Supporting Information

Metallic Conductive Luminescent Film

Jin He, Botao Ji, Somnath Koley, Uri Banin* and David Avnir*

Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem 9190401, Israel

* Email: uri.banin@mail.huji.ac.il (U.B.); davidavnir@mail.huji.ac.il (D.A.).

1. The geometrical size of QD/SiO$_2$ NPs

**Figure S1** (a) TEM image and (b) histogram of the size of CdSe/CdS QDs; (c) TEM image and (d) histogram of sizes of QD/SiO$_2$ NPs.

As the size of CdSe cores is ~3.8 nm, based on the size of CdSe/CdS QDs and QD/SiO$_2$ NPs determined in **Figure S1b** and **d**, the shell thickness of CdS and SiO$_2$ are calculated to be ~15 nm and ~16.5 nm, respectively.
2. Morphology of QD/SiO$_2$ NPs-adsorbed on Au film (QD/SiO$_2$ NPs adsorbed Au-2)

![SEM top view image of QD/SiO$_2$ NPs-adsorbed on Au film (QD/SiO$_2$ NPs adsorbed Au-2)](image)

**Figure S2.** SEM top view image of QD/SiO$_2$ NPs-adsorbed on Au film (QD/SiO$_2$ NPs adsorbed Au-2)

3. Wash cycle experiments of QD/SiO$_2$ NPs embedded and adsorbed on gold film

![Normalized PL intensities of QD/SiO$_2$@Au film and QD/SiO$_2$ NPs-adsorbed on Au film in wash cycle experiment.](image)

**Figure S3.** Normalized PL intensities of QD/SiO$_2$@Au film and QD/SiO$_2$ NPs-adsorbed on Au film in wash cycle experiment.

4. Raman mapping of QD/SiO$_2$ NPs: Embedded vs. Adsorbed

![Raman map of QD/SiO$_2$ NPs at 300 cm$^{-1}$(CdS 1LO).](image)

**Figure S4.** Raman map of QD/SiO$_2$ NPs at 300 cm$^{-1}$(CdS 1LO). (a) QD/SiO$_2$@Au film and (b) QD/SiO$_2$ NPs adsorbed Au-1.
5. **Fluorescence image obtained from the back side of QD/SiO$_2$@Au film**

![Fluorescence image](image)

*Figure S5.* Fluorescence microscopy image of QD/SiO$_2$@Au film from backside ($\lambda_{ex}$=480 nm, scale bar = 5 μm).

6. **The stability of QD/SiO$_2$ NPs to the gold electroless solution**

Quantum dot fluorescence can be quenched by Au$^{3+}$ or acid in the solution.$^1, 2$ To exclude the influence from the electroless solution, a 20 μL of QD/SiO$_2$ NPs solution were dropped into a 10 mL gold electroless solution. Luminescence and lifetime measurements were carried out after 2 hours and also just after the addition. The result – Figure S6 - shows stability of the luminescence to these conditions. It also implies that the lifetime change of QD/SiO$_2$ NPs in the QD/SiO$_2$@Au film is due to the plasmon coupling.

![Luminescence and lifetime spectra](image)

*Figure S6.* (a) Luminescence spectra of QD/SiO$_2$ NPs in gold electroless solution for 0 h and 2 h ($\lambda_{ex}$=480 nm). (b) Life time of QD/SiO$_2$ NPs in primary solution and QD/SiO$_2$ NPs in gold electroless solution for 2h.
7. Fluorescence spectra of QD/SiO$_2$ NPs in methanol with variable temperature

![Fluorescence spectra of QD/SiO$_2$ NPs in methanol with variable temperature](image)

**Figure S7.** (a) Temperature-dependent spectra of QD/SiO$_2$ NPs in methanol. (b) Wavelength shift in this temperature range. (c) The average emission intensity as a function of temperature. (d) Thermal quenching and recovery behavior of QD/SiO$_2$ NPs in methanol.

8. Evaluation of the electrical and magnetic field in QD/SiO$_2$@Au film by passing current

As the four-point probe method directly measures sheet resistance, $R_s$, the resistance of QD/SiO$_2$@Au film can be calculated from: $R = R_s L/W$, where $L$ is the length, $W$ is the width. The gold film size is 1 cm $\times$ 1.5 cm. Thus $R$ is calculated to be 1.245 $\Omega$, which leads to the voltage of $V = I \times R$ to be 0.8715 V under 700 mA.

The magnetic field 30 nm above the Au film (The QD locates) can be considered as magnetic field on infinite surface (30 nm $\ll$ 1 cm), which is described by Biot-Savart Law: $\vec{B} = \frac{1}{2}\mu_0 K \vec{x}_0$, where $\mu_0(4\pi \times 10^{-7} \text{ N} / \text{A}^2)$ is the permeability of free space, $K$ is linear current density, and $\vec{x}_0$ is vector unit. The $\vec{B}$ is calculated to be $4.396 \times 10^{-5} \text{ T} (\text{N} / (\text{A} \cdot \text{m}))$.

As the SiO$_2$ insulator shell prevents charge injection or any conductivity to the QDs
from gold substrate, passing current would induce either electric or magnetic field on the gold substrate. Firstly we excluded the magnetic field effects for two reasons: 1. the mechanism of magnetic field effect relies on the tuning of lattice symmetry by external magnetic field, which happens only in the high magnetic field (>10T), while the magnetic field generated here is estimated to ~10^{-5} T, which is far below the threshold of magnetic field effect. 2. Magnetic field is independent on the shape of the surface, while in our case the two tested morphologies – embedding and adsorption – responded to the current completely different. Secondly the electric field effect on the PL properties also requires a strong electric field (>0.1 MV/cm), while the voltage here is estimated to be only 0.9 V/cm, several orders of magnitude lower than the required level.

9. Temperature-current relation of QD/SiO₂@Au film

![Figure S8. Temperature increases as the function of current on QD/SiO₂@Au film.](image)

10. Temperature-lifetime relation of QD/SiO₂@Au film

![Figure S9. Luminescence decay profiles of QD/SiO₂@Au film. (Insets: Decay fits).](image)
11. Temperature dependent PL spectra and lifetime in QD/SiO₂ NPs adsorbed Au film

![Temperature-dependent PL spectra](image1)

**Figure S10.** (a) Temperature-dependent spectra of QD/SiO₂ NPs adsorbed Au-2 from 27.5 to 75.4 °C. (b) Wavelength shift in this temperature range. (c) The average emission intensity as a function of temperature. (d) Luminescence decay profiles of QD/SiO₂ NPs adsorbed Au-2 at 27.5 and 75.4 °C.

12. Luminescence of QD/SiO₂@Au film before heating and after cooling

![Luminescence spectra and decay](image2)

**Figure S11.** Luminescence spectra and decay of QD/SiO₂@Au film before the heating and after cooling. Full recovery of the emission spectra and lifetimes is observed.
13. Comparison of Figure 6 to profiles obtained from two other spots

![Graphs](image)

**Figure S12.** The changes in the fluorescence intensity induced by current for two additional individual fluorescent spots – compare with Figure 6.

14. Synthesis procedure of QD/SiO$_2$ NPs

(1) **Synthesis of CdSe cores**

CdSe cores were synthesized using a literature protocol. 6.0 g of trioctylphosphine oxide, 0.56 g of octadecylphosphonic acid and 0.12 g of CdO were loaded in a 100 mL flask. The flask was degassed under vacuum at 120 °C for 30 min. Then under Ar, the solution was heated to ~360 °C to dissolve the CdO until a clear solution was obtained. 1.5 mL of trioctylphosphine was injected to the flask, followed by heating the solution to 360 °C. A Se solution which was prepared by dissolving 116 mg of Se power in 0.72 g of trioctylphosphine was then injected to the flask. The reaction was quenched in 90 seconds after the injection. The nanocrystals were washed by using toluene/ethanol for three times and finally dissolved in toluene. The size of CdSe cores is ~3.8 nm.

(2) **Synthesis of CdSe/CdS core/shell QDs**

In a four-neck flask, freshly-prepared CdSe cores (50 nmol), 1-octadecane (ODE) (1.5 mL) and oleylamine (1.5 mL) were degassed for 30 min at 90 °C under vacuum. Under Ar, the flask was heated up to 310 °C. A 0.1 M cadmium precursor was prepared by diluting 0.5 M cadmium oleate in oleic acid with ODE. A 0.12 M sulfur solution was prepared by diluting 1-octanethiol in ODE. 6.0 mL of cadmium solution and 6.0 mL of sulfur solution were loaded in two syringes. At 240 °C, the two precursor solutions were added dropwise (3.0 mL/h) to the flask. After injection, the temperature was decreased to 90 °C. 12 mL of the reaction solution were withdrawn via a syringe. Then, the solution was reheated to 310 °C. The cadmium and sulfur precursor solutions were injected as above until the desired size was obtained. The solution was then cooled down to room temperature. The CdSe/CdS core/shell QDs were washed with hexane/ethanol and finally redispersed in 10 mL of hexane.
CdSe/CdS core/shell QDs were encapsulated in SiO$_2$ using a reverse-emulsion method. 100 μL of CdSe/CdS solution (0.1 nmol) were added to a mixture of 0.945 g of Triton X-100 and 0.735 g of hexanol in 5 mL cyclohexane, followed by the addition of 0.3 mL of water and 30 μL of ammonia solution (29 wt.%) successively. then 30 μL of tetraethoxysilane were added. The solution was stirred for 12 h at room temperature. 7.5 mL of acetone were added and the solution was centrifuged to precipitate the QD/SiO$_2$ NPs. Then QD/SiO$_2$ NPs were washed with methanol and water and finally dispersed in 10 mL of methanol.

References:


