

Supplementary Material (ESI) for *PCCP*  
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## **Phototransport in networks of tetrapod-shaped colloidal semiconductor nanocrystals**

**Isabella R. Franchini<sup>1</sup>, Adriano Cola<sup>2</sup>, Aurora Rizzo<sup>3</sup>, Rosanna Mastria<sup>3</sup>, Anna Persano<sup>2</sup>, Roman Krahne<sup>1</sup>, Alessandro Genovese<sup>1</sup>, Andrea Falqui<sup>1</sup>, Dmitry Baranov<sup>1&</sup>, Giuseppe Gigli<sup>3</sup> and Liberato Manna<sup>1\*</sup>**

<sup>1</sup> *Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy, E-mail: liberato.manna@iit.it*

<sup>2</sup> *IMM-CNR, Institute for Microelectronics and Microsystems – Unit of Lecce, Via Monteroni, I-73100 Lecce, Italy*

<sup>3</sup> *National Nanotechnology Laboratory of CNR-INFN, Via per Arnesano km 5, I-73100 Lecce, Italy*

<sup>\*</sup> *Present address: Department of Chemistry, University of Chicago, Chicago, IL 60637, USA*

### **Supporting information**

## 1. Chemicals, syntheses and assembly procedures

All syntheses were carried out in a standard Schlenk line set-up under nitrogen flow, and all following reactions and manipulations were carried out under nitrogen in a glove box. Also, all samples were stored in the glove box. All solvent used were anhydrous.

**1.1. Chemicals.** Trioctylphosphine oxide (TOPO, 99%), trioctylphosphine (TOP, 97%), cadmium stearate (90%), Tellurium (Te 99.999%), and selenium (Te 99.99%) were purchased from Strem Chemicals. Octadecylphosphonic acid (ODPA) and hexylphosphonic acid (HPA) were purchased from Polycarbon Industries. Cadmium Oxide (CdO, 99.5%), octadecylamine (ODA 97%), pyridine (Py, >99%), acetic acid (99.7+ %), 1.0 M hydrazine anhydrous solution in tetrahydrofuran were purchased from Sigma-Aldrich. Trimethylchlorosilane (TMS-Cl 99+%) was purchased from ABCR GmbH&Co. All solvents used were anhydrous and they were purchased from Sigma-Aldrich, used as received without further purification.

**1.2. Synthesis of the CdSe@CdTe tetrapods.** The synthesis of the CdSe@CdTe tetrapods was carried out via a seeded growth approach following a procedure previously published by our group<sup>1</sup>. Briefly, a solution was prepared which contained Te in TOP (Te/TOP, 0.6 g total weight, 10 wt % in Te) and previously synthesized spherical CdSe nanocrystals (~2-3 nm in diameter) having sphalerite structure. This solution was injected into a reaction flask containing a mixture of surfactants (TOPO, HPA, and ODPA) and CdO heated at 340 °C. After the injection, the resulting solution was kept at 340 °C for 3 minutes, after which it was cooled to room temperature. This solution was then washed by repeated precipitations (via addition of methanol) and re-dissolution in toluene. After the last washing step, the tetrapods were dissolved in 5 ml of toluene. The as-synthesized tetrapods were stored under nitrogen inside glove box.

**1.3. Surfactant exchange with pyridine.** A batch of as-synthesized tetrapods precipitated by methanol was mixed with 2 ml of pyridine. The mixture was refluxed at 120°C under stirring for 24 h to allow the exchange of the surfactants on the tetrapod surface. The nanocrystals were then precipitated with hexane, separated from supernatant by centrifugation and were re-dispersed in a mixture of chloroform and pyridine (the chloroform: pyridine volume ratio was equal to 9: 1) giving a stable colloidal solution.<sup>2</sup>

**1.4. Assembly of CdSe@CdTe tetrapods (either coated with phosphonic acids or with pyridine) with using Acetic Acid.** 250 µL of glacial acetic acid solution (5M) in toluene were added to 50 µL aliquot of the tetrapod solution (the concentration of the tetrapods was approx.  $4 \times 10^{-8}$  M both in toluene and in the mixture of solvents, see below for the details) at room temperature. The mixture was sonicated for 30 min at RT. The sonicator utilized was an Ultrasonic Cleaner CP102 (270W power). To remove an excess of unreacted acetic acid, a small amount of MeOH (roughly 10 µl of Methanol) was added till the solution turned turbid, after which the solution was centrifuged. The precipitate (tetrapod assemblies) was redispersed in toluene (or in the chloroform/pyridine mixture).

**1.5. Assembly of CdSe@CdTe tetrapods (either coated with phosphonic acids or with pyridine) using trimethylchlorosilane (TMS-Cl).** 200  $\mu\text{L}$  of the 0.5 M TMS-Cl solution in toluene was gradually added to 50  $\mu\text{L}$  aliquot of the tetrapod solution ( by consecutive additions of 50  $\mu\text{L}$  each) at room temperature. For bigger additions of TMS-Cl, the solution started to become turbid. No sonication was applied during this treatment.

**1.6. Assembly of CdSe@ CdTe tetrapods (either coated with phosphonic acids or with pyridine) using hydrazine.** A  $9.1 \times 10^{-2}$  M solution was prepared by dissolving 100  $\mu\text{L}$  of  $\text{NH}_2\text{NH}_2$  1 M in THF in 1 ml of toluene. Under gentle stirring, an aliquot of 25  $\mu\text{L}$  of the hydrazine solution was added to 50  $\mu\text{L}$  of the tetrapods solution at RT. After 1 h under gentle stirring the assemblies were formed (this was checked by TEM analysis of aliquots during the course of reaction). The reaction mixture was washed from the excess of hydrazine by addition of 10  $\mu\text{L}$  of MeOH, followed by centrifugation. The assemblies were re-dispersed in toluene (or in the chloroform/pyridine mixture).

**1.7 Preparation of concentrated solutions for the photovoltaic devices.** The concentration of the tetrapods in all the solutions used for the devices was about 60mg/mL. In these solutions, the molar ratios of additive molecules to tetrapods were the same as those used for the I-V studies. These solutions were prepared by more dilute solutions upon solvent evaporation under nitrogen flow.

## 2. Estimate of nanocrystal concentrations, average number of surfactants bound to their surface, and ratio of number of additive molecules to bound surfactants

**2.1 Determination of nanocrystal concentration:** This was possible by combining information from TEM and from elemental analysis. First, the average geometrical parameters of the tetrapods (arm diameter and length) were assessed via statistical analysis on transmission electron microscopy (TEM) images. At this point the average number of atoms of one atomic species per tetrapod was determined by building a structural model of the nanocrystal with the same geometrical parameters as determined by TEM (using software developed by us, which delivers a standard .pdb file with cell parameters, and atomic positions). Elemental analysis was then carried out (via Inductively Coupled Plasma Atomic Emission Spectroscopy) on diluted solutions of tetrapods. The samples were digested in HCl/HNO<sub>3</sub> 3:1 (v/v). This allowed to estimate the total concentration of a species, for example [Cd], in solution. By combining this information with the average number of Cd atoms per individual tetrapod ( $n_{Cd}$ ), it was possible to estimate the concentration of tetrapods ( $[tetrapods]$ ) in the sample:

$$[tetrapods] = \frac{[Cd]}{n_{Cd}}$$

More specifically, since the concentrations derived from elemental analysis are given in ppm, and the starting nanorods solution is diluted by a certain dilution factor, the concentration of tetrapods is derived as:

$$[tetrapods] = \frac{ppm_{Cd}}{1000 * M_{Cd} * n_{Cd}} * dilution$$

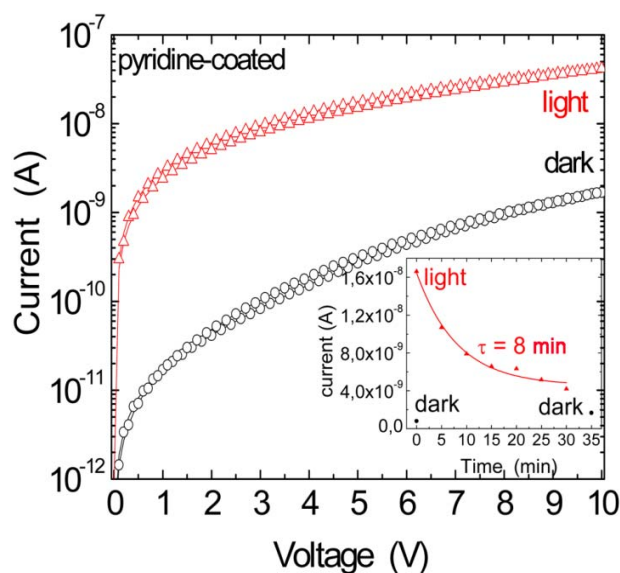
In the expression above  $ppm_{Cd}$  is the concentration in ppm of the Cd species in solution,  $M_{Cd}$  is the atomic mass of Cd, and “dilution” is the dilution factor of the solution used for the elemental analysis.

**2.2 Determination of the number of bound surfactants.** The construction of a structural model for a tetrapod allows in addition the estimate of the number of surface atoms. The .pdb file derived by our program is converted, using commercial molecular visualization software into a structure file which contains information on connectivity between atoms, for example a Cerius 2® .msi format. This file is then read again by our home-built software, which extracts from it the number of bulk atoms (namely all the atoms that have a number or nearest neighbors equal to 4 in the case of CdTe, which has tetrahedral bonding geometry) and the number of surface atoms (i.e. those that have a number or nearest neighbors less than 4). The tetrapods in our experiments had average arm length of 20 nm and width of 6 nm, as determined by statistical analysis of the series of TEM images. From the analysis of the model, each tetrapod of these geometrical parameters is found to contain in total  $7.7 \times 10^4$  atoms,  $1.8 \times 10^4$  of which are located on the surface. Of these, roughly half were Cd atoms. Assuming, by a simple model, that each surface Cd atom is bound to one surfactant molecule, and knowing the total concentration of tetrapods in the sample (see previous paragraph), we could estimate the total concentration of “bound” surfactant molecules. The molar ratios of molecules added to induce tip-to-tip aggregation and bound surfactant molecules, for the various experiments, is reported in the table below. These represent optimized values, for each treatment, in order to promote formation of the networks while still guaranteeing solubility of the networks in solution.

Treatment	[tetrapods]	[additive] (M)	[bound surfactants] (M)	[additive]/[bound surfactants]
Acetic acid	$6.7 \times 10^{-9}$	4.17	$7.2 \times 10^{-5}$	$1.2 \times 10^5$
Hydrazine	$2.7 \times 10^{-8}$	$3.0 \times 10^{-2}$	$2.9 \times 10^{-4}$	$2 \times 10^2$
Trimethylchlorosilane	$9.6 \times 10^{-9}$	0.4	$1.0 \times 10^{-4}$	$8 \times 10^3$

### 3. Transport characteristics of “as-deposited” non-annealed films

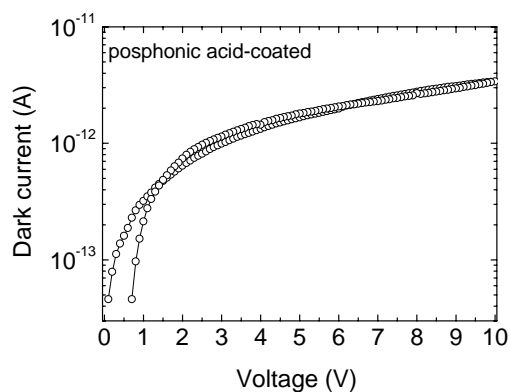
Current-voltage ( $I$ - $V$ ) characteristics under white light illumination and in the dark were first performed on the “as-deposited” (i.e. without any annealing) nanocrystal films. In pyridine-coated samples, remarkable dark currents and a significant response to the light were observed, but no saturation was seen with increasing applied voltage (Figure S1). Compared to previous studies,<sup>3</sup> here the maximum electric field (50 kV/cm) was probably too low to ensure a complete exciton ionization. Both dark and photocurrent curves were linear in a limited range of small voltages and then became slightly superlinear, which is consistent with the non-blocking behavior of the gold electrode on the nanocrystal film.<sup>4</sup> This also means that gain different than unity can occur, once the electric field is high enough that the electron collection time becomes shorter than the carrier lifetime. Current transients and hysteresis were observed during the voltage cycles, with hysteresis amplitudes depending on the timescale of the measurement and with repeating voltage cycles tending to decrease the photocurrent considerably (Figure S1, inset).



**Figure S1.**  $I$ - $V$  curves under dark (squared) and white light (cycles) for as deposited pyridine-coated tetrapod sample (non annealed). The inset shows the temporal reduction of the photocurrent taken at 1V, during successive voltage sweeps. The solid line is an exponential decay curve of 8min time constant.

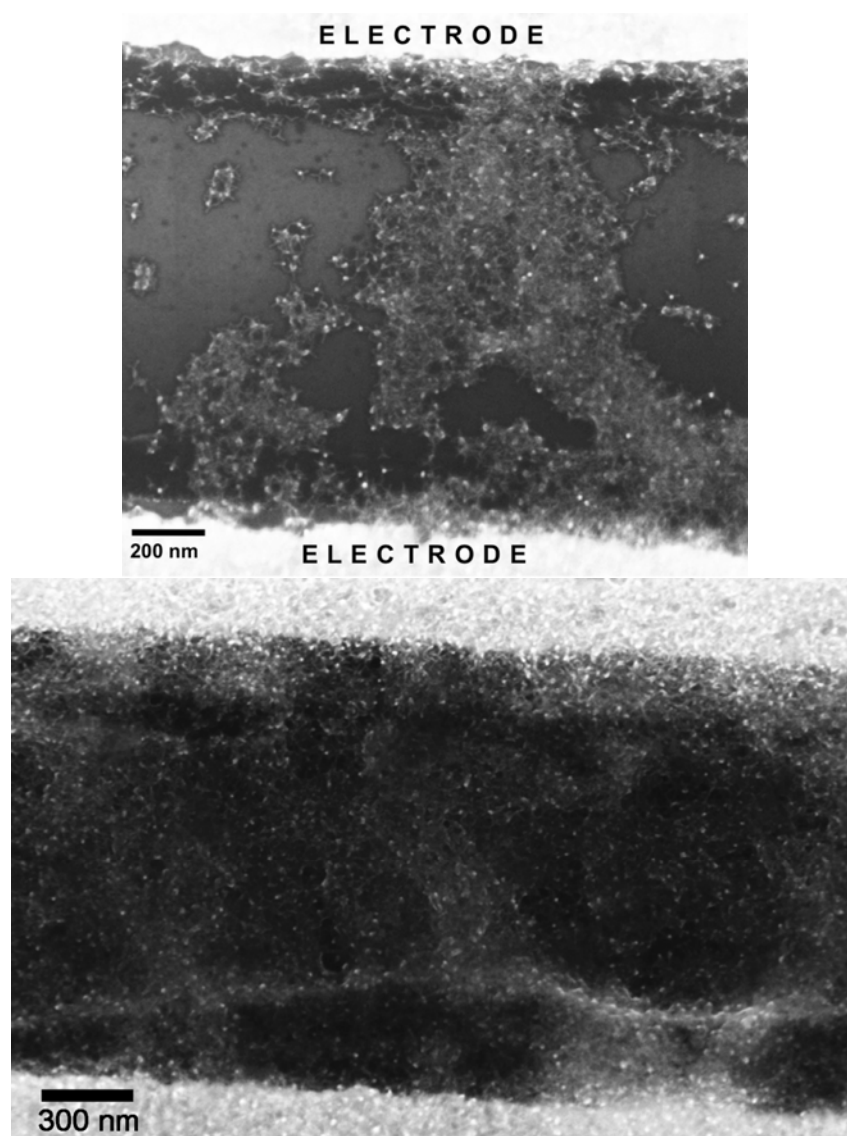
This reduction could be ascribed to charging processes in the organic molecules surrounding the tetrapod surface, as already reported for CdSe nanorods coated with trioctylphosphine oxide molecules.<sup>5</sup> In “as-deposited” films of non-assembled tetrapods coated with phosphonic acids the dark current was lower, by more than two orders of magnitude, than that from the pyridine-coated sample. Transient effects were also observed in this case and no photocurrent was recorded. It is known that the length of the molecules coating the surface of nanocrystals determines the interparticle spacing, hence the width of the potential barrier that needs to be overcome by the carriers moving in a film of

nanocrystals. Therefore the size of the ligands affects the I-V characteristics in films of nanocrystals.<sup>6</sup> The differences in currents (both photocurrents and dark currents) among the various samples prepared by us can be ascribed in part to differences in film thickness. In the present case, however, the fact that no photocurrent at all was measured on the tetrapod samples coated with phosphonic acids suggests that these large molecules are large potential barriers for the carriers.



**Figure S2.** I-V curve under dark conditions for the as-deposited phosphonic acid-coated tetrapod sample.

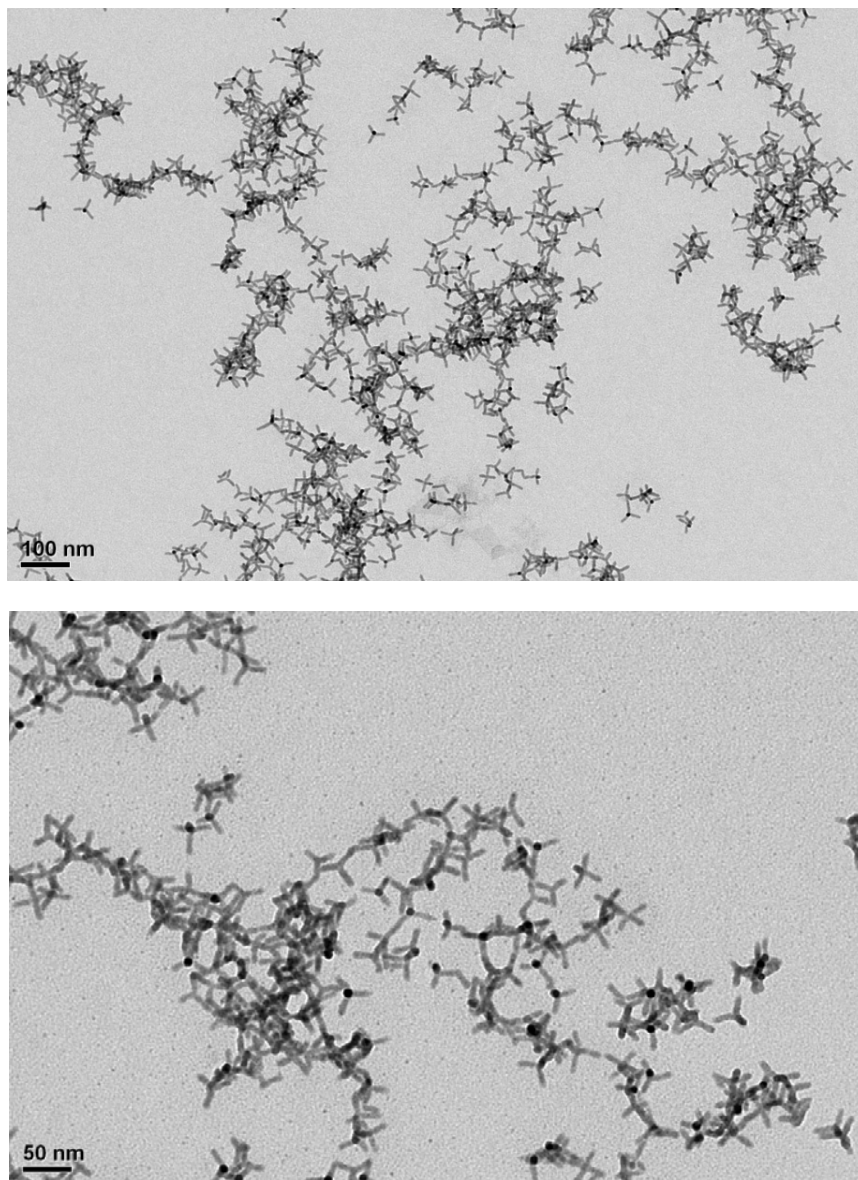
#### 4. Additional SEMs of deposited films



**Figure S3.** Typical SEM images of films of networks of phosphonic acid-coated tetrapods (obtained by hydrazine treatment) in between electrodes.



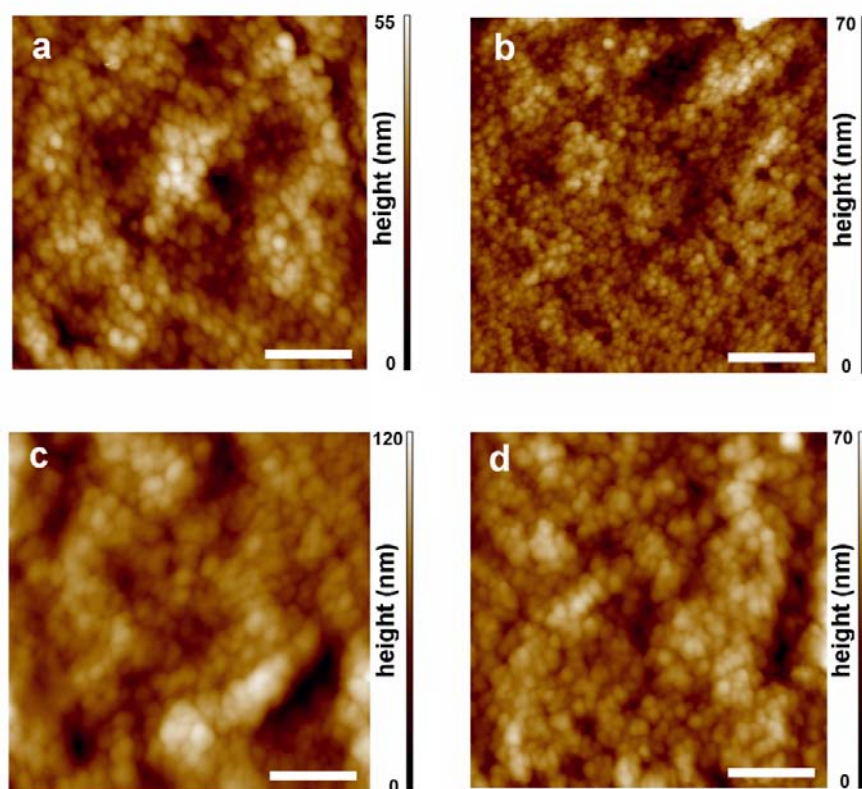
## 5. TEMs of networks before and after annealing



**Figure S4.** Top: tetrapod networks, fabricated using hydrazine, and deposited on a carbon-coated TEM grid. Bottom: a different region of the same grid, after the grid had been annealed under vacuum (approximately around  $10^{-3}$  mbar) at 450 K for 30 min.

## 5. Atomic Force Microscopy characterization of the nanocrystal films used as active layers for the photovoltaic devices

Atomic Force Microscopy (AFM) Solver Pro NT-MDT was used in a semi-contact mode to examine the morphology of the nanocrystal films made with unassembled pyridine-coated, assembled tetrapods via acetic acid, via hydrazine film, and via chlorosilane. Differences in morphology could be readily observed. As a matter of fact smaller grain are present in the sample of assembled tetrapods via acetic acid (figure S5b), while bigger grains could be observed for the sample of assembled tetrapods via hydrazine (figure S5d). These differences in the morphology can explain the difference in the PCE of the devices made with such films. Smaller grains offers a larger interface between tetrapods and C60, consequently the effective area for charge separation is bigger; this is reflected in an higher PCE for the device made with tetrapods assembled via acetic acid. The average grain size in the films of tetrapod networks assembled via hydrazine is the biggest, and consequently the efficiency is the lowest. For the samples of unassembled tetrapods and of tetrapod networks assembled via chlorosilane the grain sizes and PCEs had intermediate values.



**Figure S5.** AFM images of the different nanocrystal films used as active layer for the photovoltaic devices. (a) unassembled pyridine-coated tetrapods film; (b) networks of tetrapods via acetic acid; (c) networks of tetrapods via hydrazine; (d) networks of tetrapods via chlorosilane. The scale bars represents 500 nm.

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