

Electrophoretic deposition of ZnO nanoparticles, from micropatterns to substrate coverage

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Abstract

We report on an electrophoretic deposition (EPD) method that is suited for the preparation of both ZnO thin films and micropatterns. By applying small DC voltages between a Cu electrode and a conductive Si substrate, submersed in a suspension of ZnO quantum dots, we can cover entire substrates with ZnO layers of a tuneable thickness ranging from a few monolayers to 200 nm. The deposition occurs selectively at the cathode, which indicates that the ZnO particles have a positive charge. Atomic force microscopy was used to study the influence of the deposition voltage, time, and the quantum dot concentration on the final layer thickness. By using lithographically patterned Si substrates, the same technique enables the formation of ZnO micropatterns of variable thickness with dimensions down to 5 μm . This is done by depositing a ZnO layer on a Si substrate that is covered with a patterned, developed photoresist. After EPD, the resist is removed by submersing the substrate in the appropriate solvent without damaging the ZnO deposit. This illustrates the robustness of the layers obtained by EPD.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nowadays, colloid chemistry techniques enable the preparation of monodisperse suspensions of nanocrystals for a wide range of metal and semiconductor materials at relatively low cost [1]. Because of their size-tuneable optical and electrical properties [2, 3], and the possibility of flexible wet processing, these colloidal nanocrystals or quantum dots (QDs) are interesting building blocks for applications in biolabeling and biosensing [4], (opto)electronics [2, 5, 6], and photovoltaics [7]. Often, such applications require the assembly of individual nanocrystals into larger structures like monolayers, thin films or supercrystals. This can be achieved by different techniques, that all have specific advantages and drawbacks. Langmuir–Blodgett deposition, for instance, can be used to prepare one or a few more close packed monolayers

but is not suited to prepare thicker quantum dot films [6, 8]. Spincoating and dropcasting allow substrate coverage with quantum dot films ranging from submonolayer deposits to micrometer thick layers. However, in particular, spincoating is not compatible with local deposition processes involving the filling of templates of varying dimensions, since there is no real driving force present to direct the particles to the substrate.

With charge-stabilized colloids, electrophoretic deposition (EPD) offers an alternative to make nanocrystal assemblies that applies to both full surface coverage and local deposition. The basic idea behind EPD is that charged particles will be driven to and deposit on a surface when an electric field is applied perpendicular to the substrate [9]. It has already been shown that electrophoretic deposition is suited for the fabrication of films [10], wires [11] and micropatterns [12] of colloidal quantum dots. A typical example of QDs that are synthesized as charge-stabilized colloids are ZnO QDs prepared by alcoholic hydrolysis–

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condensation methods [11, 13, 14]. As a wide band gap semiconductor with a high exciton binding energy, ZnO is a promising material for use in short-wavelength optoelectronics such as lasers, LEDs and photovoltaics [15]. EPD of ZnO QDs has already been studied by some groups, demonstrating the formation of either micrometer thick layers over large surface areas [16–19], or patterns by using templates [19]. Also, ZnO nanowires and nanotubes can be produced by depositing ZnO QDs inside anodic alumina membranes [17].

In this paper, we present an EPD method for colloidal ZnO QDs of 2.5–4 nm in diameter. In contrast to the results in the present literature, it allows for full surface coverage with very thin, nanometer thick ZnO layers and micropatterning by means of a lithographic mask. By working in an apolar solvent mixture at relatively low ZnO QD concentration, we prepare thin ZnO layers with a thickness tuneable between a few QD monolayers to 250 nm or more. This differs from EPD processes in alcoholic media where higher QD concentrations result in micrometer thick quantum dot layers [17]. First, we demonstrate the feasibility of our approach by estimating the time needed for monolayer coverage. After demonstrating EPD of ZnO QDs in a second step, we assess the relation between deposition time, voltage, QD concentration and the thickness of the ZnO deposits. Next, we illustrate that the EPD procedure we propose can be combined with photolithography in order to prepare ZnO QD micropatterns. Therefore, we use a substrate covered with a patterned, developed resist. After EPD and resist lift-off, ZnO patterns on a Si substrate are retained. Finally, we investigate the influence of the EPD processing on the properties of the ZnO QD deposits.

2. Theory

The deposition rate of colloidal particles that are driven to a substrate by the presence of an electric field can be expressed by a relation derived from the equation of Hamaker [20, 21]:

$$\frac{dN_{\text{QD}}}{dt} = f c_{\text{QD}} A \mu E. \quad (1)$$

Here, N_{QD} is the number of deposited QDs (mol), t is the deposition time, f is a loss factor, c_{QD} is the QD concentration (mol l⁻¹), A is the exposed electrode surface (2.0×10^{-5} m²), E the applied electric field, and μ the electrophoretic mobility. If we assume that all parameters governing the deposition rate are time independent, and neglect losses ($f = 1$), we can integrate formula (1) to obtain N_{QD} as a function of time:

$$N_{\text{QD}} = c_{\text{QD}} A \mu E t. \quad (2)$$

In a close packed monolayer, the area occupied by a single QD is about equal to that of a square with sides d_{QD} . Thus, the molar number of QDs needed to cover the exposed part A of the substrate with one layer of QDs ($N_{\text{QD,mono}}$) is given by

$$N_{\text{QD,mono}} = \frac{A}{d_{\text{QD}}^2 N_A}. \quad (3)$$

Therefore, the time needed to obtain monolayer coverage of the substrate (t_{mono}) can be calculated from

$$1/t_{\text{mono}} = d_{\text{QD}}^2 N_A c_{\text{QD}} \mu E. \quad (4)$$

To estimate t_{mono} , we need an expression for the electric field and for the electrophoretic mobility. We obtain the field from the ratio $\Delta V/\varepsilon d_{\text{el}}$, where ΔV is the potential difference between the electrodes, ε the dielectric constant of the solvent, and d_{el} the distance between the electrodes. The electrophoretic mobility of the nanocrystals follows from their zeta potential. Unfortunately, the zeta potential of the QD suspensions used here could not be measured because CHCl_3 , which is used as the majority solvent (see section 3), damages the experimental setup. However, with nanometer sized particles in an almost apolar solvent, we may assume that the Debye length will be much larger than the particle diameter. Therefore, we can write the electrophoretic mobility μ as [22]

$$\mu = \frac{Ze}{3\pi\eta d_{\text{QD}}}. \quad (5)$$

Here, Z denotes the net number of elementary charges on one QD particle, e is the elementary charge, η is the viscosity of the solvent mixture (0.65×10^{-3} Pa s), and d_{QD} is the hydrodynamic diameter of the QDs. Since no organic ligands are present at the nanocrystal surface, we equate the hydrodynamic radius of the particles with the hard sphere particle radius found from transmission electron microscopy (TEM).

3. Experimental details

3.1. ZnO nanoparticles

Colloidal ZnO nanocrystals were prepared based on the wet chemical procedure by Schwartz *et al* [11]. $(\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}$ (TMAH, 2.5 mmol), dissolved in dry ethanol (5 ml), was added dropwise to a solution of $\text{Zn}(\text{Ac})_2$ (0.1 M) in dimethylsulfoxide (DMSO, 15 ml), under vigorous stirring at room temperature. With this procedure, ZnO nanocrystals ranging from 2.5 to 4.5 nm in diameter can be obtained. Absorption spectra were collected with a Cary 500 UV–vis–NIR spectrophotometer (Varian) using quartz cuvettes with an optical path length of 1 cm to determine the particle size [14, 23] and the QD concentration [23] of the suspensions used for EPD.

3.2. Suspensions for EPD

The ZnO nanocrystals as obtained after colloidal synthesis were precipitated with excess ethylacetate and resuspended in an equal volume of ethanol. For a typical EPD experiment, the ZnO QDs were resuspended in a 1:5 EtOH/ CHCl_3 mixture, with QD concentrations varying between 10 and 40 M. No extra chemical additives such as binders were used.

3.3. EPD process

A schematic drawing of the EPD cell used is shown in figure 1. Two Cu disks are used as the electrodes. The distance between the electrodes can be varied between 1 and 3 cm. An n-type Si or Au substrate, which can serve both as the cathode and as the anode, is attached to the bottom electrode. A DC voltage ranging between 20 and 100 V is applied and deposition times

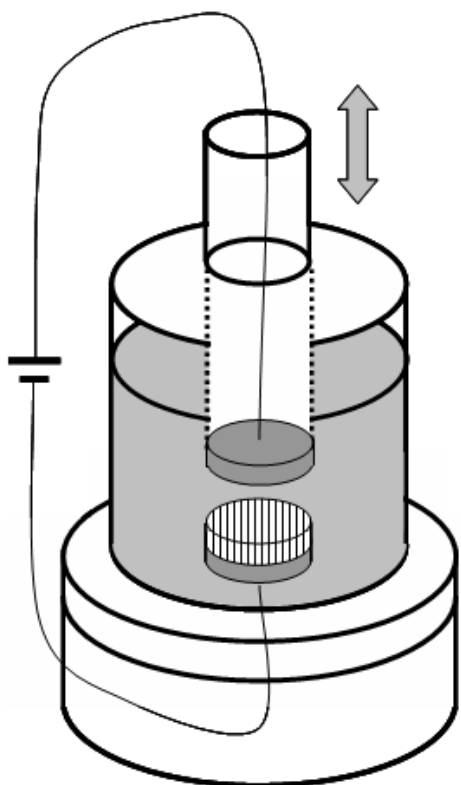


Figure 1. Schematic drawing of the Teflon cell used for EPD. Two disk-shaped Cu electrodes are used. The substrate is mounted on the bottom electrode. To decrease the contact resistance between the electrode and the Si substrate, an In–Ga eutecticum was applied. The distance between the electrodes can be varied from 1 to 3 cm.

ranging from 1 s to 60 min are used. A deposition area of 0.2 cm² is exposed to the ZnO suspension. Prior to use, the n-type Si substrates are etched for 2 min in a 2% aqueous HF solution to enhance the reproducibility of the procedure. When repeating the same ZnO QD EPD experiments on HF etched Si three times, we can reproduce a desired layer thickness within 5%. It was found that HF etching prior to deposition is crucial to achieve this reproducibility.

3.4. Photoresist

For the preparation of microstructured patterns, a negative resist (nLOF 2070, MicroChemicals) is used. After spincoating, the resist is developed with AZ-726MIF developer. The patterned substrates are postbaked at 140 °C to increase their resistance towards organic solvents. Regardless of postbaking, we found that the resist slowly detaches from the Si substrate when it is exposed to the QD suspension for more than 60 min. To remove the resist after EPD, the samples are submersed in 1-methyl-2-pyrrolidone and rinsed with EtOH.

3.5. Film analysis

The films obtained after EPD were analyzed using scanning electron microscopy and energy-dispersive x-ray (SEM/EDX) analyses (Quanta 200F, FEI) and photoluminescence spectroscopy (FS920 luminescence spectrometer, Edinburgh

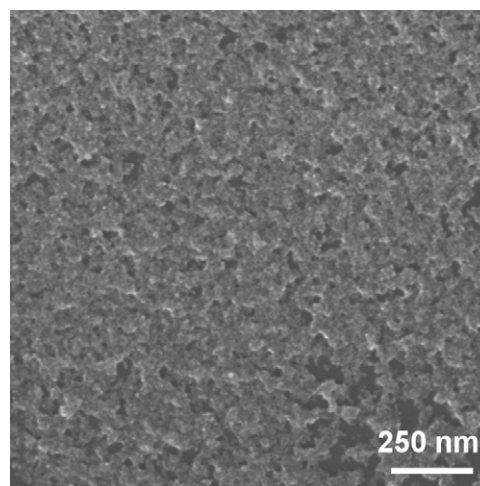


Figure 2. A SEM picture of a Si substrate attached to the cathode during EPD. The experiment was performed at 40 V for 20 min with $c_{\text{QD}} = \pm 20 \mu\text{M}$.

Instruments). The film thickness was derived from atomic force microscopy (AFM) measurements (Picoplus, Molecular Imaging) by measuring the average height profile of a scratch over the entire substrate surface.

4. Results and discussion

4.1. Surface coverage

Using the elemental charge as the net charge on a single QD and entering typical values for the different deposition parameters ($c_{\text{QD}} = 20 \mu\text{M}$, $d_{\text{QD}} = 3.5 \text{ nm}$, $\Delta V = 20 \text{ V}$ and $d_{\text{el}} = 0.01 \text{ m}$), equations (4) and (5) yield $\mu = 7.5 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $t_{\text{mono}} \sim 4 \text{ s}$. This shows that EPD of ZnO QD monolayers and multilayers should be feasible within a reasonable time span. To verify this, we started by performing an identical EPD experiment twice, the first time with the substrate attached to the cathode and the second time with the substrate mounted on the anode. Based on the timescale calculated above, we applied a DC voltage of 40 V between two electrodes submersed in an EtOH/CHCl₃ suspension containing 20 μM ZnO QDs for 20 min. This leads to the deposition of a thin layer of ZnO particles on the substrate when it is attached to the cathode, while only negligible deposits are found on the substrate connected to the anode (figure 2). Apart from demonstrating that surface coverage of substrates by ZnO QD EPD is possible, this result shows that these QDs have a positive charge when suspended in 1:5 EtOH/CHCl₃ mixtures. In the literature, both negative [18] and positive [17] particle charges were claimed for ethanolic suspensions of ZnO QDs, while no data were found for ZnO QDs suspended in apolar solvents. In our case, EPD of ZnO QDs in pure ethanolic suspensions was not successful. Possibly, this is due to an increased screening of the electric field because of the higher dielectric constant of the solvent and the increased ionic strength. This screening effect, combined with the relatively low QD concentration in our system, hinders EPD. On the other hand, working in pure

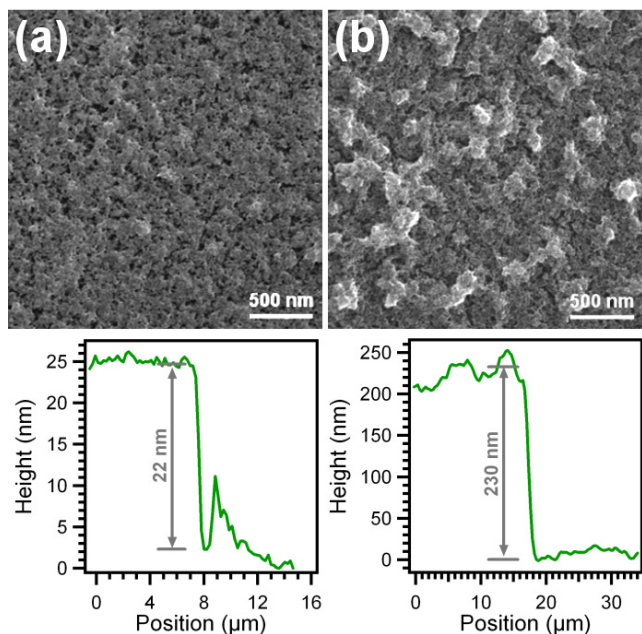


Figure 3. SEM images and height histograms as obtained from AFM on a scratch for (a) a ZnO thin layer obtained on etched Si deposited at 20 V for 20 min, $c_{\text{QD}} = 8 \mu\text{M}$, and (b) a ZnO layer deposited at 60 V for 20 min with $c_{\text{QD}} = 24 \mu\text{M}$. From the height profiles, the average height of the layers was determined to be 22 nm for (a) and 230 nm for (b).

CHCl_3 is not an option because the ZnO QDs are charge-stabilized particles which require a certain solvent polarity in order to avoid agglomeration and precipitation. By using the 1:5 EtOH/ CHCl_3 mixture, we are able to reduce the screening of the electric field, while keeping a stable colloidal suspension.

4.2. Tunable layer thickness

The number of deposited quantum dots and therefore the thickness of the quantum dot layer depends on parameters like the QD concentration, the applied voltage and the time. To assess the tunability of the layer thickness, we performed a set of EPD experiments with varying deposition time, voltage and/or quantum dot concentration. Figure 3 gives SEM pictures of a ZnO layer prepared at 20 V for 20 min, with a QD concentration of $8 \mu\text{M}$. The height profile shown in the bottom part of figure 3 is obtained by averaging all horizontal lines in an AFM image obtained for a scratched layer. In this way, we determine that the ZnO layer is ± 22 nm thick. When both the deposition voltage and the quantum dot concentration are tripled, a ZnO layer of 230 nm is deposited (figure 3(b)). The obtained ZnO layers appear as rough microstructures that may have a high specific surface area.

Figure 4 summarizes the results of a series of EPD experiments performed with varying deposition parameters. Here, the layer thickness is plotted as a function of the product of time, QD concentration, applied voltage and $1/d_{\text{el}}$. We neglect the influence of the particle size since it varies only between 3.0 and 3.2 nm in this data series. The curve has a linear slope of about $4 \times 10^{-13} \text{ m}^5 \text{ V}^{-1} \text{ s}^{-1} \text{ mol}^{-1}$, although

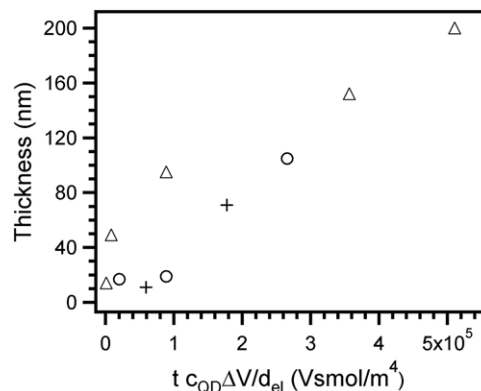


Figure 4. ZnO layer thickness as a function of the EPD parameters for experiments performed at 60 V (Δ), 40 V ($+$) and 20 V (\circ).

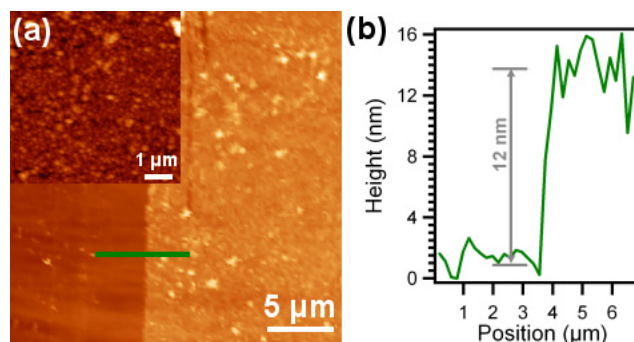


Figure 5. (a) An AFM image obtained on a ZnO layer (scratch) deposited at 60 V for 5 s with a suspension containing $24 \mu\text{M}$ ZnO QDs ($d_{\text{QD}} = 3.3$ nm). Inset: enlarged image. (b) The height profile measured for the line indicated in (a). The ZnO deposit is 12 nm thick, which complies with 3–4 ZnO QD monolayers.

some slight bending occurs at higher values of the product $t c_{\text{QD}} \Delta V / d_{\text{el}}$. This might be caused by screening effects from the ZnO layer on the electric field [17, 21].

We have estimated a theoretical value of this slope by assuming that the layer thickness equals the number of deposited monolayers multiplied by the quantum dot diameter. This leads to a value of $2 \times 10^{-11} \text{ m}^5 \text{ V}^{-1} \text{ s}^{-1} \text{ mol}^{-1}$, which exceeds the experimental one by two orders of magnitude. Yet, figure 5 shows that an EPD process performed at 60 V for 5 s with $c_{\text{QD}} = 24 \mu\text{M}$ leads to the formation of a 12 nm thick ZnO layer on the cathode. As these QDs have an average particle size of 3.3 nm, this thickness corresponds to 3–4 ZnO monolayers. Based on the experimental parameters ($c_{\text{QD}} = 24 \mu\text{M}$, $d_{\text{QD}} = 3.3$ nm, $\Delta V = 60$ V and $d_{\text{el}} = 0.01$ m), a theoretical t_{mono} of about 1 s is calculated in this case. This value agrees well with the layer thickness of 12 nm found after 5 s. This result indicates that the deposition rate is comparable to the predicted rate at the very beginning of the EPD process, but slows down considerably once a ZnO film of a few monolayers has been formed.

4.3. Micropatterns

We repeated the EPD process presented above on Si substrates, with a developed, patterned photoresist on top. Figure 6

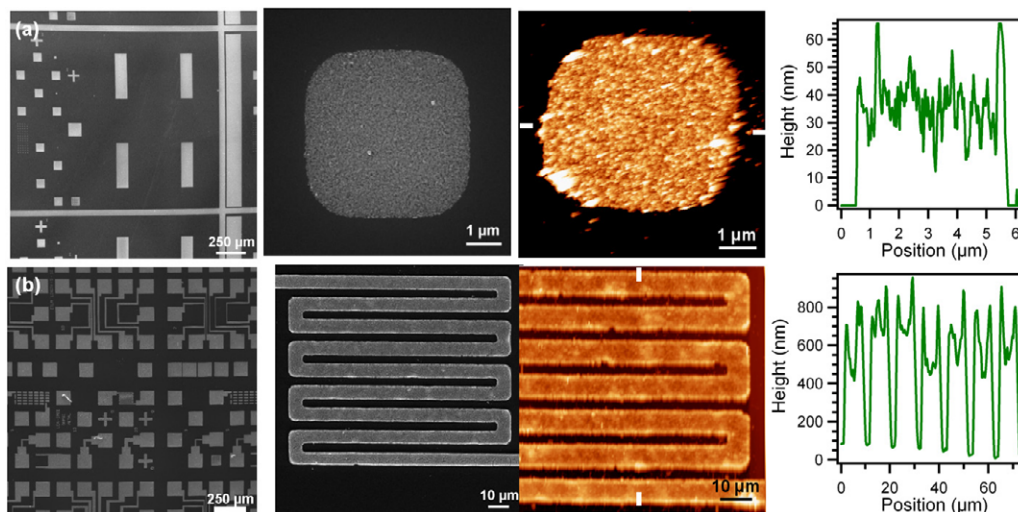


Figure 6. SEM pictures, AFM images and height profiles obtained for ZnO micropatterns prepared on photolithographically patterned substrates. The deposition parameters for the three experiments were, respectively, 20 V, 20 min, $c_{\text{QD}} = \sim 10 \mu\text{M}$ (a) and 60 V, 60 min, $c_{\text{QD}} = \sim 33 \mu\text{M}$ (b). The obtained layer thicknesses are $\sim 35 \text{ nm}$ for (a) and $\sim 400 \text{ nm}$ for (b).

shows SEM and AFM images of the resulting ZnO deposits. We observe sharply defined ZnO micropatterns that are not affected by the resist lift-off. A rounding off is found at the corners of the smallest patterns ($< 5 \mu\text{m}$). By varying the applied voltage, the deposition time and the QD concentration, we can produce microstructures ranging from 10 to 400 nm in thickness. When using the same EPD parameters, we found systematically larger values for the layer thickness of the micropatterns as compared to the completely covered substrates.

4.4. Photoluminescence

Figure 7 shows the photoluminescence (PL) spectra of a ZnO QD layer deposited at 60 V for 20 min with a thickness of $\sim 200 \text{ nm}$ and of the ZnO QD suspension used to prepare the ZnO layer. In line with the emission spectrum of the ZnO suspension, the layer exhibits a broad yellow defect emission with a maximum at $\sim 550 \text{ nm}$ and a weaker exciton emission at $\sim 350 \text{ nm}$ [24]. As compared to the ZnO suspension, we find no shift of the exciton emission, while the ratio of the band-to-band versus the defect luminescence clearly increases with the EPD layer thickness. The first observation confirms that the EPD layer is still composed of individual QDs, i.e., EPD does not lead to the formation of larger particles. The increase of the relative intensity of the exciton emission is in line with the generally accepted model of the defect luminescence of ZnO QDs, which involves the trapping of a photogenerated hole at the nanocrystal surface. Therefore, the defect luminescence will inevitably be influenced, in this case quenched, when isolated colloidal particles are assembled into a close packed QD layer.

5. Conclusions

We developed a procedure to deposit thin layers of ZnO quantum dots from colloidal suspensions by elec-

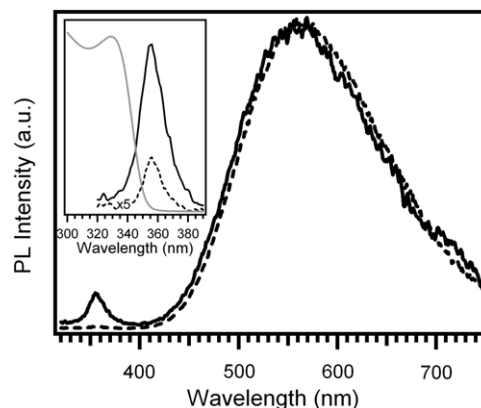


Figure 7. PL spectra obtained from a ZnO thin layer deposited at 60 V for 20 min (full) and the corresponding ZnO QD suspension (dashed). The spectra were normalized at their peak intensity. Inset: detail showing the PL spectra for the band-to-band recombination (black) and the absorption spectrum of the ZnO QD suspension (gray) ($d_{\text{QD}} = 3.3 \text{ nm}$).

trophoretic deposition. Therefore, we suspended ZnO QDs obtained via a hydrolysis–condensation reaction in DMSO/EtOH, at relatively low concentrations (10–40 μM) in an ethanol/chloroform solvent mixture (1:5 EtOH/ CHCl_3). First, we estimated the deposition parameters such as voltage, time, etc, based on theoretically calculated deposition yields and the experimental conditions. Second, we found that the particles are positively charged by analyzing whether deposition occurs on the cathode or on the anode. The influence of the applied voltage, deposition time and quantum dot concentration on the final layer thickness was studied, and ZnO layers could be prepared with a thickness ranging from a few QD monolayers to 250 nm by applying voltages ranging from 20 to 60 V. We found that for layers thicker than a few monolayers, the deposition rate is considerably smaller than our theoretical calculated value, while a few monolayers can be deposited

at the predicted rate. This points towards a strong screening of the electric field by the deposited ZnO layer. Electron microscopy and atomic force microscopy show rough quantum dot deposits. Finally, EPD Si substrates that are patterned with a developed photoresist as the cathode result in micropatterned deposits with dimensions in the μm range and a thickness varying between 10 and 300 nm. Since this method uses short deposition times, low voltages and low-cost setups, these results show that it is a convenient and versatile way to integrate charge-stabilized quantum dots in devices.

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