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# Thermally robust and blinking suppressed core/graded-shell CdSe/CdSe<sub>1-x</sub>S<sub>x</sub>/CdS 'giant' multishell semiconductor nanocrystals

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#### Abstract

We demonstrate that core/graded-shell CdSe/CdSe<sub>1-x</sub>S<sub>x</sub>/CdS giant semiconductor nanocrystals (g-NCs) have robust photoluminescence (PL) temperature response. At a size of 10.2 nm in diameter, these g-NCs undergo a PL drop of only 30% at 355 K relative to their PL intensity at 85 K. In comparison, the core/step-shell CdSe/CdS g-NCs at the same diameter exhibit 80% PL drop at 355 K. Spectral shifting and broadening were found to be, respectively, 5–10 times and 2–4 times smaller than those observed in standard CdSe core and CdSe/CdS core/shell NCs. These core/graded-shell g-NCs are largely blinking suppressed and have insignificant photoluminescence decay even after excitation at very high irradiance (44 kW cm<sup>-2</sup>) for over an hour. These types of g-NC have potential applications as the active medium for thermally robust laser devices (in the visible range) or as temperature-insensitive bioprobes for biomedical imaging.

S Online supplementary data available from stacks.iop.org/Nano/24/475705/mmedia

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

In recent years, colloidal semiconductor nanocrystals (NCs) have demonstrated the utility of their unique properties in diverse applications such as optically pumped lasers [1, 2], photovoltaic cells [3], 3D holography [4], light emitting diodes [5, 6], and a number of different bioprobes [7–9]. As a result, researchers have invested significant effort in improving these NCs' photostability, reducing their size dispersion, increasing their quantum yield, and eliminating their fluorescence intermittency. Murray *et al* have made NCs with size dispersion of less than 5% [10]. High quantum yield (50–80%) and photostable water-soluble CdTe NCs have been repeatedly demonstrated for multiple biological applications [9, 11]. In 2009 Wang *et al* demonstrated that CdSe/CdZn<sub>1–x</sub>Se<sub>x</sub>/ZnSe core/graded-shell NCs are ideal for

applications that require extremely photostable NCs that do not blink in the visible range [12].

In spite of the aforementioned achievements, NCs continue to suffer from a large photoluminescence (PL) temperature dependence. It was found previously by Bawendi *et al* that NCs' PL intensity decreases by more than 85% for 5 nm diameter CdSe/ZnS particles from 100 to 300 K [13]. Although such NCs are useful as optical temperature probes, they are not suitable for thermally robust laser devices. Recent progress has found that InAs-based self-assembled NCs can be used to create thermally robust laser diodes at  $\lambda = 1.3 \ \mu m$  [2]. However, thermally robust NCs in the visible range have remained elusive.

In this paper, we demonstrate that a certain 'giant' semiconductor nanocrystal (g-NC) could solve the aforementioned temperature-dependence problem. The g-NC is a type of nanoparticle whose large size (>10 nm in diameter) compared to standard NCs (2-10 nm) has proven beneficial in terms of suppressed blinking, longer fluorescence lifetime, and reduced photobleaching [14, 15]. We have found that  $CdSe/CdSe_{1-x}S_x/CdS$  core/graded-shell g-NCs have a robust PL temperature response. With only 30% decrease in PL as the temperature rises from 85 to 355 K, these g-NCs exhibit much better PL stability than the CdSe/CdS core/shell g-NCs (80% PL drop in the same temperature range; see figure 4). We also monitored the spectral shifting and broadening of our core/graded-shell g-NCs and found them to have better performance than the standard CdSe/CdS core/shell and CdSe core-only NCs. Our CdSe/CdSe<sub>1-x</sub>S<sub>x</sub>/CdS core/graded-shell g-NCs are largely blinking suppressed and can withstand high excitation fluence (of the order of 10 kW cm<sup>-2</sup> at  $\lambda = 532$  nm) for more than an hour without any signs of PL decay.

#### 2. Procedure

#### 2.1. Chemicals

Cadmium oxide, trace metal basis >99.99% (Sigma Aldrich 202894), cadmium acetate dehydrate, >98% (Sigma Aldrich 20901), selenium powder (Se), 100 mesh, 99.99% (Sigma Aldrich 229865), sulfur, purum >99.5% (Sigma Aldrich 84683), trioctylphosphine (TOP), 97% (Sigma Aldrich 718165), trioctylphosphine oxide (TOPO), 90% (Sigma Aldrich 346187), oleic acid, 90% (Sigma Aldrich 364525), 1-octadecene (OD), >95% (Sigma Aldrich 74740), tetrade-cylphosphonic acid (TDPA), >97% (Sigma Aldrich 736414), hexadecylamine (HDA), >98% (Sigma Aldrich 445312).

#### 2.2. Synthesis of CdSe core nanocrystal

CdSe core NCs were fabricated based on the procedure proposed by Wang et al [12]. In short, 0.08 g of TDPA, 4.00 g of TOPO and 2.51 g of HDA were placed in a three-neck flask. While heating the solution gradually to 100 °C, it was degassed and purged under argon gas via a Schlenk line for 30 min. A 1 ml TOP-Se precursor solution (previously made by adding 0.158 g Se to 2 ml TOP under argon) was added to the mixture and subsequently heated to 280 °C under continuous argon flow. As the temperature stabilized, 1.5 ml of Cd-TOP precursor solution (previously made by adding 0.08 g of CdAc<sub>2</sub> into 2 ml of TOP) was swiftly injected into the three-neck flask. The temperature of the solution dropped by 10-15 °C, and the solution changed from colorless to red. After 1 min, the flask was removed from the heating source and allowed to cool under abundant airflow. The final CdSe NCs solution has peak absorption at  $\lambda_{abs} = 555$  nm and peak emission at  $\lambda_{em} = 570$  nm.

# 2.3. Synthesis of CdSe/CdSe $_{1-x}S_x$ /CdS core/graded-shell nanocrystals

CdSe core NCs were purified by dilution with toluene and precipitation via centrifugation with methanol. This step is repeated three times before placing in a three-neck flask with 5.24 g of TOPO and 3.36 g of HDA. In separate flasks, stock solutions were prepared under continuous purging with argon (0.2 M of sulfur dissolved in OD, 0.08 M of selenium dissolved in TOP and 0.2 M of cadmium oxide dissolved in oleic acid). The synthesis of  $CdSe/CdSe_{1-x}S_x/CdS$ core/graded-shell NCs follows the SILAR approach pioneered by Peng et al with slight modification [16]. The reaction temperature was fixed at 240 °C and growth times were 10 min for all anion (S and Se) and cation (Cd) precursors. The amount of precursors needed for each monolayer of shell was calculated according to the volume increment of each shell. Initially, the Se-rich surfaces of the CdSe cores were passivated by addition of Cd oleate equivalent to one monolayer of cadmium. The reaction is allowed to progress for 20 min, followed by the addition of the anion precursor (mixture of S and Se as predetermined) constituting the first shell for the core. For the first six shells, CdSe is varied linearly in six steps towards CdS, thus completing the fabrication of graded-core  $CdSe/CdSe_{1-x}S_x$  NCs. In subsequent steps, passivating CdS shells comprising one, three, five, and seven layers were added to the graded cores, and the resulting NCs were extracted for characterization.

### 2.4. Purification of crude semiconductor nanocrystal solutions

The crude NC solutions were initially diluted in toluene solution. An equivalent volume of methanol solution was added and centrifuged under 5000 rpm for 5 min. The precipitates, which were mainly NC particles, were then re-dissolved in toluene.

#### 2.5. Sample preparation of semiconductor nanocrystals

VWR Vista Vision cover slips (0.16-0.19 mm thickness) were used as the glass substrate for the NCs. These cover slips were sonicated with acetone, isopropanol, and distilled water with each step lasting 5 min. The cover slips were then oxygen plasma cleaned for 3 min. There were two methods of sample preparation. For the purpose of observing NC blinking profile under the Zeiss microscope, a very dilute NC solution (approximately  $5 \times 10^{-13}$  mol ml<sup>-1</sup> NCs) was spin-coated at 2000 rpm for 1 min. This thin film is then transferred to our second (custom-built) fluorescence microscope for thermal endurance studies. The NC thin films used for photobleaching studies were prepared using the method of drop casting. 10  $\mu$ l of 1  $\times$  10<sup>-10</sup> mol ml<sup>-1</sup> NCs was dried on a 1  $\times$  1 cm<sup>2</sup> VWR coverslip. The concentration of core-only CdSe NCs was calculated, based on the empirical fit by Yu et al [17]. However, finding the concentration of core/shell NCs is not easy, since empirical fits for the extinction molar coefficients are not available. An alternative is to assume that no new CdS NCs were generated during core/shell NC fabrication. This assumption turned out to be reasonable, considering that no evidence of small CdS NCs was found in our TEM observations of the fabricated core/graded-shell NCs. As a result, we take that the concentration of our core/shell NCs is approximately equal to the known amount of core NCs added to the solution at the beginning of the process, divided by the volume of the final solution.



**Figure 1.** Diagram of the custom-built microscope (Thorlabs model OTKB).

#### 2.6. Zeiss fluorescence microscope

For the purpose of measuring the NCs' blinking and photobleaching properties, single NC PL was observed under an inverted wide field fluorescence microscope (Zeiss Axio Imager Z2). The photoluminescence of the NCs was collected by an oil immersion  $100 \times$  objective lens (NA = 1.45) and detected by an air-cooled EMCCD camera (Photonmax 512B) after passing an emission bandpass filter at  $655 \pm 30$  nm. The exposure time was fixed at 1 s. The camera background values were measured and accounted for in all PL measurements. A mercury arc lamp (HBO 100) was used as the source, and the excitation wavelength was fixed at 405 nm.

#### 2.7. Custom-built fluorescence microscope

In order to measure the temperature dependence of the PL spectra and the integrated intensity of NC samples, a custom-built fluorescence microscope was assembled (Thorlabs model number OTKB) with a cryogenic dewar (IR Labs HDL-14) that controls the temperature of the NC sample holder. Shown in figure 1 is a schematic diagram of the microscope layout.

A high power LED (M455L2 from Thorlabs) was used as an excitation source at  $\lambda = 450$  nm. This source initially passed a diffuser, short pass filter with a cutoff at 540 nm, and a dichroic mirror. The objective lens with an NA of  $0.6 (40 \times \text{magnification})$  focused the light to a spot size of approximately 250  $\mu$ m in diameter. For some experiments, a green laser at  $\lambda = 532$  nm was used as the excitation source and the spot size was found to be  $\sim 2 \ \mu m$  in diameter via a scanning knife edge technique. The sample placed within the cold finger (HDL-14 from IR Labs) emitted PL photons, which were collected in two different paths. The transmitted arm channels the PL signal onto a 300 ln mm<sup>-1</sup> transmission blazed grating with a blaze angle of 17.5°. The diffracted light is subsequently focused with a doublet lens onto a CCD camera (DCU224C from Thorlabs). The image acquisition system was carefully aligned with the first diffraction order

from the grating so as to acquire the PL spectrum of the NCs (see the supplementary data, figure A1 available at stacks.iop. org/Nano/24/475705/mmedia). Simultaneously, the reflected PL light from the NC sample propagated backward through a long pass emission filter with cutoff at  $\lambda = 597$  nm before arriving at a photomultiplier tube (PMT) for real time PL intensity measurements.

#### 2.8. TEM measurement

All NCs were measured using the Hitachi-8100 TEM. The samples were placed on an ultrathin carbon film on a 400 mesh copper grid (Ted Pella-01822).

#### 3. Results

#### 3.1. Characterization of 'giant' nanocrystals

Starting with 3 nm diameter core NCs, these particles grew to a size of 10 nm by sequentially adding monolayers of inorganic shells. As described in the procedure,  $CdSe_{1-x}S_x$ or CdS alloys were grown onto the CdSe cores using a modified literature procedure that is based on a successive ion layer absorption and reaction (SILAR) technique [16]. The growth of up to 10 ML was conducted over a period of 12 h to achieve reasonable control over the NCs' size variation. The shell is either single composition—ten layers of CdS (core/step-shell CdSe/CdS g-NCs), or multiple composition—five layers of linearly varying CdSe<sub>1-x</sub>S<sub>x</sub> and five layers of CdS (core/graded-shell CdSe/CdSe<sub>1-x</sub>S<sub>x</sub>/CdS g-NCs).

It is well known that, in general, adding shell layers onto core NCs tends to shift the PL spectra [18] to longer wavelengths. This indicates an expansion of the core wavefunction into the shell region and, therefore, an increase of the effective size of the core while reducing quantum confinement effects by the core NC wavefunction. By continuing to deposit shell layers, these NCs are gradually dominated by the CdS shell material. With a shell:core volume ratio of approximately 25:1, the absorption feature blue-shifts, where high absorption is seen at about 500 nm, indicative of a CdS bulk bandgap (figure 2). We denote such a transition in the absorption spectrum as the defining characteristic for our 'giant' NCs (g-NCs). Shown in figure 2 are the absorption and photoluminescence spectra of core/graded-shell (G-type) and core/shell (S-type) NCs with increasing shell layers.

TEM measurements were also conducted for the G5-5 and S10 g-NCs, and the average sizes for both g-NCs were found to be 10.2 nm with root mean square percentage error (RMSPE) as described in figure 3. The G5-5 g-NCs are slightly prolate with an aspect ratio of 1.3, as shown in the inset of figure 3(A). However, S10 g-NCs have oblate features with an aspect ratio of about 1.05.

### 3.2. Photoluminescence temperature dependence of G5-5 and S10 'giant' nanocrystals

The temperature dependent PL spectra of the G5-5 and S10 g-NCs are shown in figure 4.



**Figure 2.** (A) Absorption and PL spectra of core/graded-shell NCs (denoted by 'G') with three, six, and ten shell layers. The notation of G3 represents three layers of graded  $CdSe_{1-x}S_x$  shell with no CdS shell, G5-1 indicates five layers of graded  $CdSe_{1-x}S_x$  shell and one layer of CdS shell, and G5-5 indicates the presence of the same five graded shells plus five layers of CdS shells. (B) Absorption and PL spectra of core/shell NCs labeled as 'S' followed by the CdS shell number. Both types of NC gradually change in size from standard core/shell NCs to g-NCs as the relative absorption level suddenly increases in the 500 nm region (denoted by the blue arrow). The fact that the PL red-shifting rate decreases with added shell layers indicates that the size dependent quantum confinement effect is rapidly declining. This is also a clear indication that the NC red-shift is reaching saturation—a characteristic that is suggestive of a heavily shelled NC. The quantum yields for G5-5 and S10 were found to be 7%. This is consistent with the experimental results reported in [18].



**Figure 3.** (A) TEM image of G5-5 g-NCs. The average size is about 10.16 nm with RMSPE of 17.7%. Inset, high-resolution TEM acquisition; the G5-5 g-NC is slightly prolate with an aspect ratio of 1.3. (B) TEM image of S10 g-NCs. The average size is about 10.2 nm with RMSPE of 13.6%. Inset, high-resolution TEM acquisition of S10 g-NCs. Unlike the G5-5 g-NCs, these step-shell g-NCs are oblate, with an aspect ratio of 1.05. (C) TEM image of the CdSe core NCs from which both g-NCs were created. Similar to G5-5 nanoparticles, these NCs have an aspect ratio of 1.25. The unprotected cores have an average diameter of 3.5 nm along their major axis, with an RMSPE of 8.83%.

Although G5-5 and S10 g-NCs were found to have very similar sizes (see figure 3), the G5-5 g-NCs have a much better high temperature PL performance than the S10 g-NCs as evidenced by figures 4(C) and (D). A separate experiment confirmed that neither of these two g-NCs exhibits any photobleaching even at high excitation fluence (see figure 9). The g-NC samples were tightly locked in a vacuum chamber at  $1 \times 10^{-6}$  mbar, thereby eliminating any possibility of photo-oxidation [19-21]. Furthermore, multiple scans were done on all g-NC samples and samples were kept homogeneous over the entire glass substrate (see supplementary data, figures A3, A4 and A5 available at stacks.iop.org/Nano/24/475705/mmedia) in order to ensure that thermally induced drifting does not affect the temperature dependent PL spectra. Both g-NCs exhibit 100% reversible PL response by varying the g-NCs' temperature from 300 to 360 K (see the supplementary data, figure A2 available at stacks.iop.org/Nano/24/475705/mmedia). This indicates that our temperature dependent PL spectra are reliable.

The relative integrated PL intensity (PL normalized at 85 K, see figure 5) of different-size S-type and G-type NCs were measured using a PMT with a long-pass emission filter (cutoff at 597 nm). As a reference, the CdSe NCs (labeled as 'core') integrated PL intensities were also measured and found to be consistent with previous experiments [13]. All three G-type g-NCs under investigation exhibit robust temperature stability. The S-type and core-only NCs exhibit a weakly decreasing PL in the range of 85–275 K, then a rapid decrease is observed above 275 K. This suggests the existence of at least two temperature dependent nonradiative processes, consistent with the behavior found in previous experiments [13, 23, 29]. Among the nonradiative processes are Forster energy transfer between NCs [24], radiative relaxation [23], Auger nonradiative scattering [25, 26], thermal



**Figure 4.** Temperature dependent PL spectra of (A) S10 g-NCs and (B) G5-5 g-NCs. These spectra were collected using a high sensitivity CCD camera as described in the procedure. A transmission blazed grating (300 ln mm<sup>-1</sup>) is used to diffract different wavelengths of the PL light. The concentrations of the NC thin films immobilized on a glass substrate are kept at approximately 500 NCs  $\mu$ m<sup>-2</sup>. The excitation wavelength is 450 nm with an irradiance of 4 W cm<sup>-2</sup>. (C), (D) Actual PL images acquired from the CCD camera at different temperatures after passing through the transmission grating. These are PL spots acquired at the first diffraction order (*m* = 1) with a blaze angle of 17.5° (see supplementary data, figure A1 for calibration information available at stacks.iop.org/Nano/24/475705/mmedia).



**Figure 5.** Summary of relative intensity (PL normalized at 85 K) of different types of NC (G5-7, G5-5, G5-3, S10, S3 and CdSe core-only NCs) as a function of temperature, measured using the photomultiplier tube of our custom-built microscope.

escape from NCs [27], and trapping in defect states [28]. What we found was that, instead of the conventional decrease in the PL intensity, the G-type NCs become brighter by about 15% as the temperature rises from 85 K to approximately 250 K, before declining at higher temperatures. It is as yet unknown why these NCs behave differently; therefore, more research is needed to elucidate the underlying radiative recombination mechanism of these g-NCs.

# 3.3. Empirical fit of the temperature dependent energy bandgap and full width at half maximum linewidth of nanocrystals

The temperature dependence of the main PL resonance peak energy (equivalent to the energy gap of the NCs) is reported in figure 6(A). The experimental data were fitted with the Varshni relation [23, 29], which describes the temperature dependence of the energy gap of bulk semiconductors.

$$\Delta E_{\rm g}(T) = -\alpha \frac{T^2}{(T+\beta)}.$$
 (1)

In the above equation,  $\Delta E_g$  is the difference between the energy gap at temperature T ( $E_g(T)$ ) and the energy gap at 0 K ( $E_{g0}$ ),  $\alpha$  is the temperature coefficient (in eV K<sup>-1</sup>), and  $\beta$  is the corrected Debye temperature of the material.

It is found that the best fit for the reference core-only CdSe NCs, that is,  $\alpha = (3.21 \pm 0.2) \times 10^{-4}$  eV K<sup>-1</sup> and  $\beta = 290 \pm 40$  K, well reproduces the experimental data. These values are consistent with the values found in the literature for bulk CdSe:  $\alpha = (2.8-4.1) \times 10^{-4}$  eV K and  $\beta = (181-315)$  K [30].

The G5-5 g-NCs have minimal wavelength shift at high temperatures. Within a temperature span of 270 K (85–355 K), this type of g-NC exhibits a red-shift of approximately 7 meV (black line in figure 6(A)) which gives an  $\alpha$  value that is 5–10 times smaller than any of the conventional NCs (see supplementary data, table A1 available at stacks.iop.org/Nano/24/475705/mmedia).

The reduction in temperature sensitivity for G5-5 g-NC could be further understood by comparing with the temperature dependent energy gap of the S10 g-NCs, also shown in figure 6(A) (red data points). The S10 g-NCs initially blue-shift by as much as 20 meV, followed by a 30 meV red-shift at higher temperatures. Such unexpected behavior could be related to the prolate structure of the core-only CdSe NCs (figure 3(C)). It is found that the linear



**Figure 6.** (A)  $\Delta E_g(T)$  of the PL spectra of different samples. Solid lines are the best fit curves described by equation (1). (B)  $\Delta$ FWHM of the PL spectra of different samples. Solid lines are the best fit curves, described by equation (2).

thermal dilatation coefficient of CdS  $(3.6 \times 10^{-6} \text{ K}^{-1})$  is one half that of the CdSe material  $(7.4 \times 10^{-6} \text{ K}^{-1})$  [30, 31]. However, these values could at most induce a size variation of about 0.009 nm across the investigated temperature range, corresponding to about 1 meV difference in the peak wavelength shift, which is insufficient to explain our observed data [23]. The blue-shift of the S10 g-NCs could be attributed to the anisotropic structure of the core CdSe coated with thick layers of CdS shell. With an aspect ratio of 1.25 for the core NCs and an aspect ratio of 1.05 for the S10 g-NCs, there must exist a nonuniform pressure distribution at the core/shell interface. The largest pressure and highest nonradiative loss occurs at the major axis of the core NCs. As a result, the electron-hole pair is 'forced' to recombine radiatively at a slightly shorter dimension. Despite the speculative nature of this explanation, an assessment of the major and minor axes of the core NCs reveals that they are on average 3.5 nm and 2.8 nm, respectively (figure 3(C)). This indicates that, if the electron-hole pair recombines along the minor axis, it could blue-shift by as much as 70 meV, which is of the same order of magnitude as the observed peak wavelength shift. By creating a gradually changing core/shell interface, one could effectively minimize the thermal expansion pressure between the core and the thick shell interface. As evidenced by the G5-5 g-NCs depicted in figure 6(A), such dependence of the bandgap on temperature can be drastically reduced.

The experimental data of figure 6(B) was fitted with equation (2) below, which describes the temperature dependence of the excitonic peak broadening in bulk semiconductor materials [22, 28]:

$$\Delta\Gamma(T) = \sigma T + \Gamma_{\rm LO} (e^{\frac{E_{\rm LO}}{k_{\rm B}T}} - 1)^{-1}.$$
 (2)

Here  $\Delta\Gamma$  is the FWHM difference between the PL linewidth at temperature *T* and the inhomogeneous linewidth ( $\Gamma_{inh}$ ), which is temperature independent. While inhomogeneous broadening is due to the fluctuations in size, shape and composition of NCs, homogeneous broadening (expressed in equation (2)) is related to the exciton–phonon interactions.  $\sigma$  is the exciton–acoustic phonon coupling coefficient,  $\Gamma_{LO}$  represents the exciton–LO phonon coupling coefficient,  $E_{LO}$  is the LO-phonon energy, and  $k_B$  is the Boltzmann constant. A summary of the fitting parameters is

given in supplementary data table A2 (available at stacks.iop. org/Nano/24/475705/mmedia).

The best fit curve for our CdSe core-only NCs yields  $\Gamma_{\text{inh}} = 132 \pm 10 \text{ meV}, \sigma = 67 \pm 10 \text{ meV}, \Gamma_{\text{LO}} = 38 \pm 4 \text{ meV}$  and  $E_{\text{LO}} = 24.5 \pm 0.5 \text{ meV}$ , which are similar to the values found by Valerini *et al* for their 5 nm diameter CdSe/ZnS NCs [23]. Confirmation of the LO energy,  $E_{\text{LO}}$ , is also found from the Raman spectroscopy measurement of CdSe NCs [32, 33]; their estimated value is about 25.4 meV, which is in close agreement with our findings ( $E_{\text{LO}} = 24.5 \text{ meV}$  in table A2 available at stacks.iop.org/Nano/24/475705/mmedia).

From the experimental data, G5-5 g-NCs have a smaller temperature dependent linewidth broadening compared to all other types of NC; their  $\sigma$  value of  $15 \pm 5 \ \mu eV \ K^{-1}$  is 2–4 times smaller than that of the other NCs. In contrast, S10 has by far the largest  $\sigma$  value, which could be ascribed to the presence of some additional dephasing process, induced by surface defects or trap sites at the abrupt interface between core and shell layers [23].

## 3.4. Photoluminescence temperature response of annealed S10 g-NCs

To further verify that the improved thermal stability of G5-5 g-NCs is related to the graded material that minimizes the core/shell lattice tension, a separate experiment was conducted in which the S10 g-NCs were annealed at  $190 \,^{\circ}$ C for 18 h under vacuum. The annealing temperature is chosen to be high enough to thermally induce atomic mobilities between the CdSe and CdS materials, without causing damage to the overall nanostructure. The annealed S10 g-NCs (hereinafter denoted as the sample S10A) were gradually cooled to room temperature to prevent the formation of internal cracks due to thermal shock.

Figure 7(A) shows that the PL intensity of the S10 sample after annealing improves by more than 40% at 355 K. A fit of the experimental data in figure 7(B) to equation (2) reveals that the temperature dependent  $\sigma$  coefficient reduces from 87 ± 10 to 40 ± 6  $\mu$ eV K<sup>-1</sup>. The overall PL peak energy shift for S10A shown in figure 7(C) is only half that of the S10 sample (see supplementary data, tables A1 and A2 available at stacks.iop.org/Nano/24/475705/mmedia). This observation supports the fact that easing the lattice tension of the CdSe/CdS interface in g-NCs renders the



**Figure 7.** (A) Relative intensity (PL normalized at 85 K) of the S10 g-NCs before and after annealing. (B) Fitted  $\Delta$ FWHM experimental data as described in equation (2). The annealed sample (S10A) is about 50% less susceptible to homogeneous broadening. (C)  $\Delta E_g(T)$  of samples S10 and S10A reveal that the PL peak energy shift of S10A is less than half that of the S10 sample.



**Figure 8.** (A)–(D) The blink 'on' fraction statistics of different-size NCs, from core-only to G5-5 g-NCs. Each case has a sample size of 50 NCs. The excitation wavelength is 405 nm, with an irradiance of 2 W cm<sup>-2</sup>. (E) A sample of the blinking trajectory of G5-5. The exposure time is 1 s, and the emission filter's wavelength range is  $655 \pm 20$  nm. (F) Intensity profile of the diffraction limited spot of a single G5-5 nanoparticle captured by the EMCCD when the particle blinks 'on' and 'off'.

nanoparticles more thermally robust. However, due to the fact that only one thin film sample is used for annealing purposes, the sample size is insufficient for TEM acquisition.

#### 3.5. Blinking statistics of G5-5 g-NCs

The blinking statistics of the G5-5 g-NCs analyzed at room temperature are shown in figure 8.

The PL of G-type NCs is collected from a dilute NC thin film immobilized on a glass substrate. Based on SEM measurements, we have found that the separation between NCs is approximately 0.3  $\mu$ m (see supplementary data figures A3 and A4 available at stacks.iop.org/Nano/24/475705/mmedia). Utilizing the Rayleigh criterion, the spatial resolution of our microscope system should be about 0.22  $\mu$ m



**Figure 9.** (A) The PL intensity versus exposure time for different-size NCs. The excitation wavelength is 532 nm at 44 kW cm<sup>-2</sup>. The NC concentration is kept at approximately 8000 NCs  $\mu$ m<sup>-2</sup>. (B) Intensity profile of G5-5 g-NCs at different excitation irradiance with NC coverage of 8000 NCs  $\mu$ m<sup>-2</sup> immobilized on glass substrate. (C) Intensity profile of G5-5 g-NCs at different NC coverage. All of these measurements were acquired under the ambient environment.

 $(NA = 1.46, 100 \times \text{ objective lens})$ . This gives a probability of greater than 75% that the observed diffraction limited spot comes from a single NC.

The blink 'on' threshold is based on the following criterion [18]:

#### $I_{\rm on} > I_{\rm background} + 2.5\sigma_{\rm background}$

where for a single NC to be considered 'on', the average pixel intensity ( $I_{on}$ ) must be at least 2.5 times the standard deviation of the background noise ( $\sigma_{background}$ ) above the averaged background intensity ( $I_{background}$ ).

We measured 50 NC samples for each NC size (core, G3, G5-3 and G5-5). Based on figures 8(A)–(D), our G5-5 g-NCs have the highest probability of being nonblinking. Approximately 67% of these g-NCs are nonblinking and the remaining 30% exhibit a blink 'on' fraction of greater than 0.95. Such observations are also consistent with those of the core/step-shell CdSe/CdS g-NCs. In general, the smaller nanoparticles exhibit a higher blinking rate [14, 18, 34]. Furthermore, blinking statistics at 50 ms exposure time were also acquired and it was found that the G5-5 g-NCs blink 'on' fraction peak population reduces by only 10%, which is far better than for most core and core/shell NCs. This confirms that G5-5 g-NCs are largely blinking suppressed (see supplementary data figure A6 available at stacks.iop.org/ Nano/24/475705/mmedia).

#### 3.6. Photobleaching rates of G5-5 g-NCs

The photobleaching rates of different-size NCs are shown in figure 9(A). With increasing NC size, these graded NCs exhibit rapid reduction in photobleaching rate when illuminated with a cw laser (44 kW cm<sup>-2</sup>) at  $\lambda = 532$  nm. We found that the g-NCs (G5-1, G5-3 and G5-5) are extremely stable at high power illumination. Consistent with the extreme photostability found by Hollingsworth *et al* [17, 18], the thick shell layers prevent photo-oxidation, which is one of the main contributors to photobleaching [13, 14]. The G5-5 g-NCs were also investigated under different illumination irradiance at 532 nm and multiple NC concentrations on glass substrates; see figures 9(B) and (C). It is found that, at an NC concentration of approximately 50 NCs  $\mu$ m<sup>-2</sup>, there is about 20% PL drop at the end of 1 h under an irradiance of 44 kW cm<sup>-2</sup>. However, no signs of PL decay were found at higher NC concentration.

#### 4. Conclusion

We have demonstrated that core/graded-shell CdSe/  $CdSe_{1-r}S_r/CdS$  'giant' NCs have a robust PL temperature dependence. It is found that the thermal PL stability is approximately 1.5-3 times better than that of any other type of NC (e.g. CdSe core-only NCs, three shell layer CdSe/CdS NCs, and ten shell layers CdSe/CdS g-NCs). The peak wavelength shift and the spectral FWHM were 5-10 times and 2-4 times, respectively, smaller than their competing counterparts. The temperature robust PL property of the core/graded-shell g-NCs is believed to be related to the minimization of the core/shell lattice tension. Therefore, PL lifetime measurement is needed to better understand the electron-hole distribution differences between G5-5 and S10 g-NCs especially under different temperature conditions. In addition, TEM acquisition of the structural changes of S10 g-NCs as they are annealed will provide crucial understanding about the underlying physics of these thermally robust g-NCs. Furthermore, such g-NCs were found to be largely blinking suppressed and extremely photostable under high excitation fluence (see figures 8 and 9). Due to their extreme PL stability, these g-NCs could be ideal for use as the active medium for improved laser devices for visible range telecommunication systems [2], and possibly as temperature-insensitive bioprobes in bio-imaging applications [8].

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