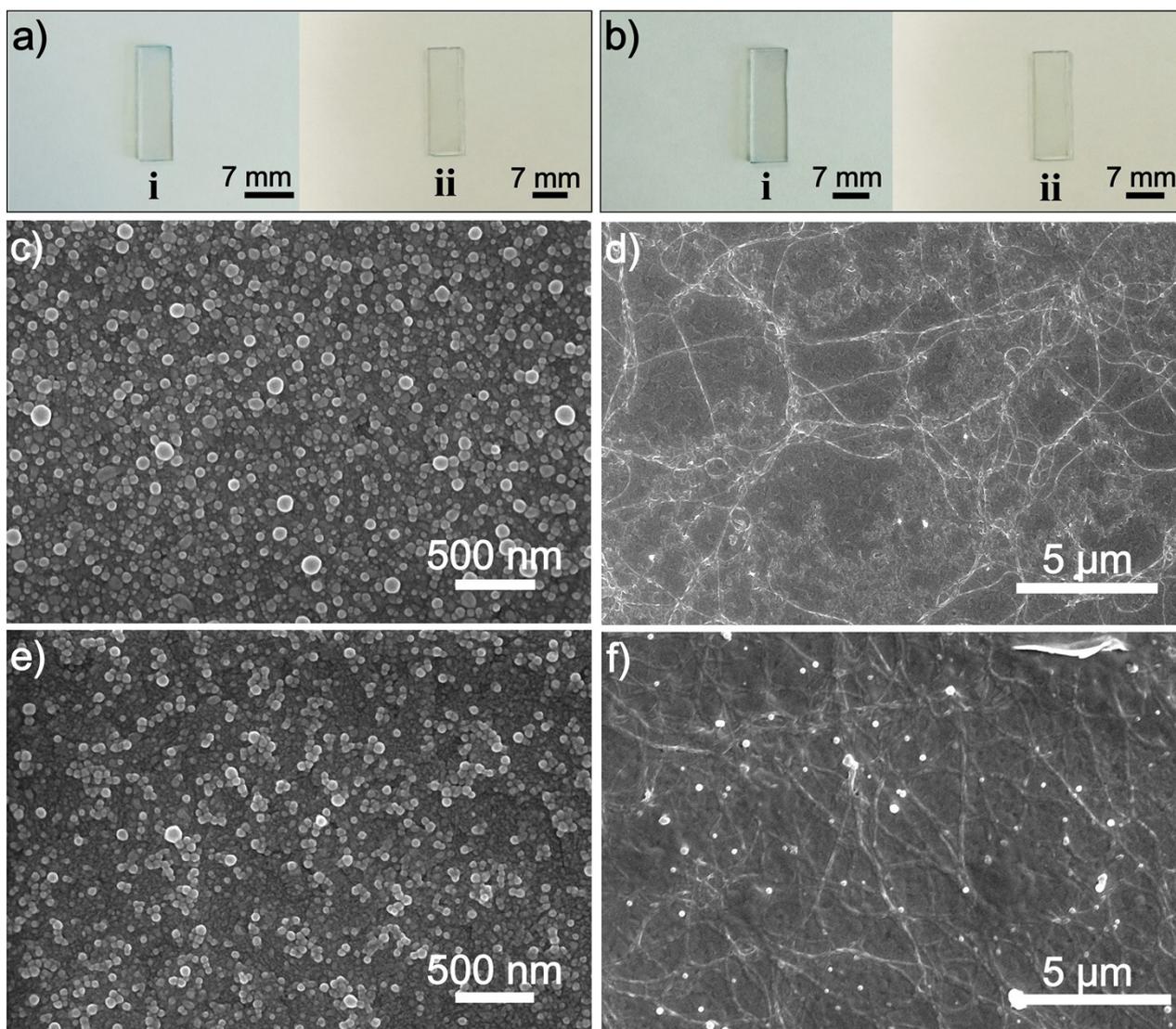


Figure S7. (a) Photo images of ITO/Nanospheres photoanode before (i) and after (ii) photocurrent response test; (b) photo images of ITO/Nanofibers photoanode before (i) and after (ii) photocurrent response test; (c, d) SEM images of ITO/Nanospheres and ITO/Nanofibers photoanodes before photocurrent response test; (e, f) SEM images of ITO/Nanospheres and ITO/Nanofibers photoanodes after photocurrent response test. The layer number of the samples mentioned above was ten.