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Layer-by-layer assembly of capped CdSe nanoparticles: Electrical bistability and memory phenomenon

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The authors demonstrate thin-film formation of capped-CdSe nanoparticles via layer-by-layer electrostatic assembly. The assembly of two types of nanoparticles in sequence—with anionic and cationic capping agents, respectively—results in thin films of CdSe nanoparticles. Devices based on such thin films demonstrate electrical bistability. The bistability, which is reversible in nature, is due to charge confinement in the nanoparticles and has an associated memory phenomenon. The devices based on the CdSe nanoparticles exhibit high on/off ratio and demonstrate read-only and random-access memory applications. © 2007 American Institute of Physics.

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Researches on semiconducting nanoparticles have started to focus different applications to meet the advancement of technology. Apart from several optoelectronic devices for photonic applications,^{1,2} the nanomaterials have demonstrated applications as electrically bistable devices and memory elements.^{3–7} In bistable or switching devices, thin films of nanoparticles exhibit two different currents or conductivities at a voltage with an ability to switch between the states. Switching from its pristine to a high one often occurs due to charge confinement in the nanoparticles.^{4,7,8} When the high conducting state is stable after withdrawal of bias that induces it, the device can be undertaken for read-only or random-access memory applications.

Thin-film formation with a control in the nanoscale is often important in fabricating difference devices. Conjugated or inert polymers as matrices for spun-cast films,⁹ pyridine group-containing suitable polymers for assembly through hydrogen bond interaction,¹⁰ trioctylphosphine oxide capped particles for self-assembly,¹¹ or polyions for layer-by-layer (LbL) electrostatic adsorption^{12–16} are frequent routes to form thin films of different nanoparticles. Thin films of nanoparticles without any matrix and having a control over their thickness in the nanoscale will hence be of utmost use. Such films will provide routes to study the intrinsic properties of the semiconducting nanoparticles. In the present article, we use different capping agents to form anionic and cationic nanoparticles that can be assembled to form all nanoparticle thin film via LbL electrostatic adsorption process. We study electrical bistability in such films for memory applications.

Mercaptoacetic acid (MAA)- and poly (diallyldimethylammonium chloride) (PDDA)-stabilized nanoparticles were synthesized following an earlier reported procedure.⁴ LbL films of CdSe nanoparticles were deposited on indium tin oxide (ITO) coated glass substrates by alternate adsorption of MAA- and PDDA-capped particles in cycles from their dispersed solutions. The dipping sequence was repeated to get a desired number of bilayers of CdSe. Here, during each dipping, a layer of nanoparticles becomes electrostatically adsorbed to the substrate and at the same time reverses the nature of surface charge for the next layer adsorption.

The LbL films were dried in vacuum at 60 °C. Thicknesses of 10- and 20-bilayer films were 50 and 100 nm, respectively. Aluminum (Al) was thermally evaporated in vacuum (10⁻⁶ bar) as top electrodes. Area of the devices was 6mm². All the electrical measurements were carried out in a shielded vacuum chamber at room temperature. Voltage was applied to the ITO electrode with respect to Al. Scan speed for current-voltage (*I-V*) characteristics was 50 mV/s.

XRD patterns of the MAA- and PDDA-capped nanoparticles show intense peaks for the (111), (220), and (311) planes of CdSe crystals.¹⁷ TEM image of the former nanoparticles resolves the diameter to be less than 5 nm (inset of Fig. 1). Electronic absorption and photoluminescence (PL) spectra of the nanoparticles are shown in Fig. 1. The MAA- and PDDA-capped particles show absorption band at 420 and 480 nm, respectively. Particle size has been calculated from the following equation:^{18,19}

$$R = \frac{h}{E_{gn} - E_{gb}} \sqrt{\left(\frac{E_{gb}}{2m^*}\right)},$$

where R is the particle size, h the Planck constant, m^* the effective mass of electron (which we assumed to be $0.2m_e$), E_{gb} the band gap for bulk, and E_{gn} is the absorption edge band for nanoparticles. The calculated diameters for the

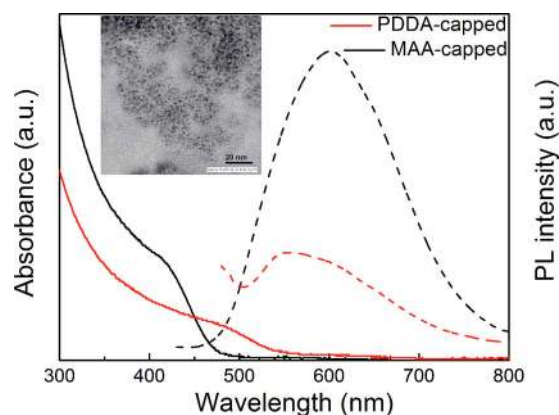


FIG. 1. (Color online) Electronic absorption and photoluminescence spectra of MAA- and PDDA-capped CdSe nanoparticles in dispersed solution. The PL spectra are shown in broken lines. Inset shows a TEM image of MAA-capped nanoparticles.

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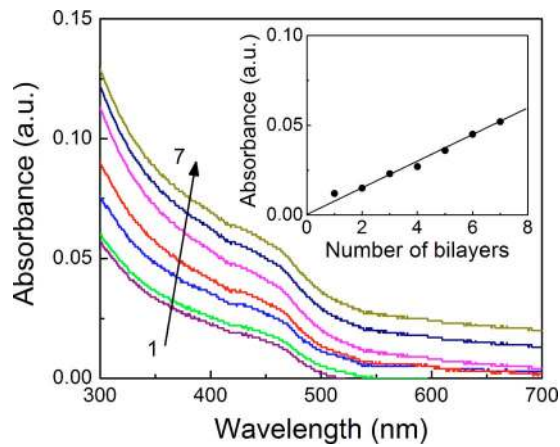


FIG. 2. (Color online) Electronic absorption spectra of LbL films of CdSe nanoparticle for different number of layers (from 1 to 10). Inset shows absorbance at peak wavelength as a function of number of layers. The straight line is a fit to points.

MAA- and PDDA-capped nanoparticles become 3 and 4.2 nm, respectively, which matches reasonably well with that obtained from TEM images. PL spectra of the nanoparticles, with excitations at 420 and 480 nm, show emission bands at 603 and 550 nm, respectively (Fig. 1). The emission band falls in the range reported in the literature.^{20,21} As expected, emission energy is low in smaller particles (MAA capped) as compared to that in PDDA-capped ones.

Growth of the LbL film has been monitored by recording electronic absorption spectrum of the film after each bilayer adsorption (Fig. 2). Here, films were grown on quartz substrates. All these spectra show a peak at 467 nm—the intensity of the band increasing with number of deposited layers. The wavelength of absorption maximum is 47 nm redshifted as compared to that in MAA-capped dispersed solution. This could be due to the formation of delocalized states via interactions among nanocrystals.^{22,23} The inset of Fig. 2 shows the absorbance of the films at 467 nm as a function of number of LbL layers of CdSe nanoparticles. A linear plot through the origin with a slope of unity confirms that the CdSe nanoparticles were adsorbed uniformly during deposition of each and every layer. The plot further confirms formation of thin films based only on the nanoparticles with a thickness control in the nanometer scale.

The I - V characteristics of devices based on 10 and 20-bilayer devices are shown in Fig. 3. The plots show that the (magnitude of) current at a negative voltage exhibits a sudden increase. In effect, current at a small negative voltage (say, -1.0 V) depends on the direction of sweep. When the bias is swept from a negative voltage, the magnitude of current is much higher as compared to that when the bias is scanned toward the negative value. The bistability is associated with a memory phenomenon. That is, during the sweep from a negative voltage, higher value of current is retained until a positive voltage switches the conductivity to a lower one. The bistability, however, is clearly observed in the negative bias direction only. Such a bistability in electrical conductance has earlier been observed in CdSe nanoparticles embedded in polymer matrices.¹⁶ The bistability—a high and a low value of current at any voltage—is considered to be due to charge confinement in the nanoparticles. The results in thin films of the nanoparticles show that the bistability is an intrinsic property of the particles.

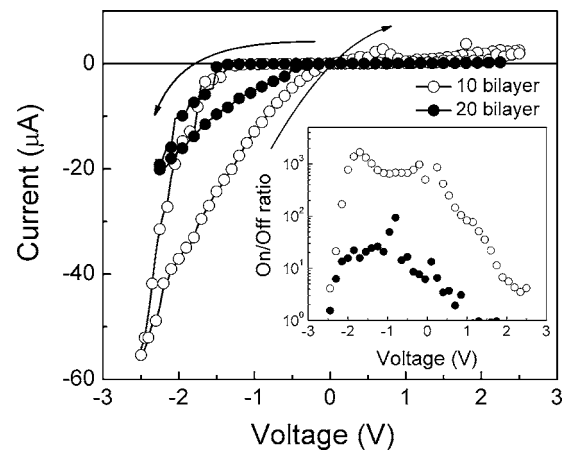


FIG. 3. Current-voltage characteristics of devices based on 10 and 20 bilayers of CdSe nanoparticles in a voltage loop. Arrows show the direction of voltage sweep. Inset shows on/off ratio as a function of voltage for the two devices.

We have studied electrical bistability in 10- and 20-layer devices. When the I - V plots for the two thicknesses are compared, the low-state current for the thinner device is expectedly higher (nearly double) as compared to that for the 20-layer device. The high-state current is also high for the thinner device. The ratio between the two at any voltage, the on/off ratio, is however more in the 10-layer device (inset of Fig. 3). The ratio, which depends on the voltage at which it is measured, reaches up to more than 2000. In the 20-layer device, all the nanoparticles might not have switched to their high state resulting in lower on/off ratio as compared to that in 10-layer case.

The bistability in these devices is reversible in nature. That is, a device can be switched reversibly for many cycles. I - V characteristics for four continuous voltage loops are shown in Fig. 4. The plot in the figure shows that both the traces corresponding low-state and high-state current have little deviation over voltage cycles. The results show the potential of the nanoparticles for random-access memory (RAM) applications.

The electrical bistability can be explained on the basis of charge confinement in the nanoparticles. Under a suitable negative voltage, the CdSe nanoparticles with higher surface charge density form percolative networks. Such networks fi-

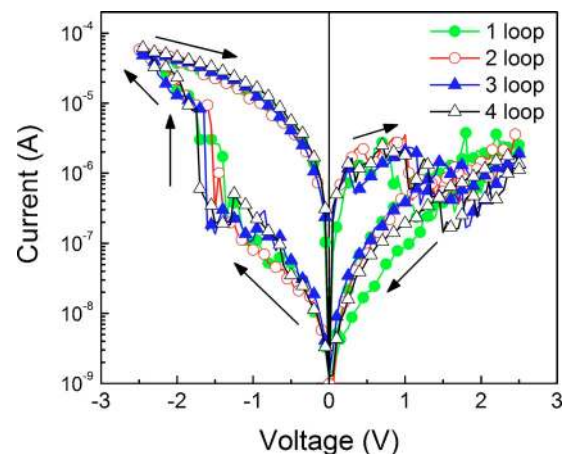


FIG. 4. (Color online) Current-voltage characteristics of a device based on 10 bilayer of CdSe nanoparticles in four consecutive voltage loops. Arrows show the direction of voltage sweep.

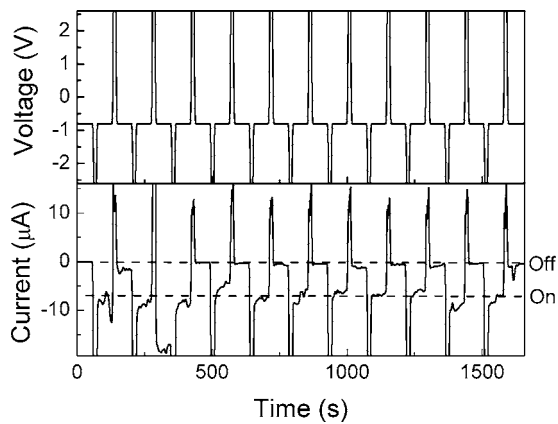


FIG. 5. Voltage and corresponding current under “write-read-erase-read” sequence of a device based on 10 bilayer of CdSe nanoparticles for RAM applications. Write and read voltage pulses were -2.6 and $+2.6$ V (10 s), respectively. The broken lines in the lower panel represent level of current under read voltage (-0.8 V, 2 s, 50% duty cycle) during probing low-conducting off state and high-conducting on state.

nally produce channels across the device resulting in a high-conducting state. The direction of bias at which the high state is reached depends on the electrode work functions so that the energy required for electron injection to the conduction band of CdSe nanoparticles is low. In the present system, electron injection from the ITO electrode to the conduction band of CdSe is favorable resulting in the high-conducting state in the negative bias.

RAM application of the devices based on thin films of the nanoparticles can best be demonstrated by switching the device to a low- and a high-conducting state repeatedly in sequence and probing the states after the each one has been induced (Fig. 5). The figure shows that the current during probing the two states in cycles substantially differed demonstrating RAM application. Read-only memory (ROM) applications can also be demonstrated in these devices. To do so, we first switched a device to its low-conducting state and probed under a small voltage for several hours. We then switched the device to its high-conducting state and probed the device in the same way. Duty cycle of the read pulse was low, so that the probing process did not interfere the states to be monitored. The currents under probe voltage in the two cases have been compared (Fig. 6). The figure shows that the

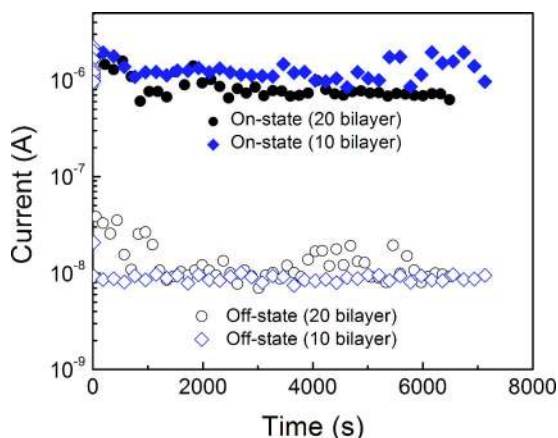


FIG. 6. (Color online) Magnitude of current under -0.8 V pulse (2 s, 6.25% duty cycle) as a function of time after a high-conducting on state and a low-conducting off state have been induced by -2.5 V and $+2.5$ V pulses (30 s), respectively. The device under assessment for ROM applications is based on 10 bilayer of CdSe nanoparticles.

current depends on the preceding voltage pulse. Amplitude of current in probing the high state is about two orders in magnitude higher than that while probing the low-conducting state. Apart from some initial decrease, the current for both the states show little or no appreciable change with time evidencing stability of nonvolatile memory of the system. The results hence clearly demonstrate that ROM applications can be achieved in thin-film devices based on CdSe nanoparticles.

In conclusion, we have deposited LbL films based on MAA-capped and PDDA-capped CdSe nanoparticles via electrostatic adsorption process. The method of using anionic- and cationic-capped nanoparticles in LbL film deposition process has resulted in thin films based only on CdSe particles with a thickness control in the nanometer scale. Devices based on such films have shown a jump in current at a suitable negative bias. Device current at a voltage has depended on the voltage-sweep direction. The ratio between the two currents, the on/off ratio, has reached up to 2000. The devices have demonstrated that the nanoparticles could be used for both ROM and RAM applications.

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