Nanoscale

Dynamic Article Links

Cite this: *Nanoscale*, 2012, **4**, 5163

www.rsc.org/nanoscale

PAPER

Energy transfer from a dye donor to enhance the luminescence of silicon quantum dots†

Folarin Erogbogbo,[ab] Ching-Wen Chang,[a] Jasmine May,[bc] Paras N. Prasad[bc] and Mark T. Swihart*[ab]

Received 25th April 2012, Accepted 18th June 2012
DOI: 10.1039/c2nr31003a

Quantum dots are known for their superior optical properties; however, when transferred into aqueous media, their luminescent properties are frequently compromised. When encapsulated in micelles for bioimaging applications, luminescent silicon quantum dots can lose as much as 50% of their luminescence depending on the formulation used. Here, we create an energy transfer micelle platform that combines silicon quantum dots with an anthracene-based dye in the hydrophobic core of 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-*N*-[methoxy(polyethylene glycol)-2000] (DSPE-PEG) micelles. These phospholipid micelles are water dispersible, stable, and surrounded by a PEGylated layer with modifiable functional groups. The spectroscopic properties of energy transfer between the anthracene donors and silicon quantum dot acceptors were analyzed based on the observed dependence of the steady-state emission spectrum on concentration ratio, excitation wavelength, pH, and temperature. The luminescence of silicon quantum dots from the core of a 150 nm micelle is enhanced by more than 80% when the anthracene dye is added. This work provides a simple yet readily applicable solution to the long-standing problem of luminescence enhancement of silicon quantum dots and can serve as a template for improving the quantum dot emission yield for biological applications where luminescence signal enhancements are desirable and for solar applications where energy transfer plays a critical role in device performance.

Introduction

Quantum dots (QDs) are semiconductor nanocrystals, 1–10 nm in diameter, that typically consist of combinations of elements from groups II and VI (CdSe, CdTe, CdS, ZnS and ZnSe), groups IV and VI (PbS and PbSe) or groups III and V (GaAs, GaN, InP and InAs) of the periodic table.[1,2] They have advantageous optical properties such as broad excitation spectra, photostability, and bright, size-dependent emission. Upon transfer from hydrophobic to aqueous solvents, their brightness and quantum yield typically decrease.[3,4] Thus, methods of enhancing their photoluminescence (PL) in aqueous media are desirable.

PL enhancement of QDs has traditionally been accomplished by altering synthesis strategies[3,4] to make the QDs more stable in aqueous environments or by combining them with plasmonic materials that can enhance their properties after synthesis. Even though synthetic measures have greatly improved the quality of emission from QDs, many encapsulation, ligand exchange, and other "hydrophobic to aqueous" conversion methods that are needed for biological applications lead to substantial reduction in luminescence intensity.

Combining QDs with plasmonic materials has shown the greatest enhancements of brightness and PL quantum yields of QDs.[5–9] However, these methods often involve the immobilization of the QDs on films or substrates, and therefore eliminate some of the advantages that come from colloidal suspensions such as those required for biological applications. Enhancing the PL of QDs with metals also requires highly controlled "spacer" sections to protect the QDs from quenching by the metals. Gao's group synthesized QDs constructed to have a plasmonic gold shell about 5 nm away from the QD core, which showed ~80–120% enhancement in emission yield compared to the QDs solubilized in water. However, the gold shell requires further modification for dispersion in water. This study and similar studies[10] are very promising for multimodal dark field and optical imaging; however they have practical limitations that arise from excessive particle loss during centrifugation to remove the polyelectrolyte that serves as a spacer between the QD and the shell. In addition, this method only works for particles of a certain size, and the additional functionalization

[a]*Department of Chemical and Biological Engineering, 303 Furnas Hall, The University at Buffalo, The State University of New York, Buffalo, New York, 14260-4200, USA. E-mail: swihart@buffalo.edu; Fax: +1 716-645-3822; Tel: +1 716-645-1181*

[b]*Institute for Lasers Photonics and Biophotonics, 458 Natural Sciences Complex, The University at Buffalo, The State University of New York, Buffalo, New York, 14260-4200, USA. E-mail: pnprasad@buffalo.edu; Fax: +1 716-645-6945; Tel: +1 716-645-4147*

[c]*Department of Chemistry, 359 Natural Sciences Complex, The University at Buffalo, The State University of New York, Buffalo, New York, 14260-3000*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2nr31003a

steps required limit their use for increasing quantum yield in water.

Energy transfer between QDs and dyes has been extensively studied for biological applications in the context of biosensors.[11–14] Most reports investigate QDs as donors to dyes, and the ability of QDs to be efficient energy acceptors from dyes has been questioned.[15] To demonstrate that QDs can be acceptors, other QDs, proteins, polymers and long-lived lanthanide complexes have been used as donors.[16–20] A recent report[16] demonstrated the use of a dye, 1,8-naphthalimide, as a FRET donor to Cd-based QDs. However, that work was done in organic solvents, with the dye bound to the QDs surface. In this work, rather than attaching the dye to the QD, we have simply co-encapsulated the dye and QD within a micelle.

Micelle encapsulation is among the most successful approaches to dispersing QDs in aqueous media.[21,22] Micelle encapsulated QDs have been demonstrated in a wide variety of applications including delivery of drugs and imaging agents. Micelles can also be used to combine multiple discrete components into multifunctional nanoconstructs that are useful for multiple applications. Few studies have considered co-encapsulation of multiple components to enhance an existing function. Because QDs are not known as efficient acceptors they have not previously been combined in the core of a micelle with dyes for emission enhancement.

Silicon quantum dots (SiQDs) are currently investigated as alternatives to conventional QDs,[23–32] because of the abundance of elemental silicon and its inherent lack of toxicity. Two studies[33,34] have shown the ability of SiQDs to serve as efficient energy transfer acceptors within a polymer film. Our group has recently shown that SiQDs can be combined with other discrete components in the core of a micelle to achieve multi-functionality.[35] Here, we use basic principles of energy transfer and micelle encapsulation to overcome one of the most important limitations of QDs in biological applications: the loss of emission yield when transferred to water. We study SiQDs co-encapsulated with vinyl anthracene (VA) in the hydrophobic core of 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-*N*-[methoxy(polyethylene glycol)-2000] (DSPE-PEG) micelles. We chose VA because it is representative of anthracene dyes, which have been tailored for many different applications,[36] and more importantly because the anthracene excitation spectrum matches the peak PL excitation wavelengths for SiQDs, yet its emission occurs at much shorter wavelengths than the SiQDs. Thus, excitation at the same wavelength typically used to excite SiQDs (~350 nm) leads to absorption by both the SiQDs and the VA. Subsequent energy transfer from VA to the SiQDs leads to enhanced luminescence from the SiQDs. We used DSPE-PEG micelles because we have previously demonstrated that they can render SiQDs useful in multiple imaging applications such as cellular labeling,[37] *in vivo* tumor targeting, sentinel lymphnode mapping, and multicolor imaging.[38]

Experimental methods

Materials

Silane (SiH_4, Voltaix, electronic grade, 99.999%), hydrofluoric acid (HF, Acros Organic, 48–51%), nitric acid (HNO_3, EMD, 68–70%), styrene (Acros 99%), DSPE-mPEG-methoxy 2000 (Avanti 20 mg ml^{-1}), and 9-vinyl anthracene (Sigma-Aldrich) were used as received if not otherwise noted. All solvents (chloroform, HPLC water, and methanol) were of reagent grade and were used without further purification.

Preparation of silicon nanocrystals

Silicon nanocrystals were prepared by high temperature CO_2 laser pyrolysis of silane in an aerosol reactor as described by Li *et al.*[26] The non-luminescent silicon nanoparticles were collected under a nitrogen atmosphere to prevent oxidation.

Preparation of photoluminescent SiQDs

The etching procedure developed by Hua *et al.*[28] was scaled up as follows. 300 mg silicon nanoparticles were dispersed in 40 ml of methanol. A mixture of 100 ml of HF (48 wt%) and 10 ml of HNO_3 (69 wt%) was added to the silicon–methanol solution. The etching process proceeded for 60–75 seconds. The color of the mixture changed from brown to orange with decreasing particle size. Once the Si NPs approached the desire emission wavelength, 400 ml of methanol was added to terminate the reaction. The particles were then collected on a PTFE filter and washed with a 1 : 3 methanol–water mixture to remove excess acid. After rinsing with pure methanol four times, the particles were added to styrene for photoinitiated hydrosilylation. All of the above processes were carried out under nitrogen. Silicon nanoparticles and styrene in a transparent vial containing a magnetic stirrer were put in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with 16 RPR-2537 Å UV tubes to initiate hydrosilylation. The reaction time is about 10 minutes for styrene. The completeness of reaction is qualitatively indicated by the clarity of the solution. The clear samples were filtered through a PTFE syringe filter with a pore size of 0.45 μm and the styrene coated silicon nanoparticles were isolated by centrifugation.

Micelle encapsulation

Dry particles were dispersed in chloroform to make a concentration of 1 mg Si QDs per ml chloroform. In micelle encapsulation, 100 μl of this dispersion (containing 0.1 mg SiQDs) and 5 mg phospholipid (DSPE PEG (2000) methoxy) were added in a 10 ml round bottom flask. A series of samples was prepared by adding 0, 5, 10, 50, or 100 μl of 0.0018 M vinyl anthracene (VA) in chloroform (containing 0.00019 μg VA per μl). Sonication was used to disperse the particles. The chloroform was then evaporated using a Labconco rotary evaporator with a 37 °C water bath. Finally, 2 ml of HPLC water was used to hydrate the lipid film formed on the reaction vials. The resulting stable dispersion was stored at 4 °C for further studies.

PL and PLE measurement

A Perkin–Elmer luminescence spectrometer (model LS50) was used to measure PL and PLE. Solution samples of functionalized SiQDs were put in a quartz cuvette for measurement. To record PL spectra, a 390 nm emission cutoff filter was added. The excitation wavelength was 350 nm and emission was scanned

from 400 nm to 900 nm. For PLE measurement, the emission wavelength was set to the maximum of the PL spectrum obtained with 350 nm excitation. The excitation wavelength was then scanned from 300 nm to 800 nm.

Temperature study

The SiQD/VA micelle dispersions were heated in a quartz cuvette in a water bath. Samples were removed at 20 °C, 25 °C, 35 °C, 45 °C, 55 °C, 65 °C, 75 °C, 85 °C, and 95 °C, and PL was immediately measured.

pH study

50 μl of SiQDs/VA micelle dispersion was extracted from each solution sample (samples with 0 μl, 5 μl, 10 μl, 50 μl, and 100 μl VA) and diluted by 2 ml of a solution prepared from HCl or NaOH to yield solutions with pH ranging from 1 to 13. The PL of each sample was measured immediately and again after 24 hours.

Electron microscopy

The size was characterized by high-resolution transmission electron microscopy using a JEOL 2010 HRTEM.

Results and discussion

Fig. 1 illustrates the strategy of surface functionalization of SiQDs. This process stabilizes the luminescence of the SiQDs.

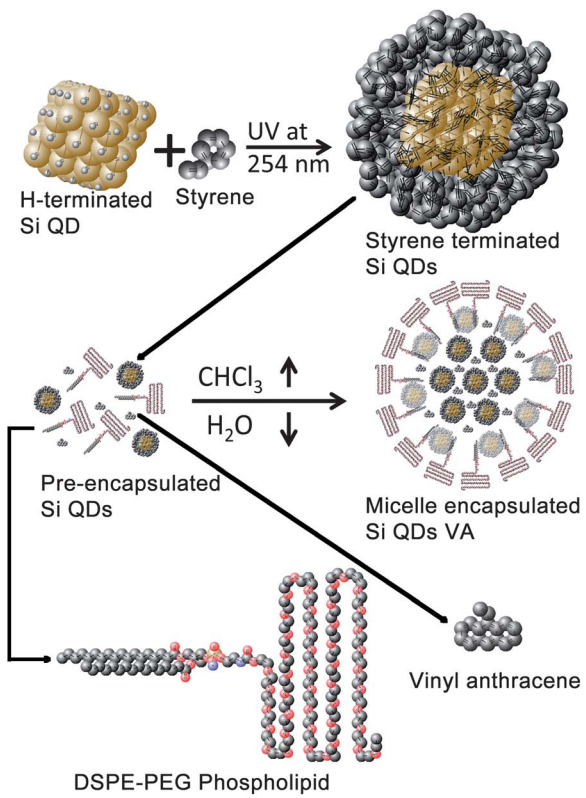

Fig. 1 Schematic of surface functionalization of SiQDs. (The image is not drawn to scale.)

During the photoinitiated hydrosilylation process, styrene was attached to the SiQD surface *via* reaction of surface SiH moieties with the terminal double-bond of styrene. The functionalized SiQDs are hydrophobic and dispersible in chloroform or other nonpolar solvents. Fig. 1 also shows the co-encapsulation of these hydrophobic SiQDs and vinyl anthracene (VA) into the hydrophobic core of DSPE PEG micelles. The donors, VA, and the acceptors, SiQDs, are spatially colocalized by premixing them and then encapsulated by using a 1 : 50 mass ratio of SiQD to DSPE-PEG. The parameters of the process are varied by changing mass ratios of dye to SiQDs.

Fig. 2a and b show the TEM images of SiQDs. The size of the SiQD micelle ranges from 100 nm to 150 nm and is similar for micelle-encapsulated SiQDs with VA in Fig. 2c and d.

The PL and PLE spectra of SiQDs and VA are shown in Fig. 3a. The overlap of the VA emission spectrum and the SiQDs excitation spectrum is highlighted because it meets the requirements for energy transfer. Excitation of VA near 355 nm produces emission peaking at 428 nm. Therefore, when the micelles containing both VA and SiQDs were excited at 350 nm, both direct absorption by the SiQDs and absorption by VA followed by energy transfer to the SiQDs are possible. Fig. 3b shows extinction spectra of SiQDs and VA, alone and co-encapsulated in micelles. The extinction spectrum of co-encapsulated SiQDs and VA (MSiQDs-VA) is approximately the sum of the spectra of the micelles with SiQDs or VA alone. Note that these extinction spectra include contributions from scattering as well as from absorption, but that the scattering contribution should be approximately the same in all cases.

Fig. 4a shows the intensity change of PL from micelles containing SiQDs and varying amounts of VA. Over this range of concentration ratios, the emission peaks observed for VA alone are absent because of energy transfer to the SiQDs. As the amount of VA is increased, intensity of the SiQD emission also increases. The normalized intensity of SiQDs without any VA is 0.5 and the intensity goes up to 0.6, which is about 14% increase in emission area of the original sample, with 0.005 ml VA added

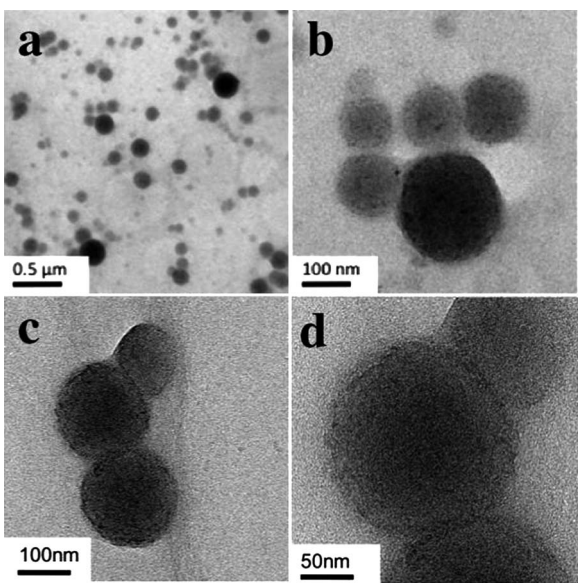

Fig. 2 TEM images of (a and b) SiQD micelle, and (c and d) MSiQDs-VA.

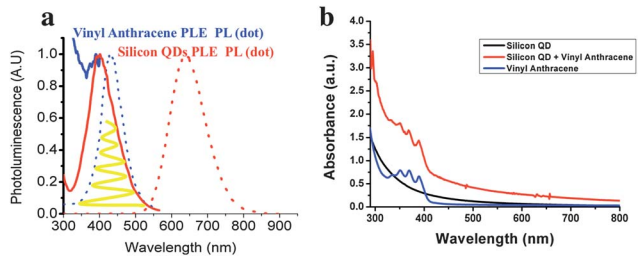

Fig. 3 (a) PL and PLE spectra of SiQDs and VA. (b) Absorbance of Si QD micelles, VA micelles, and SiQDs and VA micelles.

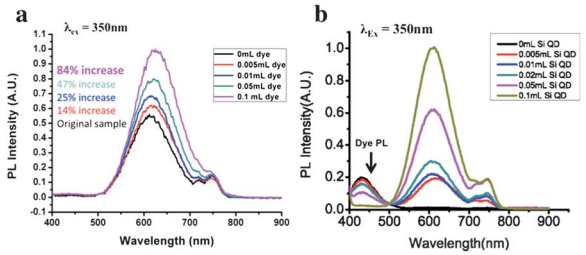

Fig. 4 (a) The PL trend of a certain amount of SiQDs with different amounts of VA co-encapsulated in micelles. (b) The change of PL of a certain amount of VA with a different amount of SiQDs co-encapsulated in micelles.

(the mass ratio of silicon to VA is 1050 : 1). The intensity of SiQDs keeps increasing when 0.01 ml (SiQDs to VA mass ratio 525 : 1), 0.05 ml (SiQDs to VA mass ratio 105 : 1) and 0.1 ml VA (SiQDs to VA mass ratio 53 : 1) are added and the SiQD intensity increases by 84%. The disappearance of the VA's emission peak is depicted in Fig. 4b. The PL spectra shown are from micelle configurations with a constant amount of VA, the donor, premixed with various amounts of SiQDs added and encapsulated in micelles. The spectrum of VA alone without SiQDs has a peak at 430 nm. When adding SiQDs into micelles, the emission peak of SiQDs at 620 nm emerges and the VA emission peak at 430 nm decreases due to energy transfer to SiQDs. Fig. 4b also reveals that as the SiQD content of the micelle increases, the PL intensity of the VA drops until it is no longer detectable. This indicates that SiQDs are efficient acceptors of energy that is transferred from VA.

The PL wavelengths with the highest increases in area due to energy transfer from VA to SiQDs are analyzed in Fig. 5. Fig. 5b is derived from Fig. 5a in order to compare the SiQD PL intensity that corresponds to the emission wavelengths of 580 nm, 620 nm, and 700 nm. As the wavelength shifts to the red

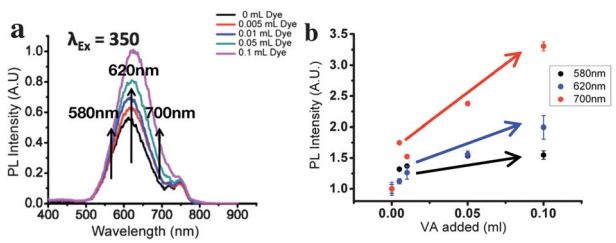

Fig. 5 (a) Original spectra of SiQDs and VA micelles (MSiQDs-VA) with varying amounts of VA. (b) PL comparison of MSiQDs-VA at 580 nm, 620 nm, and 700 nm.

the more energy seems to be transferred from the VA. The emission at 700 nm increases by about 250% compared to the 50% increase at 500 nm. This is reasonable because the excitation spectra of SiQDs would shift as the PL shifts to the red, thereby increasing the overlap of the effective energy transfer area. This may also have a beneficial impact for near infrared emitting particles that emit at 700 nm or higher.

Fig. 6 validates that the increase in PL intensity of the SiQD micelles is associated with energy transfer from VA. The PL of micelles containing a constant amount of silicon and increasing amounts of VA reveals that at 350 nm, the excitation wavelength of VA, the PL increases sharply, whereas at 380 nm, 400 nm and 430 nm no sharp increase is noticed.

The stability of micelle encapsulated SiQDs with varying amounts of VA was examined as a function of pH and temperature. Fig. 7 shows the variation of PL intensity of the MSiQD-VA in HPLC water after the sample is heated to different temperatures. Although the PL intensity fluctuates from 20 °C to 95 °C, there is no clear reduction of PL for SiQD micelles and MSiQDs-VA. This measurement was surprisingly stable and indicates that the energy transfer from VA to SiQDs is not particularly thermosensitive at these concentrations.

Fig. 8 illustrates the stability of MSiQDs-VA under different pH. The PL intensity is pH dependent. Even though the PL of SiQDs is known to increase with decreasing pH values,[39] it is surprising to see that the PL intensity increased so drastically from pH 3 to pH 1. As shown in Fig. 8a, luminescence at 620 nm

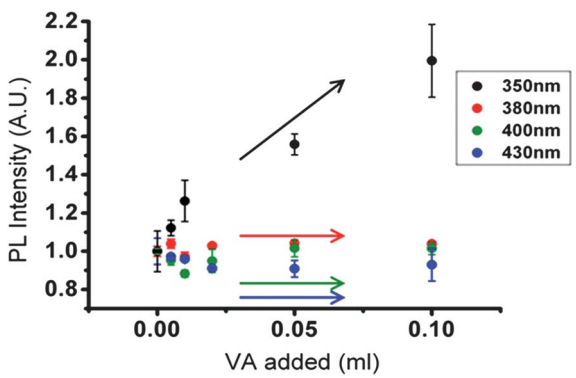

Fig. 6 By exciting MSiQDs-VA at different wavelengths, energy transfer between SiQDs and VA can be proved.

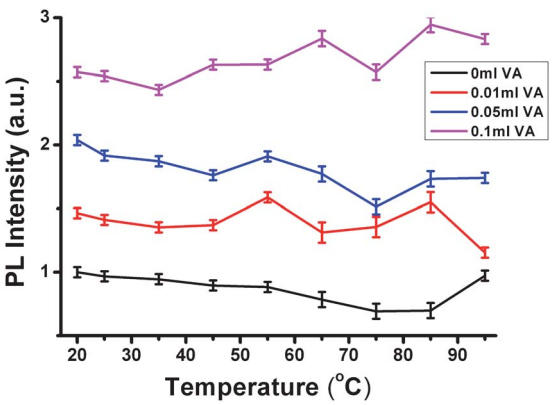

Fig. 7 PL of MSiQDs-VA under different temperature.

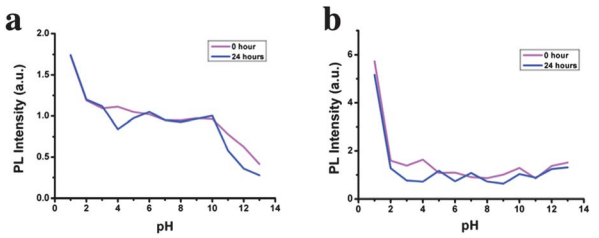

Fig. 8 (a) PL of MSiQDs-VA under different pH. (b) PL of VA from MSiQDs-VA under different pH. VA helps to intensify the PL of MSiQDs-VA in acidic environment.

increases at low pH. This increase may be due to the combination of Si QD emission increasing under acidic conditions and the energy transferred from VA. The PL intensity is stable between pH 3 and pH 10 and starts to descend at pH 11. After 24 hours, the PL intensity is relatively similar at neutral to acidic conditions. This suggests the micelle encapsulated MSiQD-VA is stable under acidic pH conditions after 24 hours. Fig. 8b shows the PL at 430 nm under different pH, which correlates to the emission of VA. It suggests that VA emission intensity increases at lower pH. This suggests that there is an increase in energy transfer under extremely acidic conditions because the emission intensity of VA in micelles increases. A surprising cumulative effect gives rise to the increase in emission of MSiQD-VA at low pH.

This work shows SiQDs to be very capable acceptors from dye donors, thus resulting in an enhanced emission yield from SiQDs. Toxicity has been the main comparison point between silicon and cadmium based QDs; however, with the addition of this work, SiQDs will have a known advantage of being acceptors from dye donors when compared to cadmium based QDs. Even though there are reports of SiQDs with QY's as high as 70%, silicon has a reputation as a low yield emitter. The QY of silicon is still generally a lot lower than that of cadmium based QDs and the method reported here might make it more competitive for sensitive applications. The micelle encapsulation method overcomes limitations of direct functionalization of QDs to dyes and the favorable spatial distribution allows energy transfer to occur in micelles. Vinyl compounds can be reacted to the surface of SiQDs; however the 254 nm photo-initiated reactions common with silicon compounds may bleach the dye before it has any effect. The protocol here is simple and offers precise control even though no complicated "spacers" or distance formulations are needed to take advantage of energy transfer from a dye to the QDs. This report also opens the door for the anticipation of new and exciting spectroscopic properties of SiQDs if they are studied in a nanoconstruct containing two-photon dyes and up converted nanophosphors. SiQDs are also desirable for photovoltaics because of their low toxicity and the existing infrastructure for silicon in the semiconductor industry. Vacuum deposition techniques and spin-coating can be applied to fabrication of thin films with SiQDs for solar cell applications; however the efficiencies are still low. Incorporating effective donors into silicon constructs would be hard to control when placing multiple energy transferring components into a system; hence we envision the use of nanostructured micelles, although they will not be made from DSPE PEG, that can be used for controlled energy transfer events on a thin film surface.[40] Overall, this work may have impact for SiQDs in bioapplications and photovoltaics.

Conclusions

SiQDs luminescence can be enhanced by energy transfer from an organic dye. The observed increase in emission intensity was as large as 250% near 700 nm emission wavelength. This can be used to combat the emission yield drop typically associated with conversion of SiQDs to water-dispersible forms. It may have implications in areas where silicon is viewed as an inefficient emitter or where its properties as an acceptor can enhance photovoltaic efficiency.

Acknowledgements

This study was supported by grants from the NCI RO1CA119397, the Ford Fellowship grant #10995602-1-57847, and the John R. Oishei Foundation.

Notes and references

1 P. N. Prasad, *Biophotonics*, Wiley-Interscience, Hoboken, NJ, 2003.
2 P. N. Prasad, *Nanophotonics*, Wiley-Interscience, Hoboken, NJ, 2004.
3 S. F. Wuister, I. Swart, F. van Driel, S. G. Hickey and C. de Mello Donegá, *Nano Lett.*, 2003, **3**, 503–507.
4 R. Xie, U. Kolb, J. Li, T. Basché and A. Mews, *J. Am. Chem. Soc.*, 2005, **127**, 7480–7488.
5 J.-H. Song, T. Atay, S. Shi, H. Urabe and A. V. Nurmikko, *Nano Lett.*, 2005, **5**, 1557–1561.
6 O. Kulakovich, N. Strekal, A. Yaroshevich, S. Maskevich, S. Gaponenko, I. Nabiev, U. Woggon and M. Artemyev, *Nano Lett.*, 2002, **2**, 1449–1452.
7 E. Hwang, I. I. Smolyaninov and C. C. Davis, *Nano Lett.*, 2010, **10**, 813–820.
8 J. S. Biteen, L. A. Sweatlock, H. Mertens, N. S. Lewis, A. Polman and H. A. Atwater, *J. Phys. Chem. C*, 2007, **111**, 13372–13377.
9 K. Munechika, Y. Chen, A. F. Tillack, A. P. Kulkarni, I. J.-L. Plante, A. M. Munro and D. S. Ginger, *Nano Lett.*, 2010, **10**, 2598–2603.
10 M. M. Maye, O. Gang and M. Cotlet, *Chem. Commun.*, 2010, **46**, 6111–6113.
11 S. Huang, Q. Xiao, Z. K. He, Y. Liu, P. Tinnefeld, X. R. Su and X. N. Peng, *Chem. Commun.*, 2008, 5990–5992.
12 B. Tang, L. H. Cao, K. H. Xu, L. H. Zhuo, J. H. Ge, Q. F. Li and L. J. Yu, *Chem.–Eur. J.*, 2008, **14**, 3637–3644.
13 V. R. Hering, T. E. S. Faulin, E. R. Triboni, S. D. Rodriguez, D. L. Bernik, R. I. Schumacher, V. P. Mammana, A. Faljoni-Alario, D. S. P. Abdalla, G. Gibson and M. J. Politi, *Bioconjugate Chem.*, 2009, **20**, 1237–1241.
14 I. L. Medintz and H. Mattoussi, *Phys. Chem. Chem. Phys.*, 2009, **11**, 17–45.
15 A. R. Clapp, I. L. Medintz, B. R. Fisher, G. P. Anderson and H. Mattoussi, *J. Am. Chem. Soc.*, 2005, **127**, 1242–1250.
16 D. H. Xu, X. Huang, W. Zhang, G. Chen, W. Zhu and X. Zhong, *ChemPhysChem*, 2010, **4**, 3167–3171.
17 P. O. Anikeeva, C. F. Madigan, S. A. Coe-Sullivan, J. S. Steckel, M. G. Bawendi and V. Bulovic, *Chem. Phys. Lett.*, 2006, **424**, 120–125.
18 N. Hildebrandt, L. J. Charbonnière, M. Beck, R. F. Ziessel and H.-G. Löhmannsröben, *Angew. Chem., Int. Ed.*, 2005, **44**, 7612–7615.
19 M. Achermann, M. A. Petruska, S. Kos, D. L. Smith, D. D. Koleske and V. I. Klimov, *Nature*, 2004, **429**, 642–646.
20 N. N. Mamedova, N. A. Kotov, A. L. Rogach and J. Studer, *Nano Lett.*, 2001, **1**, 281–286.
21 *Quantum Dots*, ed., M. Bruchez and C. Z. Holt, Humana Press, Totowa, New Jersey, 2007.
22 B. Dubertret, P. Skourides, D. J. Norris, V. Noireaux, A. H. Brivanlou and A. Libchaber, *Science*, 2002, **298**, 1759–1762.
23 H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki and T. Nakagiri, *Appl. Phys. Lett.*, 1990, **56**, 2379–2380.
24 J. P. Wilcoxon, G. A. Samara and P. N. Provencio, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **60**, 2704–2714.
25 G. Ledoux, J. Gong, F. Huisken, O. Guillois and C. Reynaud, *Appl. Phys. Lett.*, 2002, **80**, 4834–4836.

26 X. G. Li, Y. Q. He, S. S. Talukdar and M. T. Swihart, *Langmuir*, 2003, **19**, 8490–8496.
27 S. M. Liu, S. Sato and K. Kimura, *Langmuir*, 2005, **21**, 6324–6329.
28 F. J. Hua, M. T. Swihart and E. Ruckenstein, *Langmuir*, 2005, **21**, 6054–6062.
29 C. S. Yang, R. A. Bley, S. M. Kauzlarich, H. W. H. Lee and G. R. Delgado, *J. Am. Chem. Soc.*, 1999, **121**, 5191–5195.
30 D. S. English, L. E. Pell, Z. H. Yu, P. F. Barbara and B. A. Korgel, *Nano Lett.*, 2002, **2**, 681–685.
31 G. Belomoin, J. Therrien, A. Smith, S. Rao, R. Twesten, S. Chaieb, M. H. Nayfeh, L. Wagner and L. Mitas, *Appl. Phys. Lett.*, 2002, **80**, 841–843.
32 Z. Yamani, S. Ashhab, A. Nayfeh, W. H. Thompson and M. Nayfeh, *J. Appl. Phys.*, 1998, **83**, 3929–3931.
33 N. Liu, H.-Z. Chen, F. Chen and M. Wang, *Chem. Phys. Lett.*, 2008, **451**, 70–74.
34 N. Liu, M.-M. Shi, X.-W. Pan, W.-M. Qiu, J.-H. Zhu, H.-P. He, H.-Z. Chen and M. Wang, *J. Phys. Chem. C*, 2008, **112**, 15865–15869.
35 F. Erogbogbo, K.-T. Yong, R. Hu, W.-C. Law, H. Ding, C.-W. Chang, P. N. Prasad and M. T. Swihart, *ACS Nano*, 2010, **4**, 5131–5138.
36 H. Lu, B. Xu, Y. Dong, F. Chen, Y. Li, Z. Li, J. He, H. Li and W. Tian, *Langmuir*, 2010, **26**, 6838–6844.
37 F. Erogbogbo, K. T. Yong, I. Roy, G. X. Xu, P. N. Prasad and M. T. Swihart, *ACS Nano*, 2008, **2**, 873–878.
38 F. Erogbogbo, K.-T. Yong, I. Roy, R. Hu, W.-C. Law, W. Zhao, H. Ding, F. Wu, R. Kumar, M. T. Swihart and P. N. Prasad, *ACS Nano*, 2011, **5**, 413–423.
39 F. M. Dickinson, T. A. Alsop, N. Al-Sharif, C. E. M. Berger, H. K. Datta, L. Siller, Y. Chao, E. M. Tuite, A. Houlton and B. R. Horrocks, *Analyst*, 2008, **133**, 1573–1580.
40 S. I. Yoo, S. H. Bae, K.-S. Kim and B.-H. Sohn, *Soft Matter*, 2009, **5**, 2990–2996.

