

NANO EXPRESS

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Functionalized silicon quantum dots by *N*-vinylcarbazole: synthesis and spectroscopic properties

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Abstract

Silicon quantum dots (Si QDs) attract increasing interest nowadays due to their excellent optical and electronic properties. However, only a few optoelectronic organic molecules were reported as ligands of colloidal Si QDs. In this report, *N*-vinylcarbazole - a material widely used in the optoelectronics industry - was used for the modification of Si QDs as ligands. This hybrid nanomaterial exhibits different spectroscopic properties from either free ligands or Si QDs alone. Possible mechanisms were discussed. This type of new functional Si QDs may find application potentials in bioimaging, photovoltaic, or optoelectronic devices.

Keywords: Silicon quantum dots; *N*-vinylcarbazole; Surface modification; Spectroscopic property

Background

Silicon (Si) is one of the most important semiconductor materials for the electronics industry. The energy structure of bulk Si is indirect bandgap, which is greatly changed by the quantum confinement effect for small enough Si nanocrystals (NCs) called Si quantum dots (QDs), making Si QDs fluorescent with a tunable spectrum. Excellent spectroscopic properties, such as high quantum yield, broad absorption window, and narrow fluorescent wavelength, contribute to a rapid development in Si QD research [1]. Nontoxicity to the environment and the use of an economic source material are other two merits for the application of Si QDs in optoelectronics [2,3], solar energy conversion [4,5], biology [6-8], splitting water [9], etc. Si QDs can be prepared using a variety of techniques such as wet chemical reduction [10-18], metathesis reaction [19], disproportionation reaction [20,21], thermal annealing of Si-rich SiC [22], electrochemical etching [23], plasma synthesis or plasma-enhanced chemical vapor deposition (PECVD) [24-27], and high-temperature hydrogen reduction method [28-32]. Because Si QDs are chemically active, their surface should be passivated for further use.

Molecules with alkyl chains and -CH₃, -COOH, or -NH₂ ends have been widely employed as surface ligands to enhance the stability of Si QDs [28-36]. These ligands help prevent the oxidation of silicon and enhance the dispersibility of Si QDs in organic or aqueous solution. In addition to the surface protection, optoelectronic functional molecules as ligands of Si QDs are attracting increasing interest in recent years for the crucial role of the ligands to the interfacial related process in optoelectronic or light-harvesting devices. Kryschi and co-workers showed that 3-vinylthiophene ligands may act as surface-bound antennae that mediate ultrafast electron transfer or excitation energy transfer across the Si QD interface via high-energy two-photon excitation [37,38]. They also reported that for 2- and 4-vinylpyridine-terminated Si QDs, ultrafast excitation relaxation dynamics involving decay and rise dynamics faster than 1 ps were ascribed to electronic excitation energy transfer from an initially photoexcited ligand state to Si QD conduction band states [39]. Larsen and Kauzlarich and their co-workers investigated the transient dynamics of 3-aminopropenyl-terminated Si QDs [40]. A formation and decay of a charge transfer excited state between the delocalized π electrons of the carbon linker and the Si core excitons were proposed to interpret one-photon excitation. Zuilhof et al. reported Si QDs functionalized with a red-emitting ruthenium complex to exhibit Förster resonance energy transfer (FRET) from Si QDs to

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the complex [41]. The ligands on the Si surface may also induce optoelectronic interactions to other QDs such as CdSe QDs, e.g., Sudeep and Emrick found that hydrosilylation of Si QDs provides a corona of phosphine oxides that may serve as ligands for CdSe QDs [42]. This surface functionalization of the Si QDs was proved a key to the photoluminescence quenching of CdSe QDs, as conventional (alkane-covered) Si QD samples give no evidence of such optoelectronic interactions. Recently, we reported 9-ethylanthracene-modified Si QDs showing dual emission peaks that originate from the Si QD core and the ligands [43]. In this report, we demonstrate the synthesis and surface modification of Si QDs with *N*-ethylcarbazole, using hydrogen-terminated Si QDs and *N*-vinylcarbazole as the starting materials. Both anthracene and carbazole are fluorescent molecules and organic semiconductors. The main difference is that anthracene is an electron transport material while carbazole is a hole transport material. This difference is important for the structure design of optoelectronic or photovoltaic devices utilizing these Si QD-based hybrid materials. *N*-vinylcarbazole and its derivatives as a class of typical optoelectronic molecules show abundant attractive properties and can be applied in dye, optics, electronics, and biology [44–48]. *N*-vinylcarbazole is also the monomer precursor of poly(*N*-vinylcarbazole) (PVK) polymer which is widely used as a hole transport or electroluminescent material in organic optoelectronic devices [49–51]. The *N*-ethylcarbazole-modified Si QDs (referred to as 'N-ec-Si QDs' for short) exhibit photoluminescence quite different from freestanding *N*-vinylcarbazole- or hydrogen-modified Si QDs. This hybrid nanomaterial was characterized and investigated by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL), and PL lifetime measurement.

Methods

Materials and equipment

N-vinylcarbazole (98%), HSiCl_3 (99%), and mesitylene (97%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Analytical-grade ethanol (99.5%) and hydrofluoric acid (40% aqueous solution) were received from Sinopharm Chemical Reagent Co., Ltd. (SCRC; Shanghai, China). All reagents were used as purchased without further purification. The XRD spectrum was performed on a Bruker D8 Advance instrument (Bruker AXS GmbH, Karlsruhe, Germany) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). TEM images were obtained on a JEM-2100 transmission electron microscope with an acceleration voltage of 200 kV (JEOL, Ltd., Akishima, Tokyo, Japan). The FTIR spectra were measured by a Bruker VECTOR 22 spectrometer (Bruker, Germany) with KBr pellets. The PL and excitation spectra were collected by a Hitachi F-4600 fluorescence spectrophotometer (Hitachi, Ltd.,

Chiyoda-ku, Japan). The UV-vis absorption spectra were measured by a Shimadzu UV-2700 UV-vis spectrophotometer (Shimadzu Corporation, Kyoto, Japan). The PL lifetime was obtained on a Zolix Omni- λ 300 fluorescence spectrophotometer (Zolix Instruments Co., Ltd., Beijing, China).

Synthesis of hydrogen-terminated Si QDs

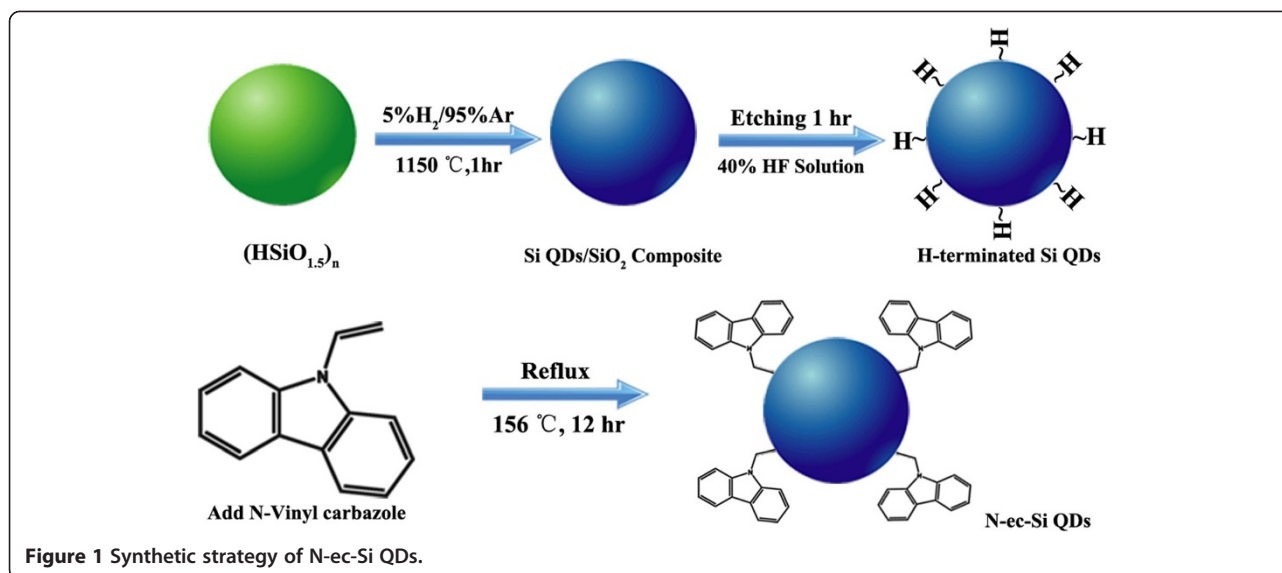
Si QDs were synthesized by reduction of $(\text{HSiO}_{1.5})_n$ powder with hydrogen [28,29]. Typically, 5 mL of HSiCl_3 (49.5 mmol) was added to a three-neck flask equipped with a mechanical stir bar, cooled to -78°C in an ethanol bath, and kept for 10 min, using standard Schlenk techniques with N_2 protection. With the injection of 20 mL H_2O by a syringe, a white precipitate formed immediately. After 10 min, the white $(\text{HSiO}_{1.5})_n$ was collected by centrifugation, washed by distilled water, and dried in vacuum at 60°C . In the reduction step, $(\text{HSiO}_{1.5})_n$ (1.10 g) was placed in a corundum crucible and transferred to a tube furnace. The sample was heated to $1,150^\circ\text{C}$ and maintained for 1.5 h with a heating rate of $5^\circ\text{C}/\text{min}$ under a slightly reducing atmosphere containing 5% H_2 and 95% Ar ($\geq 99.999\%$). After cooling to room temperature, a light brown product of Si/SiO₂ composite was collected. The Si/SiO₂ composite (50 mg) was grinded with a mortar and pestle for 10 min. Then the powder was transferred to a Teflon container (20 mL) with a magnetic stir bar. A mixture of ethanol (1.5 mL) and hydrofluoric acid (40%, 2.5 mL) was added. The light brown mixture was stirred for 60 min to dissolve the SiO₂. Finally, 5 mL mesitylene was added to extract the hydrogen-terminated Si QDs into the upper organic phase, forming a brown suspension (A), which was isolated for further surface modification.

Modification of Si QDs by functional organic molecules

N-vinylcarbazole (1 mmol) was dissolved in 15 mL mesitylene and loaded in a 50-mL three-neck flask equipped with a reflux condenser. Then 2 mL Si QDs (A) was injected by a syringe. The mixture was degassed by a vacuum pump for 10 min to remove any dissolved gases from the solution. Protected by N_2 , the solution was heated to 156°C and kept for 12 h. After cooling to room temperature, the resulting Si QDs were purified by vacuum distillation and then washed by ethanol to remove excess solvent and organic ligands. The as-prepared brown solid product was readily re-dispersed in mesitylene to give a yellow solution.

Results and discussion

The synthesis route of N-ec-Si QDs is summarized in Figure 1. The HSiCl_3 hydrolysis product $(\text{HSiO}_{1.5})_n$ was reduced by H_2 at $1,150^\circ\text{C}$ for 1.5 h. In this step, the temperature and time are crucial in controlling the size of Si QDs. The higher the temperature and the longer

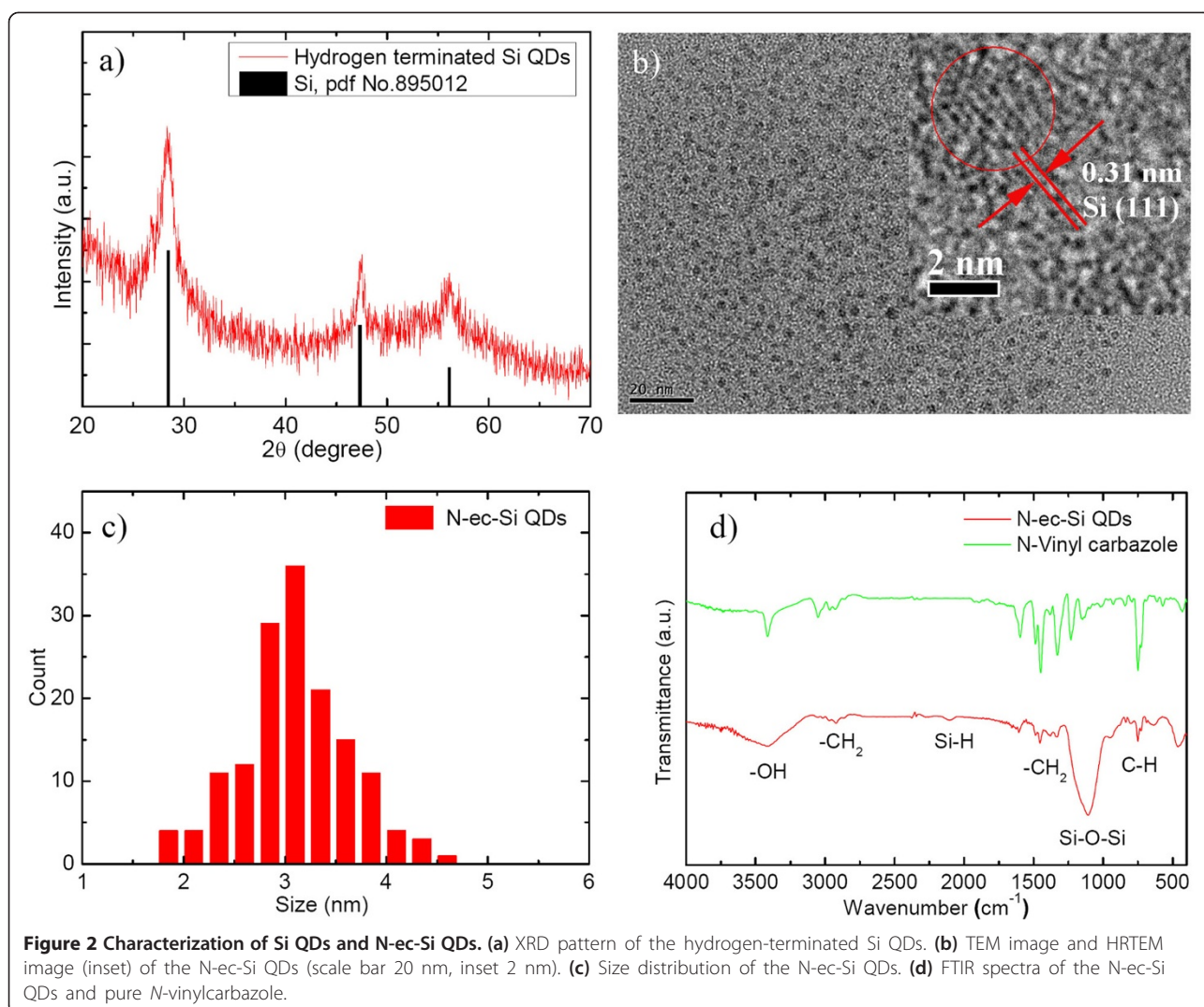


the reduction time, the bigger the sizes of Si QDs. The following HF etching procedure also plays a key role for the size tuning of the Si QDs. HF not only eliminates the SiO₂ component and liberates the free Si QDs but also etches Si QDs gradually. Another contribution of HF etching is the modification of the surface of Si QDs with hydrogen atoms in the form of Si-H bonds, which can be reacted with an ethylenic bond or acetylenic bond to form a Si-C covalent bond [28-32].

The hydrogen-terminated Si QDs are characterized by XRD (Figure 2a). The XRD pattern shows broad reflections (2θ) centered at around 28°, 47°, and 56°, which are readily indexed to the {111}, {220}, and {311} crystal planes, respectively, consistent with the face-centered cubic (fcc)-structured Si crystal (PDF No. 895012). Figure 2b and its inset show typical TEM and high-resolution TEM (HRTEM) images of N-ec-Si QDs, respectively. A *d*-spacing of approximately 0.31 nm is observed for the Si QDs by HRTEM. It is assigned to the {111} plane of the fcc-structured Si. The size distribution of N-ec-Si QDs measured by TEM reveals that the QD sizes range from 1.5 to 4.6 nm and the average diameter is about 3.1 nm (Figure 2c). In the FTIR spectrum of N-ec-Si QDs, a series of characteristic vibrations from Si QDs and carbazole are observed (Figure 2d). The weak vibration resonance centered at 2,090 cm⁻¹ can be assigned to the coupled H-Si-Si-H stretching or monohydride Si-H bonds. This result shows that the Si-H bonds were only partially replaced by Si-C because of the rigid and steric effect of the *N*-vinylcarbazole molecule. Compared to the IR spectrum of *N*-vinylcarbazole, similar vibrational peaks can be found in the spectrum of N-ec-Si QDs. The CH₂ symmetric and asymmetric stretching vibrations in the range 2,920 to 2,850 cm⁻¹, the CH₂ bending vibration at approximately 1,450 cm⁻¹, and the aromatic group

vibration bands at approximately 750 cm⁻¹ can be assigned to the surface-modified *N*-ethylcarbazole (-NC₁₄H₁₂) ligands. This indicates the successful modification of *N*-vinylcarbazole onto the Si QDs. It should be noticed that the Si-O-Si vibration band at 1,000 to 1,200 cm⁻¹ is recorded, suggesting possible oxidation of the Si QD surface. This may due to the steric effect of carbazole, that is, the Si QD surface cannot be fully protected by the ligand, in which some Si-H remained and encountered oxidation when exposed to air.

Figure 3a shows the absorption spectra of *N*-vinylcarbazole and N-ec-Si QDs. The absorption band at 320 to 360 nm of the N-ec-Si QDs is assigned to the carbazole ligand. It suggests that ligands can be employed to enhance the absorption of pure Si QDs, therefore providing a potential strategy to increase the light-harvesting efficiency of QDs in solar cells [52,53]. Upon excitation at 302 nm, the N-ec-Si QDs and *N*-vinylcarbazole show intense emission bands at approximately 358 nm and approximately 366 nm, respectively (Figure 3b). In comparison with *N*-vinylcarbazole, the emission in the N-ec-Si QDs exhibits a blueshift of 8 nm and a shoulder peak at approximately 372. When carbazole was linked to the surface of Si QDs by Si-C bond by the hydrosilylation reaction, the vinyl group in *N*-vinylcarbazole was transformed into an ethyl group. Therefore, the conjugate system of the molecule reduced from *N*-vinylcarbazole to carbazole, inducing a bigger electronic bandgap. In addition, the ligand to QD bonding would enhance the structural rigidity of the ligand. These reasons may contribute to the blueshift of the PL spectrum. Commonly, the extension of molecular conjugated orbitals of a ligand to the attached materials would lead to a redshift. In N-ec-Si QDs, the ethyl group formed through the hydrosilylation reaction separates the conjugated part,



the carbazole group, from the silicon nanocrystal, which prevents or weakens the interaction of the carbazole group with the electronic wave functions of the Si QDs. Therefore, a redshift is prohibited. A similar blueshift was also demonstrated in our recent work for 9-ethylanthracene modified on Si QDs [43].

The N-ec-Si QDs and *N*-vinylcarbazole show distinct excitation spectra within the range of 280 to 360 nm (Figure 3c), indicating that the energy structure of N-ec-Si QDs is different from *N*-vinylcarbazole. PL decay curves of N-ec-Si QDs and *N*-vinylcarbazole were investigated at room temperature in mesitylene solution (Figure 3d). The PL decay curves are fitted to the exponential function

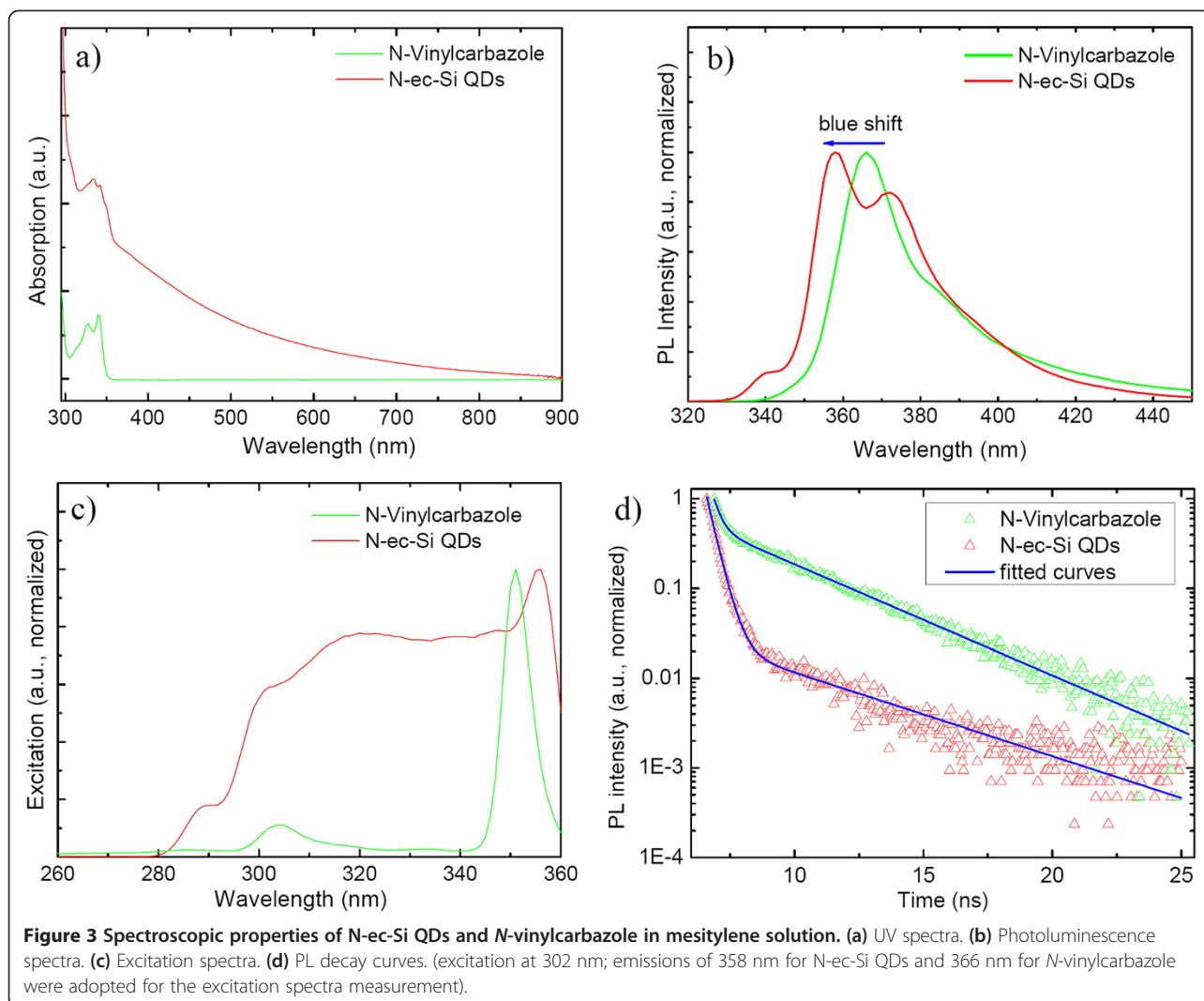
$$I(t) = \sum_{i=1}^n A_i \exp(-(t-t_0)/\tau_i) \quad (1)$$

where τ_i is the PL decay lifetime, A_i is the weighting parameter, and $n = 2$. The fitting parameters are given in

Table 1. The average lifetime is determined by the equation [54]

$$\tau_{av} = \frac{\sum_{i=1}^n (A_i \tau_i^2)}{\sum_{i=1}^n (A_i \tau_i)} \quad (2)$$

The average PL decay lifetime of N-ec-Si QDs is 1.4 ns, much shorter than that of *N*-vinylcarbazole which is 3.2 ns. The lifetime diversity may be influenced by many factors. First, the hydrosilylation reaction induces the transformation of the molecule structure. Second, the *N*-vinylcarbazole dispersion state in the mesitylene is not clear. Possible π - π packing of the molecules may lead to a redshift. Support can be found in the fact that N-ec-Si QDs show a more symmetric PL spectrum to the absorption spectrum than *N*-vinylcarbazole exhibits. Third, the interaction of the ligands with the Si-QDs and interaction between the modified ligands are inevitably encountered [55]. Additionally, the oxidation of the

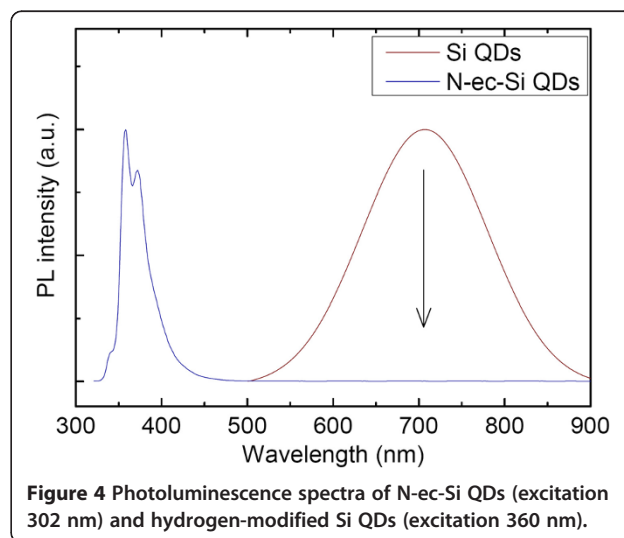


silicon surface may induce additional non-radiative pass-ways for the excitation. All of these factors would lead to PL lifetime shortening [56]. Unlike alkyl ligands or 9-ethylanthracene-modified Si QDs, the fluorescence from hydrogen-terminated Si QDs was quenched after the carbazole modification (Figure 4). It may be induced by the interaction of carbazole with the Si QDs. The fluorescence quantum yield of N-vinylcarbazole and N-ec-Si QDs was estimated to be 26.6% and 11.2%, respectively, by using Coumarin 540 dye in methanol as a reference (91%) [57]. The decrease of the quantum yield could be a result from fast non-radiative relaxation of the excited

Table 1 Fitting parameters of the PL decay curves

Sample	Emission (nm)	τ_1 (ns)	τ_2 (ns)	a_1^a	a_2^a	R^2	τ_{av} (ns)
N-vinylcarbazole	366	0.27	3.5	0.58	0.42	0.998	3.2
N-ec-Si QDs	358	0.35	4.6	0.98	0.02	0.997	1.4

$$^a a_i = \frac{A_i}{\sum_{j=1}^n A_j}, i = 1, 2, n = 2.$$



states, induced by the interaction of the ligands to Si QDs or surface states, which also could be an interpretation for the lifetime shortening. From the molecular design aspect, the functional group modified by a long alkyl tail with an ethyl or vinyl end would be an ideal ligand structure in which the Si QDs and the functional group are spatially separated. Also, the flexibility of the long alkyl chain exhibits a smaller steric effect. The surface of Si QDs could be more effectively protected, thus preserving the fluorescence of the Si QD core.

Conclusions

In conclusion, N-ec-Si QDs were successfully prepared and characterized. Spectroscopic properties were investigated and discussed. The absorption, excitation, PL, and PL decay properties of N-ethylcarbazole ligands on the Si QD surface are significantly different from those of N-vinylcarbazole in solution. Hopefully, the synthesis strategy could be extended for the syntheses of a series of Si QDs containing various optoelectronic functional organic ligands, with application potentials ranging from optic, electronic, and photovoltaic devices to biotechnology.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

JWJ and GW contributed equally to the manuscript. XZY and XXX designed the research. JWJ, GW, and XXX carried out the experiments and drafted the manuscript. All authors read and approved the final manuscript.

Acknowledgements

This work was supported by the Major State Basic Research Development Program of China (Grant Nos. 2013CB922102 and 2011CB808704), the National Natural Science Foundation of China (Grant Nos. 91022031 and 21301089), and Jiangsu Province Science Foundation for Youths (BK20130562).

Received: 1 July 2014 Accepted: 1 August 2014

Published: 7 August 2014

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doi:10.1186/1556-276X-9-384

Cite this article as: Ji et al.: Functionalized silicon quantum dots by N-vinylcarbazole: synthesis and spectroscopic properties. *Nanoscale Research Letters* 2014 **9**:384.

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