Creating Nanopatterns with Electrophoretically Mobile Quantum Dots

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ABSTRACT

Our research group is interested in making chemical patterns with a feature size of a few nanometers using quantum dots (Qdots) on a self-assembled monolayer (SAM). In this study, we quantified the electrophoretic mobility of cadmium selenide Qdots in polyacrylamide gels. These Qdots display excellent photocatalytic and photoemission properties arising from the quantum confinement effects. By varying the orientation of the electric field, we plan to electrophoretically move the Qdots as "pens" on a photocatalytically reactive SAM to create complex nanopatterns. Since Qdots are synthesized and stabilized in non-polar organic solvents, surface ligands, such as diethylaminoethanethiol, are used to impart a charge on the surface, making them water-soluble. The effective surface charge, or the zeta potential, of these charged Qdots of two different size ranges was determined using polyacrylamide gel electrophoresis (PAGE). The free solution mobility was found to be $1.9 \times 10^{-4} \pm 0.5$ cm^2/V-s for 3.9 nm Qdots and $2.0 \times 10^{-4} \pm 0.4$ cm^2/V-s for 2.3 nm Qdots. The zeta potential at room temperature was 27 ± 6 mV for 3.9 nm Qdots and 30 ± 5 mV for 2.3 nm Qdots under a 3.75 V/cm field strength and 5 mA current in a pH 7.1 buffer. The magnitude of these zeta potentials is comparable to those reported in literature. Using these data as guidelines, electrophoresis of Qdots preadsorbed on SAMs is currently underway.

CONCEPTS

- Electrophoretically move multiple Qdots as "pens" on SAM surface with electric field (Electrophoresis)
- Photocatalytically reduce azides to amines with Qdots when irradiated with light of specific wavelengths (Photocatalysis)*
- Simultaneous electrophoresis and photocatalysis produce nanopatterns (Figure 1)

*Warrier, *Photochem. Photobiol. Sci.*, **2004**, 3, 859-863

Concept of Nanopatterning

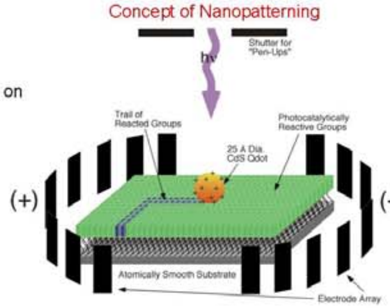

Figure 1: Positively charged Qdots are driven by electric field on SAM while photocatalysis is taking place

APPLICATIONS / ADVANTAGES

- Circuitry with feature size of Qdot dimensions
- Discontinuities between patterns can be obtained via electrophoresis with no photocatalysis
- Surface nano-templating (nano "etch-and-sketch")
- Low cost

DEMONSTRATION OF CONCEPT

- Synthesized and solubilized oleic acid-capped CdSe Qdots in toluene
- Synthesized and solubilized trioctylphosphine oxide (TOPO) capped core-shell Qdots in toluene#
- Replaced hydrophobic surface ligands with 2-(*N,N'*-diethylamino)ethanethiol (DEAET) caps to solubilized Qdots in water (Figure 2)
- Adjusted pH to manipulate surface charge density of Qdots in water
- Prepared polyacrylamide gel at various total acrylamide concentration (%T) with cross-linking percentage of 9.9%
- Concentrated aqueous Qdot solutions were placed into loading well and let settle for ~ 30 minutes
- Obtained Qdot mobility at 3.5 V/cm field strength and buffer pH of 7.1 (Figure 3)

#Bhattacharjee, *Physica E*, **2006**, 3, 388-393

Exchange of Surface Ligands

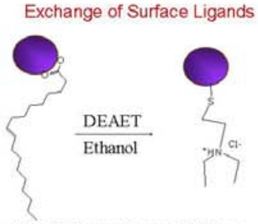

Figure 2: Oleic acid caps on Qdots are replaced with DEAET

Schematic of Gel Electrophoresis

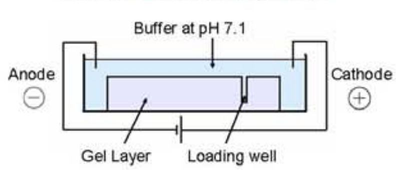

Figure 3: Positively charged Qdots are expected to move from the cathode to anode

QDOT MOBILITY ON SAM

- Methyl-terminated SAM-on-silicon surface was shown to be hydrophobic
- Preadsorbed amine-derivatized Qdots onto methyl-terminated SAM-on-silicon for ~ 6 hours
- Surface became hydrophilic where the Qdots were adsorbed
- Applied an electric field of ~1.5 V/cm across the SAM for over 20 hours in buffer (Figure 4)
- Monitor Qdots' movements by locating the hydrophilic area on surface

Schematic of Surface Electrophoresis

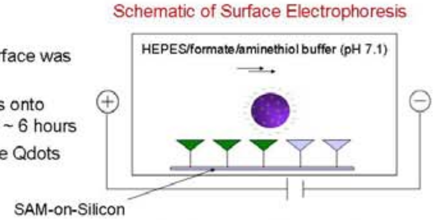

Figure 4: Positively charged Qdots move from cathode to anode on the SAM surface

QDOT CHARACTERIZATION

- Quantum confinement effects allow the determination of Qdot core diameter (Figures 5,6,7,8)+
  - Smaller Qdot → Larger band gap → Shorter wavelength absorbed
  - Estimate Qdot diameter with first absorption peak
- Photoluminescence (PL) peak characterizes the Qdot monodispersity (Figures 6,7,8)
  - Smaller PL FWHM → Higher monodispersity

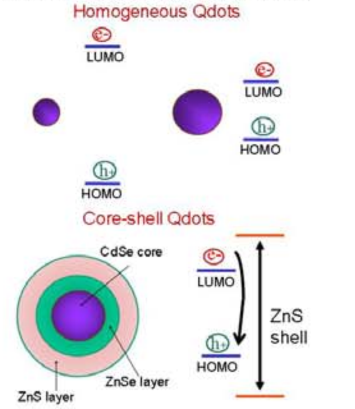

Figure 5: Qdots exhibit blue shift with decresaing core diameter. Core-shell Qdots were prepared with two layers (ZnSe ans ZnS) on top of the core made of CdSe

+Warrier, *Photochem. Photobiol. Sci.*, **2004**, 3, 859-863

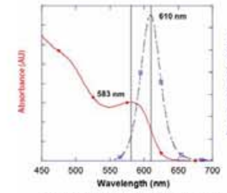

Figure 6: Homogeneous 3.9nm (583nm abs.) Qdots

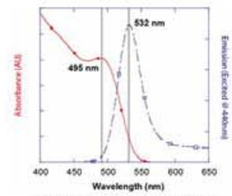

Figure 7: Homogeneous 2.3nm (495nm abs.) Qdots

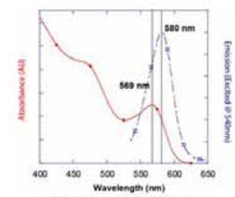

Figure 8: ~3.8nm core-shell (569nm abs.) Qdots

QDOT MOBILITY IN POLYACRYLAMIDE GELS

Figure 9: Amine-derivatized Qdots of 3.9nm (red) and 2.3nm (yellow) move toward anode (right) in 3.5%T gel (left) and 7%T gel (right)

$$\log M = \log M_0 - K_R T$$

Equation 1: M is the mobility, M_0 is the free solution mobilty, K_R is the retardation coefficient and T is total acrylamide concentration

What Exactly is Zeta Potential?

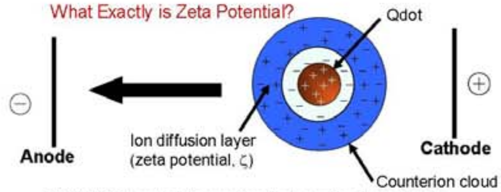

Figure 10: Zeta potential, proportional to the surface charge density, was determined (Equation 2)§. Zeta potential is measured across the ion diffuse layer, which is neutral overall

$$M_0 = \frac{2\varepsilon\zeta}{3\eta_s} H(kR)$$

Equation 2: M_0 is the free solution mobility, ε is the solvent dielectric constant, ζ is the zeta potential, η_s is the solvent viscosity, H(kR) is Henry's function, approximated by 1.5.

§Pons, *J. Phys. Chem. B*, **2006**, 20308-20316

Homogeneous Qdots Follow Mobility Model (Equation 1)

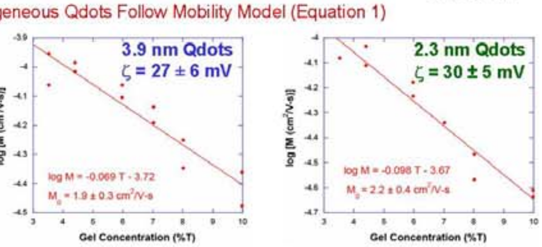

Figure 11: Qdot mobility was measured at various %T and free solution mobility, M_0, was extrapolated from y-intercept§

CONCLUSION

- Monodisperse CdSe Qdots were synthesized in high-boiling organic solvents
- Amine-derivatization produced positively charged, water soluble Qdots
- Zeta potentials of Qdots were determined from polyacrylamide gel electrophoresis
- Electrophoresis experiments for both in gel and on SAM surfaces are underway

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