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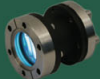
Room temperature-dipolelike single photon source with a colloidal dot-in-rod

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We propose colloidal CdSe/CdS dots in rods as nonclassical sources for quantum information technology. Such nanoemitters show specific properties such as strongly polarized emission of on-demand single photons at room temperature, dipolelike behavior and mono-exponential recombination rates, making us envision their suitability as sources of single photons with well defined quantum states in quantum cryptography based devices. © *2010 American Institute of Physics*. [doi:10.1063/1.3291849]

The development of efficient fully polarized single photon sources (SPSs) operating at room temperature is a cutting-edge research field.[1–3] The main application of SPSs is undoubtedly quantum information technology and in particular private keys distribution based on single photon fluxes of well defined quantum states.[4–6] Nonclassical light emission has been demonstrated from several nanometre-sized materials, such as single molecules,[7] defects in diamonds,[3] quantum dots,[8] single atoms in microcavities,[9] and more recently from elongated nanostructures such as carbon nanotubes[10] and quantum dots embedded in quantum wires.[11] Among these propositions, Stransky–Krastanov grown structures are catching the attention of scientific community[8,11] but are still limited by the operating temperature, far from 300 K. On the other hand, wet-chemically synthesized colloidal core/shell nanocrystals (NCs) are promising emitters for room temperature applications, due to the well separated allowed quantum energy states,[12,13] the low cost synthesis, the broad tunable emission range, and the compatibility with planar nanofabrication technology.[2,14–16] Although these emitters suffer from drawbacks, recent advances in fabrication succeeded in obtaining enhanced emission and almost suppressed blinking.[17,18] In 2001, elongated NCs [so called nanorods (NRs)] have been suggested as appealing room-temperature light emitters.[19] In particular, CdSe/CdS dots-in-rods (DRs), obtained by surrounding a spherical CdSe core with an elongated CdS shell[20] turn out to be very promising quantum emitters by virtue of their interesting ensemble polarization properties and therefore the expected dipolelike emission. In addition, they exhibit short lifetime and quantum efficiency of ~75% (further improved by surrounding the nanocluster with additional ZnS shell layers).[21] Compared to core NRs, the use of a CdS shell,

having low lattice mismatch with the CdSe core, minimizes the influence of surface traps between core and shell on the radiative recombination process, which occurs in the low band gap core.[22] This avoids the well known increase of the average radiative lifetime of the system due to the interaction of excitons with surface traps.[23]

In this work we propose colloidal CdSe/CdS DRs as suitable fully polarized single photon sources for quantum information technology applications. We first show the non-classical behavior of the light emitted by an isolated DR, then, by time and polarization resolved spectroscopy, we assess its polarization properties and we deduce the physical processes involved in the experiment. By exploiting their dipole nature we also measured the orientation of the DRs on the substrate by means of a defocused imaging technique, showing that DRs are suitable nanosources for quantum cryptography algorithms based on a single photon flux with a well defined quantum state, such as BB84 and B92.[4,5]

CdSe/CdS DRs were prepared by using the seeded growth approach proposed in Ref. 20 with a rod length l ~50 nm and a core diameter c ~2.7 nm. A typical output of the synthesis is reported in Fig. 1(a). A nanomolar solution of DRs in toluene was drop-casted on a glass coverslip thus obtaining a superficial DR density lower than 0.1 DR/μm^2. The sample was analyzed by a confocal microscopy system. A picosecond-pulsed excitation laser diode (wavelength 404 nm, pulse width ~50 ps) was focused on a single DR and time- and polarization-resolved spectroscopy and single photon counting measurements were performed by means of a high-sensitivity Hanbury–Brown and Twiss setup, based on a pair of avalanche photodiodes (APDs). The signals from the photodiodes were elaborated by a data acquisition card, used in two different configurations. All measurements were performed at room temperature.

In the start-stop mode, the delays between the received photons on the two APDs provide the measurement of the

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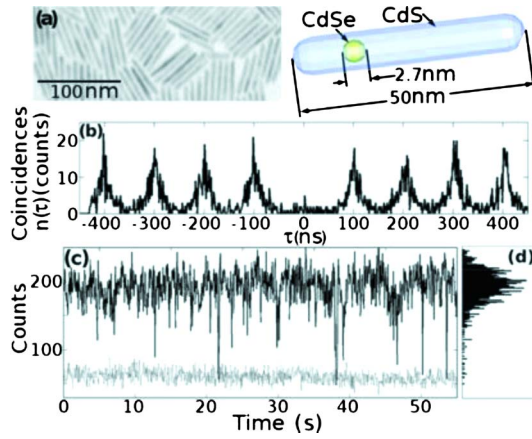
FIG. 1. (Color online) (a) Transmission electron microscope image and sketch of the synthesized DRs. (b) Autocorrelation function for unpolarized detection obtained with a laser repetition rate $\nu=5$ MHz. (c) Example of a typical time resolved signal detected from a DR with a time binning of 100 ms. The gray dotted line represents the noise time trace. (d) Intensity distribution corresponding to (c).
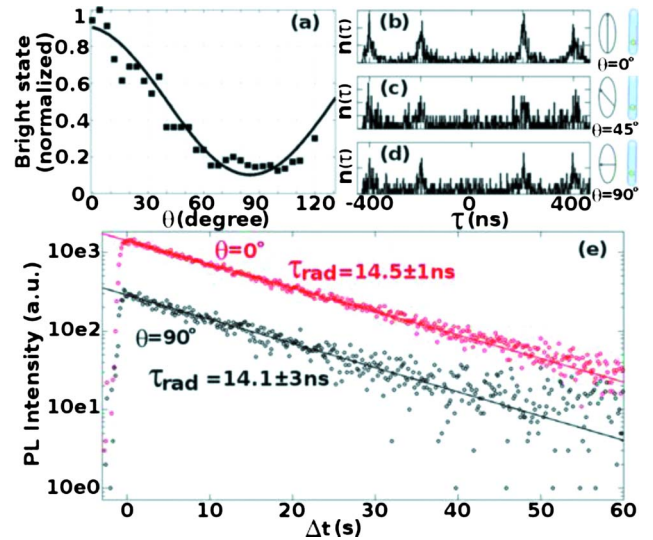

FIG. 2. (Color online) (a) Mean value of the bright state as a function of the polarization detection angle. The square dots represent experimental data, the solid line is the $\rho(\theta)$ fitting function. [(b)–(d)] Coincidence histogram $n(\tau)$ for three different value of θ. (e) Radiative decay curves in logarithmic scale detected for $\theta=0°$ and 90°.

coincidence histogram $n(\tau)$, proportional to the second order autocorrelation function $g^2(\tau)=\langle I(t)I(t-\tau)\rangle/[\langle I(t)\rangle\langle I(t-\tau)\rangle]$, where I(t) is the collected signal and τ is the delay between the received photons. $g^2(\tau)$ is a fundamental parameter to evaluate a SPS and to identify an isolated nanocrystal: indeed if $g^2(0)=0$, that is no photons are detected with zero delay, we can infer that I(t) is a flux of single photons. A typical result of this measurement on a single DR is reported in Fig. 1(b). The negligible area of the $g^2(t)$ function around zero delay is the evidence that the system emits two or more photons at the same time with a negligible probability, computed to be ~0.02. Besides inferring that there are no multiple emitting DRs in the investigated area, this is the evidence that no more than one photon is emitted by each DR and that never two excitons are allowed to radiatively recombine per each excitation pulse. This finding can be assigned to the ability of Auger processes to suppress the radiative recombination of multiexcitonic states. When a laser pulse excites various electron hole pairs, they recombine nonradiatively through Auger processes until only one electron hole pair remains. Therefore, considering the coincidences histogram reported in Fig. 1(b), we can infer that multiexcitonic emissions, detrimental for the realization of advanced optical sources emitting single photons on demand, is avoided in the nanoclusters under investigation at the used pump regime (mean power ~1 μW).

Moreover, it is well known in literature that in strongly confined quantum emitters, such as colloidal NCs, two excitons localized in the same nanometer-sized core region feel a mutual interaction, thus generating a biexcitonic system.[24] Bi-excitons assume specific characteristics, such as different recombination energy, quadratic dependence from excitation power and faster decay time, with respect to the single exciton.[24] As shown in the following, besides the information inferred by the coincidences histogram, we can also have a confirmation about the single excitation pulse-single emission behavior of our DRs by measuring its radiative decay curve, where the presence of a biexcitonic system would lead to a nonmonoexponential trend.

By triggering the data acquisition card with the laser pulses (laser triggered mode), we recorded individual photon

events with their absolute arrival times and their delays from the synchronization pulse. The typical time resolved photoluminescence (PL) trace of a single DR emission and the corresponding intensity distribution are displayed in Figs. 1(c) and 1(d), respectively. These curves clearly show only one emission level, identified as a bright state, in contrast to what observed in Ref. 25 in a charged CdSe/CdS NC, in which a nonradiative Auger process and a low efficient radiative process, usually referred to as gray state, are in competition. In our case, the absence of gray states, traps, and biexcitonic processes let us predict that a monoexponential decay behavior, only due to the single exciton recombination, is the dominant physical process involved in the quantum system under investigation.

In order to analyze the polarization properties of a single DR the mean emission intensity of the bright state has been measured for several detection polarization angles θ; when $\theta=0°$ (90°) only the light polarized along (perpendicular to) the rod axis is collected. As shown in Fig. 2(a) these mean values are well fitted by the curve $\rho(\theta)=d\cos^2(\theta)+(1-d)/2$, with a degree of linear polarization $d=(I_\parallel-I_\perp)/(I_\parallel+I_\perp)$ reaching $\sim80\%$ ($I_\parallel$ and $I_\perp$ are the intensity at $\theta=0°$ and 90°). In order to confirm that the photon flux is antibunched for every component of the polarization vector, we measured the autocorrelation function for several values of θ. Representative results of these measurements are shown in Figs. 2(b)–2(d). Clear antibunched emission was obtained for each polarization, showing that by changing the polarization detection angle the nonclassical light flux is preserved.

The decay rate of the PL has been also measured. Two typical decay curves are reported in Fig. 2(e) for $\theta=0°$ and 90°. Both curves show a monoexponential decay function $A_r\exp\{-(t-t_0)/\tau_r\}$ with the best fit decay constant τ_r ~14.5 ns. This result, coupled to the antibunching behavior and to the time resolved PL, is a further evidence that in the investigated temporal range no secondary radiative processes such as biexcitonic emission or gray recombination processes are involved in the fluorescence of the CdSe/CdS DR.
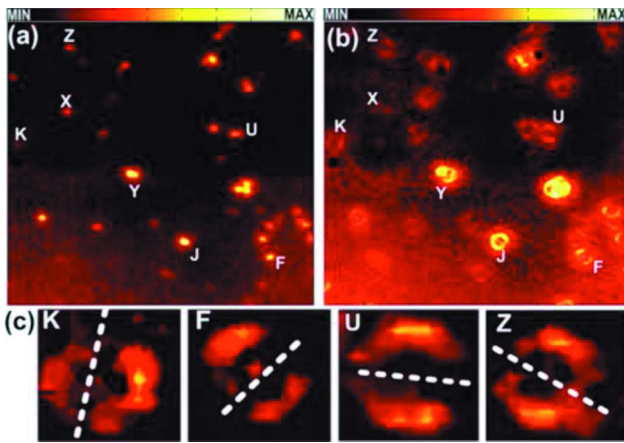
FIG. 3. (Color online) (a) Focused microscope images on an area of 50 ×50 μm^2. (b) Defocused microscope images of the same area shown in (a) when the objective is 500 nm far from the focal point. (c) Detail of four isolated DRs oriented along four different directions.

In order to determine the dipole orientation in each DR, a defocused microscope technique[26] has been adopted: when a high numerical aperture microscope objective is moved from the focal point, an omnidirectional emitter on the sample plane is identified by means of concentric defocusing lines around the original focused spot. On the contrary, when the radiation diagram is dipolelike and the dipole is parallel to the microscope coverslip, the circular behavior is substituted by two arcs around the position of the investigated object. Figures 3(a) and 3(b) display the PL images collected with a high numerical aperture oil objective (NA=1.40) for different focal points. The focused image [Fig. 3(a)] shows the presence of several isolated DRs (for example Z, U, K, and F) and some clusters composed by more than one nanoparticle, for example Y and J, as demonstrated by the fact that their emission does not exhibit antibunching. By moving the microscope objective 500 nm far from the focal point [Fig. 3(b)] we detected the defocused images by means of a high quantum efficiency CCD. The single DRs Z, U, K, and F are characterized by two well defined defocusing curves. The defocused pattern can be used to identify the orientation of the DR (and therefore the orientation of the polarization vector) on the substrate by connecting the two minima of the defocusing lines as shown is Fig. 3(c) for K, U, F, and Z nanocrystals. This is not the case of the DR clusters Y and J in Fig. 3(a). Since these clusters are composed by a few DRs the resulting radiation patterns originate by a combination of dipolelike diagrams.

Here we have shown that a defocused microscope technique can be exploited to identify the orientation of randomly deposited DRs. Reasonably, this approach allows to choose a proper set of four well oriented DRs as a base for cryptography algorithms after a random deposition of the emitters. Further improvements exploiting alignment techniques[20] could also allow to control the orientation of DRs also during the deposition, thus increasing the potential of such emitters as room temperature nanosources for effective quantum cryptography systems.

In summary, we propose colloidal CdSe/Cds DRs as nonclassical emitters for quantum information technology. We assessed the absence of radiative biexcitonic recombination and gray states reporting complete and fully polarized

photon antibunching, showing the suitability of these nanoemitters as dipolelike, room temperature, and polarized single photon sources. The possibility to identify the orientation of a single DR on the substrate suggests a viable strategy for the implementation of quantum information algorithms based on polarized single photon fluxes.

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