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COMMUNICATION

Electrically-driven Assembly of CdTe Quantum Dots into Photoconductive Microwires

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A low strength AC electric field applied across a drying aqueous CdTe nanoparticle suspension above 100 μm gap interdigitated electrodes allows rapid assembly of photoconductive microwires. The fabrication procedure is scalable for commercial photoelectronic applications as it does not require organic solvents, lengthy ligand-removal procedures, expensive microfabrication or any sophisticated instrumentation.

Quantum dots (QDs) are presumably the most studied nanomaterials in the current global energy landscape due to their unique positioning in the photovoltaic and semiconductor industry.[1] As a consequence, methods that enable rapid QD assembly into functional mesoscopic architectures and nanoscale devices that can be harnessed in the emerging fields of optoelectronics[2] and nanobiotechnology[3] have also garnered significant attention. In the past two decades, many techniques have been reported which allow the facile self- and directed-assembly of nanoparticles in external fields.[4] One of the pioneering works by Kotov's group showed self-assembly of CdTe nanoparticles into freely suspended nanowires under tightly controlled experimental conditions of pH, light and particle-capping ligand concentrations.[5] The particle assembly process was, however, slow and took place over several days. The same group recently illustrated an alternate technique for QD microwire formation across 2 μm electrodes using dielectrophoresis (DEP), reducing the fabrication time to only a couple of hours.[6]

DEP, in general, is one of the most widely used techniques for on-chip assembly of a wide range of particle types.[7] The DEP force scales with the particle size (r), field gradient (∇E_{rms}^2), and the effective polarizability of the particles with respect to the surrounding medium ($\mathrm{Re}|K(w)|$) as $\langle F_{DEP} \rangle = 2\pi\varepsilon_m r^3 \mathrm{Re}|K(w)|\nabla E_{rms}^2$ (**see SI for details**).[8] For small particles below ten nanometer size range, dispersive forces due
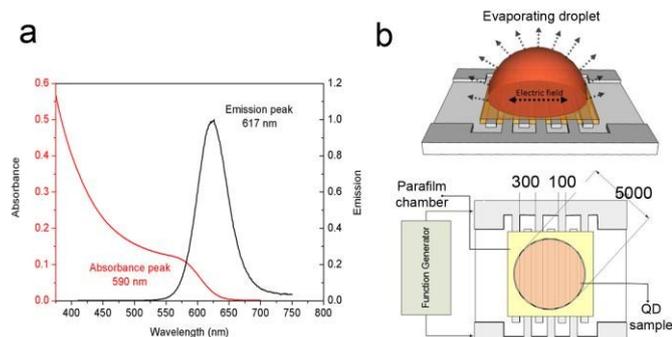
to Brownian motion largely dominate over the size-dependent DEP-induced dipolar interactions by several orders of magnitude unless the nanoparticles are made of highly polarizable metals like Au, Ag or Pd (dielectric constant infinite). Therefore, DEP assembly becomes a real challenge for alignment of 2 - 5 nm quantum-confined nanocrystals which have an effective dielectric constant of only ~ 11. This is unless one uses (i) highly miniaturized electrodes to generate large electric field gradients of strength ~ 10 V/μm, (ii) non-polar organic solvents to somewhat enhance the effective polarizability of the particles and avoid bubble formation due to Joule heating, and (iii) anisotropic particles like nanorods to aid in one-dimensional alignment.[9] Further to this, size-selective precipitation and controlled removal of particle surface capping ligands is needed to both impart intrinsic dipolar asymmetry to the nanoparticle surface and to reduce the overall effects of steric hindrance.[10] Achieving all the above conditions is not only practically difficult but also renders the entire semiconducting microwire formation process unscalable for high-throughput production of photovoltaics.

In this communication, we demonstrate a simple, one-step benchtop strategy for QD assembly into photoconductive microwires using IDEs (platinum on glass) with gap sizes as large as 100 μm. These electrodes can be fabricated in any standard laboratory with basic microfabrication and sputtering facilities. Thioglyocolic acid (TGA)-capped CdTe nanoparticles of size 3.6 nm were synthesized using a standard protocol, and their size and concentration were determined from the absorption spectra shown in **Fig.1a** (also see **SI**).[11] The particles were resuspended in water without performing size-selective precipitation and 10 μL of this aqueous suspension was deposited above the IDEs (**Fig. 1b**). The microdroplet was then allowed to dry in the presence of an externally applied AC electric field such that no bubble formation took place during the evaporation process. Control experiments were performed under identical conditions in the

absence of electric fields. The entire experiment was carried out by maintaining the surface temperature of the electrodes at 35 °C using a hot plate (humidity ~ 55 %). No sophisticated environmentally-controlled chambers were employed as reported in earlier studies.[6,9c,9d]

Figure 1. a) Absorption and photoluminescence spectra of the CdTe QDs used in our experiments. The FWHM of the emission peak is 57 nm. (b) Side view of the drying droplet (top) and top view of the experimental setup (bottom). The units for electrode gap sizes are all in microns.

The electrode chips were imaged upon drying using an optical fluorescence microscope (Olympus BX53) and a CCD camera (Pixelfly, PCO). In the DEP-dried samples, QDs arranged into a meshed network of one-dimensional microstructures which extended away from the electrode edges toward the glass surface bridging across the electrodes (**Fig. 2a**). This network formation was observed throughout the entire surface area of the drying chamber (~ 20 mm²). A large proportion of the QDs were also deposited on the electrode surface especially along the edges where the electric field intensity was the highest. No such microwire assembly took place anywhere in the control samples where instead, a majority of the particles got collected uniformly at the outer rim of the droplet's three-phase contact line forming a bright ring structure on the chip due to the well-known coffee-stain effect **(Fig. 2b & Fig. S1)**. An earlier study by Rakovich *et al.*[12] demonstrates that it is possible to form hundreds of micrometer-long QD microwires at the drying periphery of an evaporating droplet but in our experience, only the electric field allows modulation of the assembly process in terms of uniform coverage and alignment of the wires between the electrodes which is essential for any photoelectronic application.

We hypothesize that the capillary forces operating during evaporation play a key role in the microwire assembly process. These forces are responsible for rapidly bringing the particles close together such that beyond a minimum critical aggregate size, DEP forces overcome the thermal forces in order to align the particles into chains (**see SI for calculations).** This hypothesis is supported by the fact that a key component in the assembly process is a set of iterative rehydration steps without which the bridging of the electrodes cannot be achieved (**Fig. S2**). Just before the droplet is about to dry completely, the chamber is refilled with ultrapure DI water in order to increase the effective time for nanoparticle aggregation. This rehydration step is repeated a number of times and can be optimized for any given set of

system conditions to enable efficient microwire formation spanning the electrodes. The extent of particle aggregation was confirmed by scanning electron microscopy (SEM) (Zeiss EVO 50) which showed visible morphological differences between the electric field-exposed and control samples. The particles were more fused and aggregated in the DEP-dried samples as compared to the relatively well-dispersed arrangement in the control substrates (**Fig. 2c and d**).
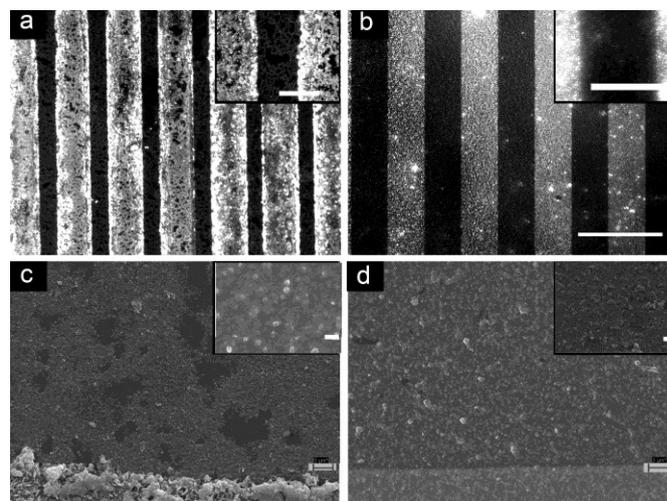
To check if the microwire assembly process is not just an artefact of a faster drying process due to the thermal heat generated by applying the electric field, we carried out an additional experiment in which we matched the drying time of a non-rehydrated DEP sample to that of an air-dried control sample. The time of drying was maintained constant by keeping the surface temperature of the control slide higher (~ 60 °C) than the one with DEP using a hot plate. In this case, as usual we saw the appearance of big QD aggregates but no discernable microwire network formation which further confirmed the role of DEP in the microwire assembly process.


Figure 2. Fluorescence microscopy images of five times rehydrated 0.3 μM samples: (a) DEP-dried (12 V, 10 kHz) showing microwire assembly and (b) air-dried without electric field. Scale bars represent 250 μm. Insets with scale bars corresponding to 100 μm show zoomed-in images of the samples. Corresponding SEM images of the (c) DEP-dried and (d) air-dried samples highlighting topological differences in the particle aggregate formation especially near the electrode edges. Scale bars represent 3 μm in the larger images and 1 μm in the insets.

The fabricated microbridges displayed red luminescence, characteristic to the colour of the original single QDs, suggesting that the particles retained their size-dependent quantum-confinement and did not fuse or recrystallize after organization into larger dimensions. This may happen if the surface ligands prevent the nanoparticles to approach each other beyond a critical distance at which the excitation transfer and other quantum mechanical effects between the nanoparticles can take place. Detailed photoluminescence studies are currently underway to understand the role of capping ligands in our system. We also measured the photoresponsive current-voltage (I-V) properties of the semiconducting microwires as a function of particle concentration by applying a voltage sweep of -25 to 25 V using a Keithley 2611A sourcemeter. At the lowest CdTe concentration of 0.1 μM, photoelectric currents of up to 15 μA were measured for samples

illuminated with a 6 Watt UV lamp (Ultraviolet fluorescence analysis cabinet, Scientech) (**Fig. 3a,b**). The samples were placed 15 cm from the light source. The current values compare well with the ones reported in literature.[6] No currents were registered in the absence of UV radiation or in the control air-dried samples both with and without UV exposure.

When the nanoparticle concentration was increased to 0.5 μM, the magnitude of the photocurrents in the UV-illuminated samples rose to 100 μA as expected but there was also a significant residual current generated in the samples kept in dark (**Fig. 3c,d**). Since the particle surfaces are not in actual contact, this electronic jump behaviour was ascribed to the quantum tunneling effects between neighboring particles or due to the presence of salts which may remain upon drying of ultrapure DI water. At an even higher CdTe concentration of 1 μM, the number of nanoparticles between the electrode surface became so excessively high that it caused current flow (up to 8 mA) even in the UV-illuminated control samples (**Fig. S3**). The control samples kept in dark showed 30 times less current indicating the versatile tunability of our process to fabricate structures which display a wide electrical range keeping with the demands of the light sensors and optoelectronics industry. We have not yet looked in-depth into the results of non-zero current at zero voltage and the diode-like knee and breakdown voltage but these effects have been reported previously in literature for CdTe solar cells.[13] Such photovoltaic effects are noteworthy and show promising applications in these fields.
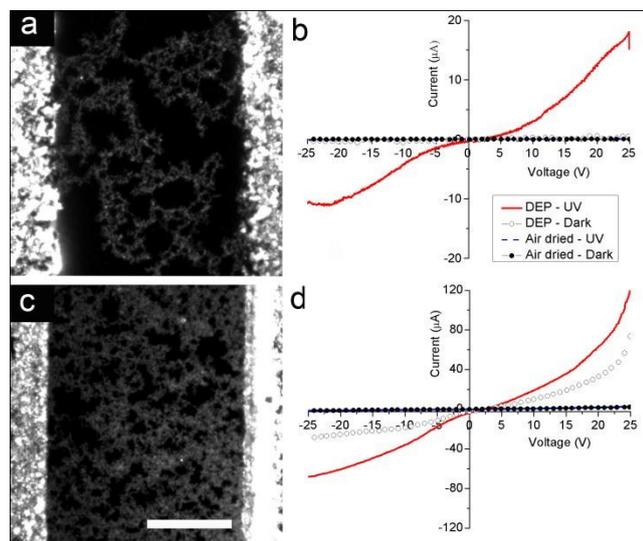
Figure 3. Concentration-dependent fluorescence images and I-V measurements of microwire networks formed from (a, b) 0.1 μM and (c, d) 0.5 μM aqueous CdTe suspensions. A DEP condition of 12 V, 10 kHz and five rehydration steps were used in all the cases. The scale bar is 25 μm.

Conclusions

We have demonstrated a simple and cost-effective method to fabricate tens of micrometer long optically-active semiconducting wires on IDE-coated glass substrates which can potentially be used in new generation nanoelectronic devices. The assembly was governed by the relative contributions from electrical, thermal and capillary forces in a drying droplet, the dynamics of which was simply modulated using an undergraduate laboratory electrical setup and a hot plate. The most crucial component in the particle size evolution process was a set of iterative rehydration steps which allowed gap sizes as big as five orders of magnitude larger than the particle size to be bridged using < 0.25 V/μm electric fields. The electronic density of the microwire networks was attained in the broad μA to mA range by simply varying the nanoparticle concentration in the initial suspension. We believe that temperature, voltage, frequency, design of the capping ligand and the number of rehydration steps can all be independently tuned to achieve in-situ nanoparticle assembly at any lengthscale. This can have far-reaching implications on the current strategies for microfabrication of miniaturized devices.

Notes and references

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Low energy, low cost quantum dot nanocrystal assembly into one-dimensional microwires for optoelectronic device applications.