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RAPID COMMUNICATION

Whispering gallery mode emission at telecommunications-window wavelengths using PbSe nanocrystals attached to photonic beads

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Abstract

We report the selective chemical attachment of infrared emitting PbSe nanocrystal quantum dots onto micron-scale glass photonic beads. Upon optical excitation, photoluminescence from the shell of nanocrystals is seen to couple into the high-Q 'whispering gallery' modes of the bead via the evanescent optical field, resulting in a series of sharp peaks being observed at wavelengths of around 1550 nm. Theoretical modelling gives a close agreement with the data for angular modes corresponding to $l \sim 120$. This work demonstrates the potential of narrow-bandgap II–VI semiconductor nanocrystals for use in a wide range of telecommunications-window photonics applications.

Semiconductor nanocrystals, or 'quantum dots', are nanometre-sized, roughly spherical, chemically synthesized particles of II–VI and III–V materials, which have attracted great interest due to the regime of extreme quantum confinement possible when the particle dimensions are smaller than that of the bulk-exciton Bohr radius [1–3]. Such quantum dots exhibit discreet electronic states and strongly size-tuneable optical transitions [4]. In addition, the inherent control over surface chemistry of these colloidal materials make them ideal for solution processing and liquid phase deposition techniques. These unique and advantageous properties have attracted a diverse range of potential applications, ranging from optical gain media [5] and photonics [6] to molecular electronics [7]. One particular area of current interest is in the synthesis and characterization [8–10] of quantum dots with luminescence which may be size-tuned to coincide with the technologically important 1.3–1.55 μm region of the spectrum, the so-called 'telecommunications window'.

In this paper, we consider the great potential for the use of PbSe nanocrystals (a narrow bandgap II–VI material) as an active medium in photonic devices operating at telecoms-window wavelengths, by demonstrating the coupling of photoluminescence (PL) into high-Q 'whispering gallery' modes (WGMs) of a glass photonic-bead as a paradigm. Micron-scale silica or polymer spheres, synthesized by sol-gel or emulsion polymerization techniques respectively, have an interesting ability to behave as optical microcavity resonators [11]. Multiple total internal reflection at the interface of the sphere allows the formation of resonant 'whispering gallery'

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modes, with Q-factors as high as 10^3–10^8, resulting in a drastic redistribution of the optical density of states, relative to free space [12]. A microsphere resonator, acting as a 'photonic bead', leads to a significant alteration of the spectral, spatial and temporal characteristics of embedded or coupled emitters. These properties make photonic beads candidates for a wide range of applications, such as novel laser cavities and oscillators [13].

The PbSe nanocrystals used in these experiments were synthesized via our recently reported organometallic-precursor route [14], with which it is routinely possible to achieve infrared emitting samples with a PL efficiency of up to 60% in solution and with a particle size distribution of less than 10%. In brief summary, this involved the solvothermal precipitation of PbSe from Pb(II) oleate and trioctylphosphine-selenide precursors at 100 °C, using diphenylether as co-ordinating solvent. The resultant nanoparticles have an organic capping matrix predominantly of oleic acid and were isolated by centrifugation and drying. The solution absorption and PL spectra of the sample used in these experiments are shown in the inset to figure 2. The mean size of the PbSe nanocrystals may be inferred, from the peak absorption wavelength [14], as being around 8.4 nm in diameter and the PL band, Stokes-shifted from the absorption, is seen to extend between around $\lambda = 1400$ nm and 1650 nm, encompassing a substantial portion of the telecoms-window wavelengths. A further important characteristic of these samples is the efficiency of PL emission (or 'quantum-yield') in the solid, close-packed form. It is expected that the efficiencies for films will be significantly reduced compared to the solution values, due to the effects of energy transfer between emitters, leading to an increased likelihood of PL quenching at surface states or traps on the nanocrystals [15]. For this measurement, thin films of the PbSe nanocrystals were drop-coated onto glass substrates from toluene solution. Using an integrating sphere technique to collect the PL over all solid angles from these films and to measure the comparative absorption of laser pump light, it was possible to make a quantitative, self-consistent calculation of PL efficiency [16]. It was found that typical efficiencies were of the order of 5–6% for newly prepared samples, decreasing to 1–2% after storage in dark conditions for several months. These values compare favourably with those reported in the literature [17] and indicate the robust shelf-life of our samples.

In contrast to previously reported methods of directly doping microspheres with chromophores and/or fluorophores during a polymerization process [18], we have developed a technique of direct attachment of the colloidal nanocrystals onto the surfaces of glass beads. Although the precursor-doping techniques enable the infiltration of emitters throughout the physical extent of polymer spheres and hence the coupling of emitted light directly into resonant modes, problems may arise with the variable shape-integrity of the beads, especially at high doping fractions. This is most likely due to the lack of stabilization of the particles that are generated, with the added dopant material causing enhanced agglomeration. Our method of attachment of nanocrystals to glass beads provides a convenient way of coupling PL emission to WGMs, via the evanescent optical field, and this technique can be readily applied to either visible emitting

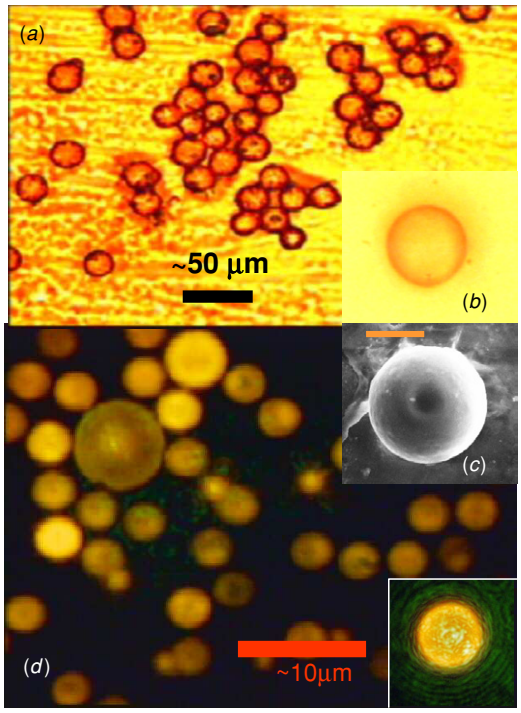

Figure 1. (*a*) Optical microscope image of 20 μm diameter glass beads coated with PbSe nanocrystals, using a broadband white-light illuminator in transmittance mode and a $\times 20$ objective. An image of a single bead under $\times 100$ magnification is shown in (*b*). (*c*) shows a single bead viewed with a scanning electron microscope (SEM), with the scale bar being ~ 10 μm in length. (*d*) Photoluminescence (in real colour) from an ensemble of ~ 5 m diameter beads, coated with CdSe/ZnS core-shell nanocrystals, viewed in a microscope coupled to a CCD camera. Laser illumination was at $\lambda = 524$ nm and an RG550 filter was used to avoid co-detection of the pump light. The inset shows the PL from a single bead under $\times 100$ magnification, focusing on the front surface of the bead.
(This figure is in colour only in the electronic version)

(e.g. CdSe) or infrared emitting PbSe samples. The beads used in our experiments were commercially purchased 20 μm diameter, borosilicate-glass spheres. A sample of the PbSe (or CdSe) nanoparticles was dispersed into a near-saturated solution (1:1 methanol and hexane, 15 mg mL^{-1}, total vessel volume of 1.5 ml) and 50 mg of the borosilicate-glass beads was added to this mixture. After sonication, the samples were left mixing for 2 h at room temperature. The methanol:hexane mixture is incompatible; so there is a gradual precipitation of nanoparticles from the methanol phase onto the beads, which act as deposition sites. Once there, the nanocrystals robustly attach to the beads, in any polar solvent medium, as they are completely insoluble due to the oleic acid capping layer. The resultant suspension was filtered, washed carefully with methanol and dried. In figure 1(*a*), a microscope image of the nanocrystal-coated beads is shown. Using a standard white-light illumination source in transmission mode the beads have a deep-reddish appearance, due to the strong absorption of the PbSe nanocrystals across the visible spectrum. In figure 1(*b*), a single bead is imaged under higher magnification and we estimate that the nanocrystal layer thickness is, at most, a few hundred nanometers. The scanning electron micrograph (SEM) image, shown in figure 1(*c*), further illustrates the

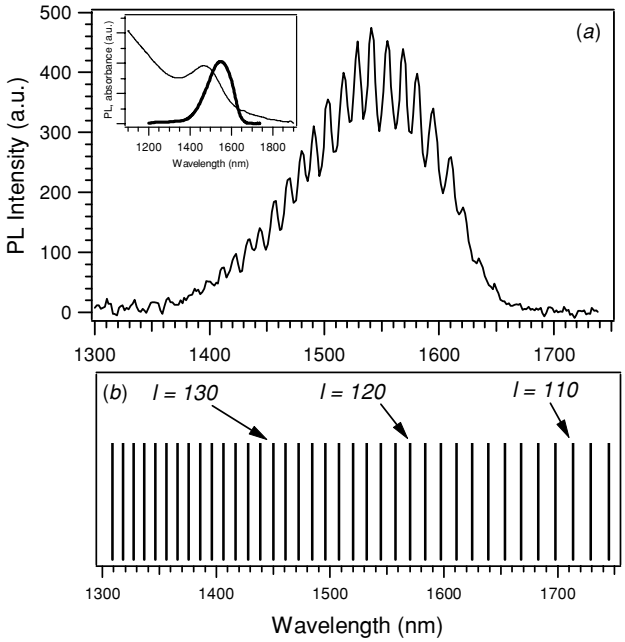

Figure 2. (*a*) Photoluminescence spectrum for a single photonic bead, coated with PbSe nanocrystals. Narrow whispering gallery modes (WGMs) are clearly present within the broad nanocrystal PL spectrum. Absorption and photoluminescence (bold line) spectra of the PbSe nanocrystals used, after dispersal into a solution of tetrachloroethylene (C_2Cl_4), are shown in the inset. (*b*) Theoretical spectral positions of the angular (l) modes of a 20 μm diameter silica bead, closely matching the experimental spacing.

smoothness and uniformity of the coating produced by this method, with slight undulations of the surface being visible on sub-micron length scales. Indeed, an advantage of this technique over other QD-to-bead attachment combinations is that the high Q-factor of the WGMs, which is highly sensitive to the roughness of the high refractive-index outer coating as well as the shape of the sphere, can be retained. Figure 1(*d*) shows microscope images of the PL observed from 5 μm beads coated with alkylamine-capped CdSe/ZnS 'core-shell' nanocrystals [3], which emit around $\lambda = 570$ nm in this particular case. We note also that several beads have a concentric variation in PL intensity, as might be expected from WGM-coupled emission.

An ensemble of the beads coated with PbSe nanocrystals was dispersed in methanol and drop-coated onto a glass microscope slide. PL measurements on the beads were carried out by coupling a few milliwatts of a $\lambda = 658$ nm, continuous-wave (CW) diode laser excitation source onto the sample inside a microscope, using a $\times 100$ microscope objective. The laser spot size in the focal plane was of the order of a few microns, allowing individual beads to be photo-excited. PL was collected co-linearly through the microscope, focused into a multimode fibre, coupled into a monochromator and detected using a Peltier-cooled InGaAs CCD array, with a spectral resolution of around 3–4 nm across a wide range of $\lambda = 850$ nm to 1750 nm. All experiments were performed using unpolarized light, in air and at room temperature. The PL spectrum detected from one of the coated beads is shown in figure 2(*a*), showing a series of sharp peaks with the envelope of peak intensities closely matching the original inhomogeneously-broadened profile of the QD PL spectrum. We attribute the presence of these sharp peaks to PL from the PbSe nanocrystals being efficiently coupled into resonant WGMs of the bead. Subtraction of the normalized PL spectrum from these data indicates that there are no significant issues of re-absorption of luminescence or waveguiding effects within the thin nanocrystal layer, indicating that the nanocrystal layer does not itself constitute a discrete optical component of the system. No signs of photobleaching with time were observed, nor any spectral redistribution of intensity as a function of power, within the damage-threshold range of our sample. We note that optical gain or stimulated emission effects [19, 20] are expected to be absent at these CW pump energies, even given the high degree of optical feedback achievable in the WGMs of such structures [5, 10].

The properties of WGMs can be described in terms of three mode indices, n, l and m, where n is the number of field maxima in the radial direction, l describes the multiplicity of angular nodes present, with each l mode consisting of $(2l + 1)$ degenerate azimuthal m modes. For spheres of 20 μm diameter, in the 1.5 μm wavelength regime and for nanocrystals confined to the outer shell, only $n = 1$ radial modes are expected to be important for collecting photoluminescence. These modes are confined just inside the outer perimeter of the sphere, and have the largest optical field overlap to the PbSe quantum dots. An estimate for the energy separation of angular (l) modes in the sphere can be derived by assuming a multiple of half-wavelengths must fit around the interior equator:

$$2\pi R\eta = l\lambda/2, \tag{1}$$

where the refractive index of the glass sphere $\eta = 1.46$ and R is the radius of the sphere. The Q-factor of the resultant angular modes may also be estimated from the number of round trips, based upon losses in reflection at the interface, as being of order 5000. The expected mode separation of $\Delta\lambda = \lambda^2/4\pi Rn = 13.1$ nm fits well with the experimental mode separation of 13.4 nm, in the vicinity of $\lambda = 1550$ nm, implying that we observe modes in the approximate range of $l = 114$–132 (figure 2(*b*)) with any residual differences being due to tolerance in the exact of radius and symmetry of the bead. With the experimental resolution employed, it was not possible to directly measure the Q-factor of the WGMs, although by de-convolution of the measured linewidths of $\Delta\lambda \sim 6$ nm, it may be inferred that $Q \geqslant 1000$. Similarly, the observation of any substructure within the l modes, such as split m modes due to imperfections in the spherical integrity or birefringence between TE and TM polarizations, is also expected to be beyond the experimental limits of resolution.

As a further tool to understanding the optical field patterns associated with WGMs in our beads, we present a model based on Mie scattering theory [21]. The well-known decomposition of harmonic EM waves inside and outside a dielectric sphere reveals the electric field to be evanescent upon leaving the sphere, converting to a travelling wave within the propagation length of the decaying mode. We display the results of our model for the $l = 100$ mode with TE polarization in figure 3(*a*), showing the field profile and evanescent field in the vicinity of the bead. No significant birefringence

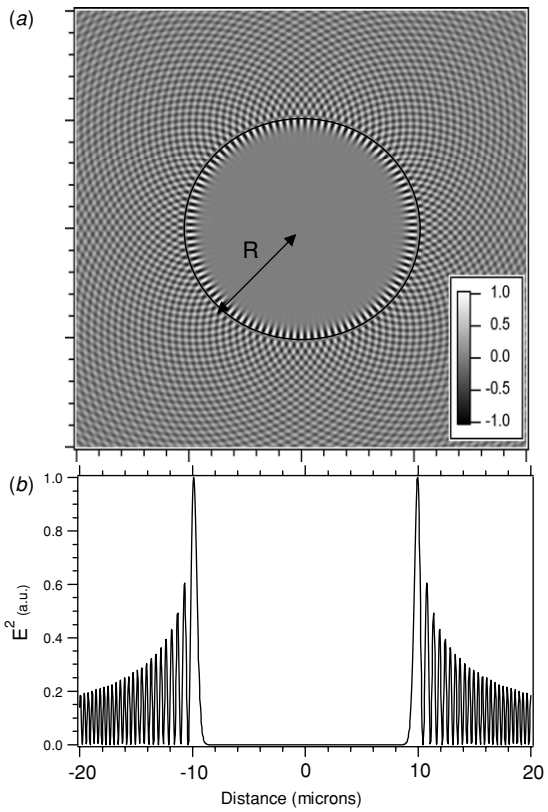

Figure 3. (*a*) A two-dimensional section of the optical field profile derived from a Mie scattering model of the $l = 100$ TE WGM (arbitrary scale). The radius of the sphere is marked on for clarity. (*b*) Optical intensity along a radial direction, showing the evanescent mode leakage beyond the dielectric/air interface.

for a spherical bead was predicted within the computational limits of this model. Figure 3(*a*) clearly shows the expected angular distribution of nodes and anti-nodes within the bead corresponding to a WGM. Plotting the optical intensity along a radial direction (figure 3(*b*)) shows the considerable extent of evanescent modes beyond the dielectric/air interface, providing a mechanism by which emitters attached within a few hundred nanometers of the sphere surface can couple light efficiently into the WGMs. We note that the macroscopic refractive index contrast between bead and coating is not of crucial importance, given the evanescent nature of this coupling. One future direction of these experiments may be to use serial dilution techniques, or an equivalent modification of the attachment chemistry, in order to reach a regime where a single nanocrystal is strongly-coupled to a WGM of the photonic bead via the evanescent field [22]. This would represent a novel system in which to observe strong exciton–photon coupling, or related quantum electro-dynamical (QED) effects. More interesting for telecom applications is the use of combined microdevices with ultra-low-threshold lasers pumped by simple light emitting diode arrangements for high efficiency coherent emitters. Wavelength multiplexing of such WGM microlasers can be achieved by assembling them on top of multiple gratings [23] with periods commensurate with the internal field profile shown in figure 3(*a*); the grating determines which whispering gallery mode operates, as the mode that couples to it the least will have the lowest losses.

In conclusion, we report a method for the chemical attachment of infrared emitting PbSe nanocrystals onto micron-scale glass photonic beads, using a ubiquitous and convenient solution processing technique. Photoluminescence from the nanocrystals is seen to couple into the high-Q whispering gallery modes of the bead, resulting in a series of sharp peaks observed at wavelengths around 1550 nm. Theoretical modelling of the angular WGMs gives a close agreement with the data for modes corresponding to $l \sim 120$, $n \sim 1$, with the nanocrystal coating within a region where the optical field of the WGMs is still substantial. This work is a clear demonstration of the use of narrow-bandgap II–VI semiconductor quantum dots, such as PbSe nanocrystals, in a telecommunications-window photonics application. We anticipate further progress in combining the many desirable properties of semiconductor nanocrystals with technologically important infrared applications.

References

[1] Alivisatos A P 1996 *Science* **271** 933
[2] Yoffe A D 2001 *Adv. Phys.* **50** 1
[3] Peng X, Schlamp M C, Kadavanich A V and Alivisatos A P 1997 *J. Am. Chem. Soc.* **119** 7019
[4] Kuno M, Lee J K, Dabbousi B O, Mikulec F V and Bawendi M G 1997 *J. Chem. Phys.* **106** 9869
[5] Klimov V I and Bawendi M G 2001 *MRS Bull.* **26** 998
[6] Finlayson C E, Ginger D S and Greenham N C 2000 *Appl. Phys. Lett.* **77** 2500
[7] Klein D L, Roth R, Lim A K L, Alivisatos A P and McEuen P L 1997 *Nature* **389** 699
[8] Battaglia D and Peng X 2002 *Nano Lett.* **2** 1027
[9] Du H, Chen C, Krishnan R, Krauss T D, Harbold J M, Wise F W, Thomas M G and Silcox J 2002 *Nano Lett.* **2** 1321
[10] Schaller R D, Petruska M A and Klimov V I 2003 *J. Phys. Chem.* B **107** 13765
[11] Woggon U, Wannemacher R, Artemyev M V, Möller B, Lethomas N, Anikeyev V and Schöps O 2003 *Appl. Phys.* B **77** 469
[12] Gotzinger S, Menezes L de S, Benson O, Talapin D V, Gaponik N, Weller H, Rogach A L and Sandoghdar V 2004 *J. Opt.* B **6** 154
[13] Cai M, Painter O, Vahala K J and Sercel P C 2000 *Opt. Lett.* **25** 1430
[14] Finlayson C E, Amezcua A, Sazio P J A, Walker P S, Grossel M C, Curry R J, Smith D C and Baumberg J J 2005 *J. Mod. Opt.* **52** 955
[15] Crooker S A, Hollingsworth J A, Tretiak S and Klimov V I 2002 *Phys. Rev. Lett.* **89** 186802
[16] de Mello J C, Wittmann H F and Friend R H 1997 *Adv. Mater.* **9** 230
[17] Sargent E H 2005 *Adv. Mater.* **17** 1
[18] Artemyev M V and Woggon U 2000 *Appl. Phys. Lett.* **76** 1353
[19] Snee P T, Chan Y, Nocera D G and Bawendi M G 2005 *Adv. Mater.* **17** 1131
[20] Lu S, Jiang D, Jia R, An L, Bian L, Liang X, Ma B and Sun B 2002 *J. Phys: Condens. Matter* **14** 6395
[21] Grandy W T and Brandt R K 2000 *Scattering of Waves from Large Spheres* (New York: : Cambridge University Press)
[22] Artemyev M V, Woggon U, Wannemacher R, Jaschinski H and Langbein W 2001 *Nano. Lett.* **1** 309
[23] Tai C Y, Unal B, Wilkinson J S, Ghanem M A and Bartlett P N 2004 *Appl. Phys. Lett.* **84** 3513