Electrically-driven Assembly of CdTe Quantum Dots into Photoconductive Microwires

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I. Synthesis of TGA-capped CdTe nanoparticles

CdTe nanocrystals were synthesized by slightly modifying a previously reported method.[1] Cadmium solution was prepared by dissolving 1.0 mmol $Cd(ClO_4)_2.6H_2O$ and 1.3 mmol TGA in 100 mL Milli-Q water with continuous stirring. The pH of the solution was maintained at 12.0 by addition of a few drops of 1 M NaOH solution. Argon gas was passed through the solution for about 20 min followed by passage of H_2Te gas (generated by adding HCl solution to ZnTe) along with the inert gas for about 10 to 15 min until a change in the colour of the Cd-solution was observed. The colour change indicated the formation of CdTe nanocrystal precursors at this stage. During the synthesis process, the precursor solution becomes acidic, so some NaOH was added to bring back the pH of the solution back to 12.0 again. The solution was refluxed at 100 ºC under open-air conditions with a water condenser. Size of the CdTe nanocrystals was controlled by the duration of refluxing and monitored by recording the absorption (UV-2600 UV-visible spectrophotometer) and fluorescence spectra (Perkin Elmer LS-55 spectrometer). Finally CdTe nanoparticles were precipitated and redispersed in Milli-Q water.

II. Bulk sample characterization and calculations for CdTe NP diameter and concentration

The size and concentration of the CdTe nanoparticles were calculated using a known procedure in the literature.[2] The absorbance (A) of the CdTe nanoparticle suspension was measured as a function of wavelength of light using UV-visible spectroscopy as shown in Fig. 1a in the main text. According to Beer-Lambert's law, the absorbance of a solution is directly proportional to the concentration of the solution (c) and the path length traversed by the incident beam of light (L),

$$A = \epsilon\, c\, L$$

where, ϵ is the extinction coefficient which scales with the particle diameter. The particle diameter (d in nm) and concentration (c in M) were calculated from the below two equations

$$d = \left(9.8127 \times 10^{-7}\right)\lambda_{EP}^3 - \left(1.7147 \times 10^{-3}\right)\lambda_{EP}^2 + (1.0064)\lambda_{EP} - 194.84$$

$$A_{EP} = 3450 \times d^{2.4} \times c \times L$$

where, λ_{EP} (nm) is the wavelength of the first excitonic absorption peak and A_{EP} is the absorbance at λ_{EP}. Calculations for our system gave values of 1.4 μM for concentration and 3.58 nm for the size of the nanoparticles.

III. Electrode cleaning procedure

Platinum on glass interdigitated electrodes were washed with MilliQ water and acetone prior to each experiment, and then dipped in Piranha solution (3:1 mixture of concentrated H_2SO_4 and 30% pure H_2O_2) for 30 min. The electrodes were dried using a nitrogen purge and then encapsulated in a 5 mm wide and 120 μm thick Parafilm® chamber in order to contain the solution.

IV. Comparison between Brownian and DEP forces

The Brownian force on particles can be approximated as $F_B = k_B T/d$. For $d = 3.6\,nm$ and $T = 308$ K, $F_B = 1.21$ x 10^{-12} N. The time-averaged DEP force on particles can be calculated using the Maxwell-Wagner equation as, $\langle F_{DEP}\rangle = 2\pi\varepsilon_m r^3 \mathrm{Re}|K(w)|\nabla E_{rms}^2$ where, ε_m is the medium permittivity, r is the particle radius, ∇E_{rms}^2 is the gradient of square of the root mean square electric field and $\mathrm{Re}|K(w)|$ is the Clausius-Mossotti factor defined as $\mathrm{Re}|K(w)| = \dfrac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} + \dfrac{\varepsilon_m \sigma_p - \varepsilon_p \sigma_m}{\tau_{MW}\left(\sigma_p + 2\sigma_m\right)^2\left(1 + \omega^2 \tau_{MW}^2\right)}$. Here, ω is the field frequency, ε_p is the particle's dielectric permittivity, σ_p and σ_m are the particle and medium conductivities, respectively, and τ_{MW} is the Maxwell-Wagner charge relaxation time given as $\tau_{MW} = \dfrac{\varepsilon_p + 2\varepsilon_m}{\sigma_p + 2\sigma_m}$.[3]

The gradient of the electric field can be found out using $\nabla E_{rms} = \dfrac{\partial E}{\partial x}$ where, E = $E_0 e^{-x/c}$ is the electric field intensity assuming that the electric field decays exponentially at the surface. E_0 is the applied electric field across the electrodes (max. 0.25 V/μm) and c is the total microdroplet height (~ 100 μm). The dielectric constant of water taken as $\epsilon_m = 78.5$ (at 298 K) is virtually independent of frequency of the applied electric field up to 40,000 MHz[4].

2

The conductivity of water is taken as 5.5 µS/m. The complex permittivity of the TGA-stabilized CdTe QDs is described as[5]

$$\varepsilon_p = \varepsilon_{TGA} \left(\frac{(\frac{R_2}{R_1})^3 + 2\frac{\varepsilon_{CdTe} - \varepsilon_{TGA}}{\varepsilon_{CdTe} + 2\varepsilon_{TGA}}}{(\frac{R_2}{R_1})^3 - \frac{\varepsilon_{CdTe} - \varepsilon_{TGA}}{\varepsilon_{CdTe} + 2\varepsilon_{TGA}}} \right)$$

where, R_1 is the radius of the CdTe core (1.8 nm) and R_2 is the radius of the TGA-capped particles (2.4 nm). It is known from the literature that $\varepsilon_{TGA} = 2.25$ and $\varepsilon_{CdTe} = 11$. Using the above equation, we obtain ε_p as 4.36. Assuming CdTe bulk conductivity of the order of medium conductivity, the Clausius Mossotti factor can be calculated as 0.46. Based on the above experimental values, F_{DEP} is calculated to be equal to 4 x 10^{-21} N at 1 µm above the bottom surface which is many orders of magnitudes smaller than the Brownian force. The DEP force further reduces as we move away from the bottom electrodes.
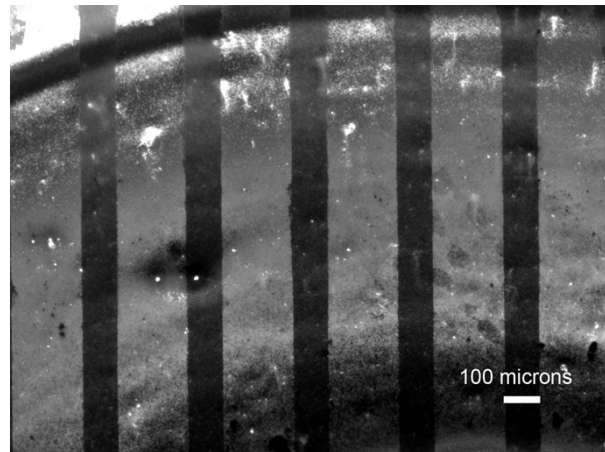

Figure S1. Bright ring formation on the outer rim of the droplet's three-phase contact line when it is dried without electric field.
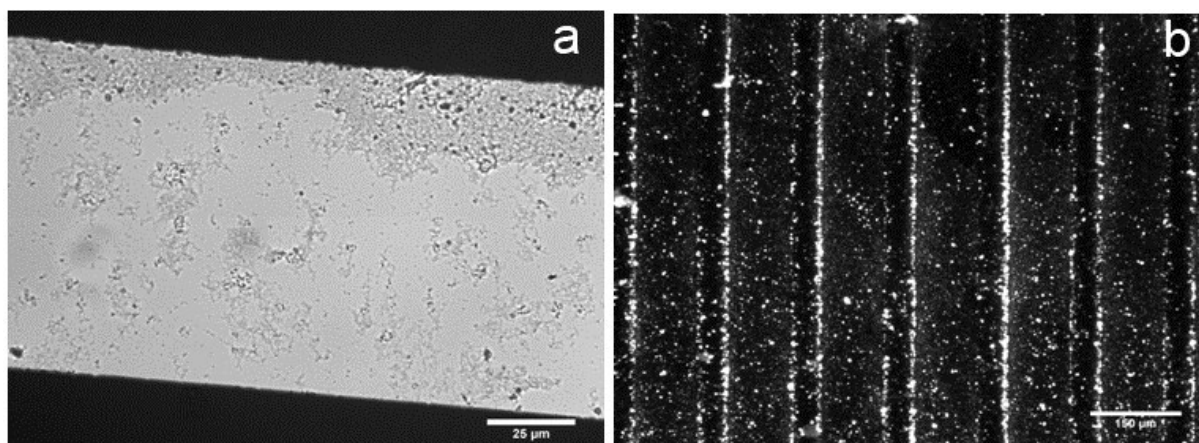
Figure S2. Electric field-driven assembly of CdTe QDs in the absence of any rehydration step. (a) In DI water using 0.1 V/µm and 10 kHz. Scale bar represents 25 µm. (b) In toluene using 3 V/µm and 10 kHz. Scale bar represents 150 µm. In both cases, particle assembly began at the edges but the electrodes remained unbridged due to lack of sufficient time for complete microwire formation.
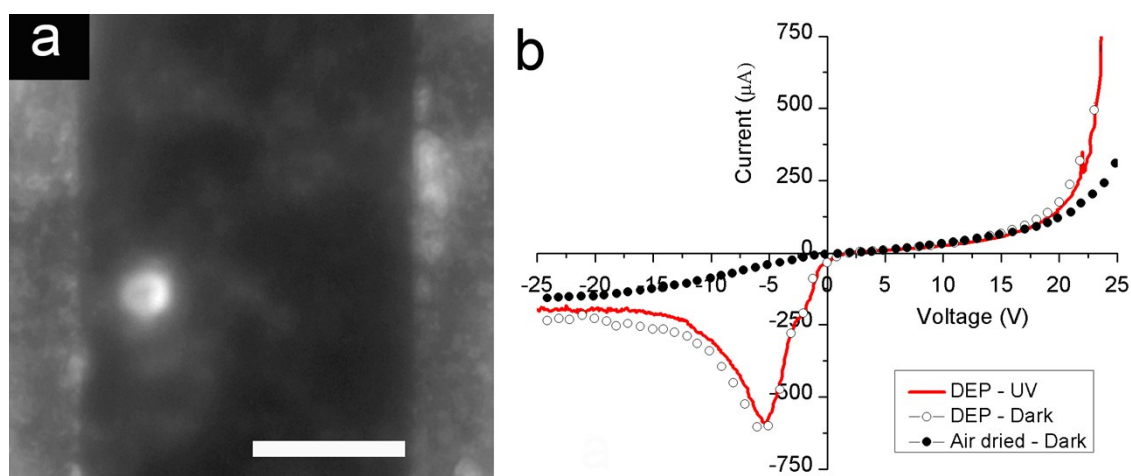

Figure S3. (a) Concentration-dependent fluorescence image and (b) I-V measurement of 1 µM aqueous CdTe suspension used to form microwires at 12 V and 10 kHz electric field conditions. The number of rehydration steps were kept at five. The poor visibility of microwires in (a) is attributed to the oversaturation of intensity leading to poor contrast with the background. The scale bar is 25 µm. The highest current was measured up to 8 mA at 25 V.

References

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