ACS NANO

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ARTICLE

Silicon Nanoparticles with Surface Nitrogen: 90% Quantum Yield with Narrow Luminescence Bandwidth and the Ligand Structure Based Energy Law

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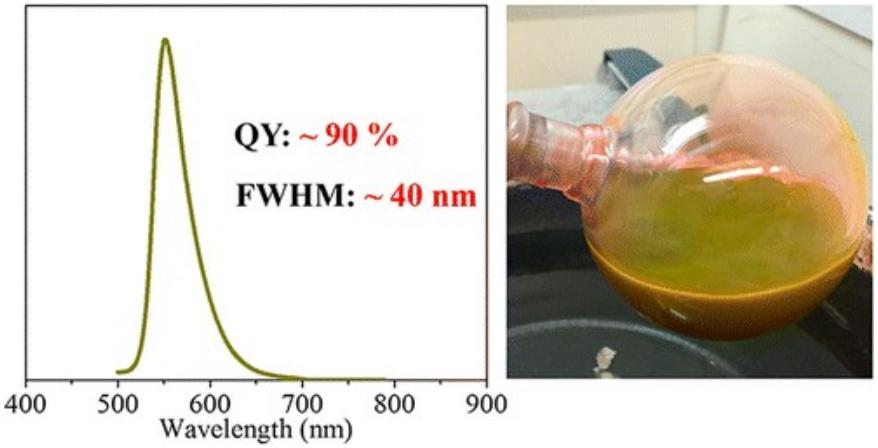
ACS Nano, **2016**, *10*(9), 8385-8393



Sandeep Bose
1-10-16

Introduction

- Gaining light from silicon has long been a dream for the scientific community.
- Silicon based highly efficient light emitting or amplifying material would be of great significance not only for the development of next technological frontiers-silicon photonics and optoelectronics as silicon is the core of photovoltaics and microelectronics.
- It is also used as an alternative material for typical cadmium-based quantum dots and commercial organic dyes in light-emitting or bioimaging applications due to silicon's intrinsic merits of least toxicity, low cost, and high abundance.
- However, improving Si NPs' photoluminescence (PL) performance to achieve ultrahigh quantum yields (QYs) and narrow luminescence bandwidth is still a major target.
- High QYs up to 60% have been reported from plasma-based synthesis but only for large-size Si NPs, and the QYs drop significantly for those smaller sized NPs that emit visible light.
- Besides, previous Si NPs usually show broad PL bandwidths (full width at half-maximum (fwhm) 70−150 nm), which is probably a result of the inhomogeneous broadening from different sizes of Si NPs in the sample.
- To date, there has been no report of Si NPs simultaneously possessing ultrahigh QY and narrow PL bandwidth, which hinders Si NPs from being applied in many areas such as parallel detection in biolabeling or high color rendering index LEDs.

In this paper

- They have synthesized surface nitrogen-capped Si NPs with PL quantum yield up to 90% and narrow PL bandwidth (full width at half maximum (fwhm) ≈ 40 nm), which can compete with commercial dyes and typical quantum dots.

- Studies were made to unveil the influence of particle size, structure, and amount of surface ligand on the PL of Si NPs.

- A general ligand-structure-based PL energy law for surface nitrogen-capped Si NPs is identified in both experimental and theoretical analyses.

- PL mechanisms were discussed (Transient absorption spectroscopy was done to prove the existence of surface states).

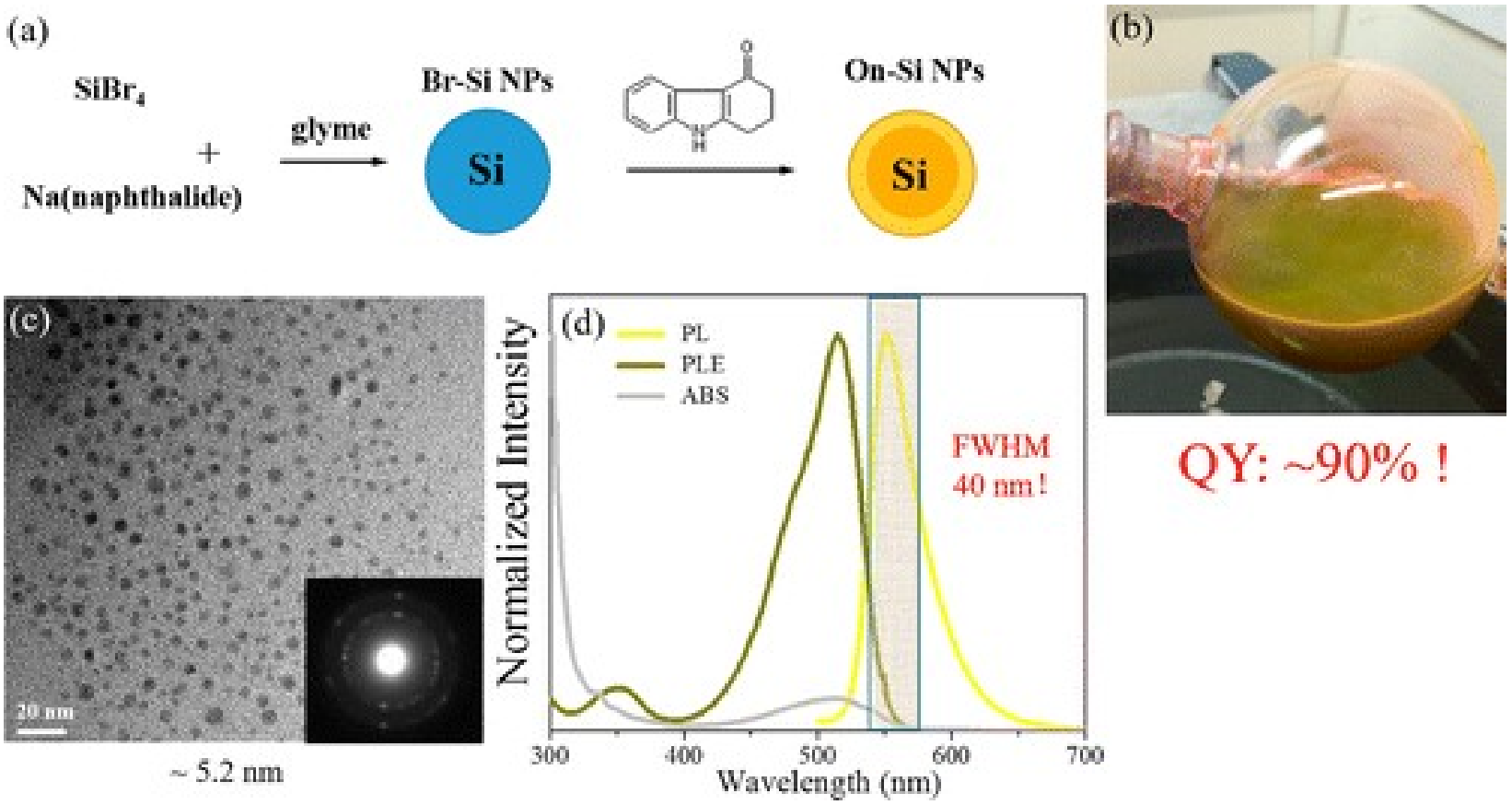


Figure 1. Synthesis of yellow-emitting On-Si NPs with exceptional PL properties. (a) Scheme of the solution reduction synthesis and surface modification to make yellow-emitting Si NPs with ultrahigh quantum yield and narrow PL bandwidth. (b) Photograph of Si NPs in glyme under ambient light after the reaction. (c) TEM graph of On-Si NPs with an average diameter of 5.2 nm. Inset is the selected-area electron diffraction pattern of the On-Si NPs. Multiple rings are consistent with diamond lattice Si (111) at 3.1 Å and (220) at 2.0 Å. (d) PL, PLE, and Abs spectra of the On-Si NPs. The fwhm of the PL peak is very narrow (only 40 nm) (scale bar in TEM image: 20 nm).

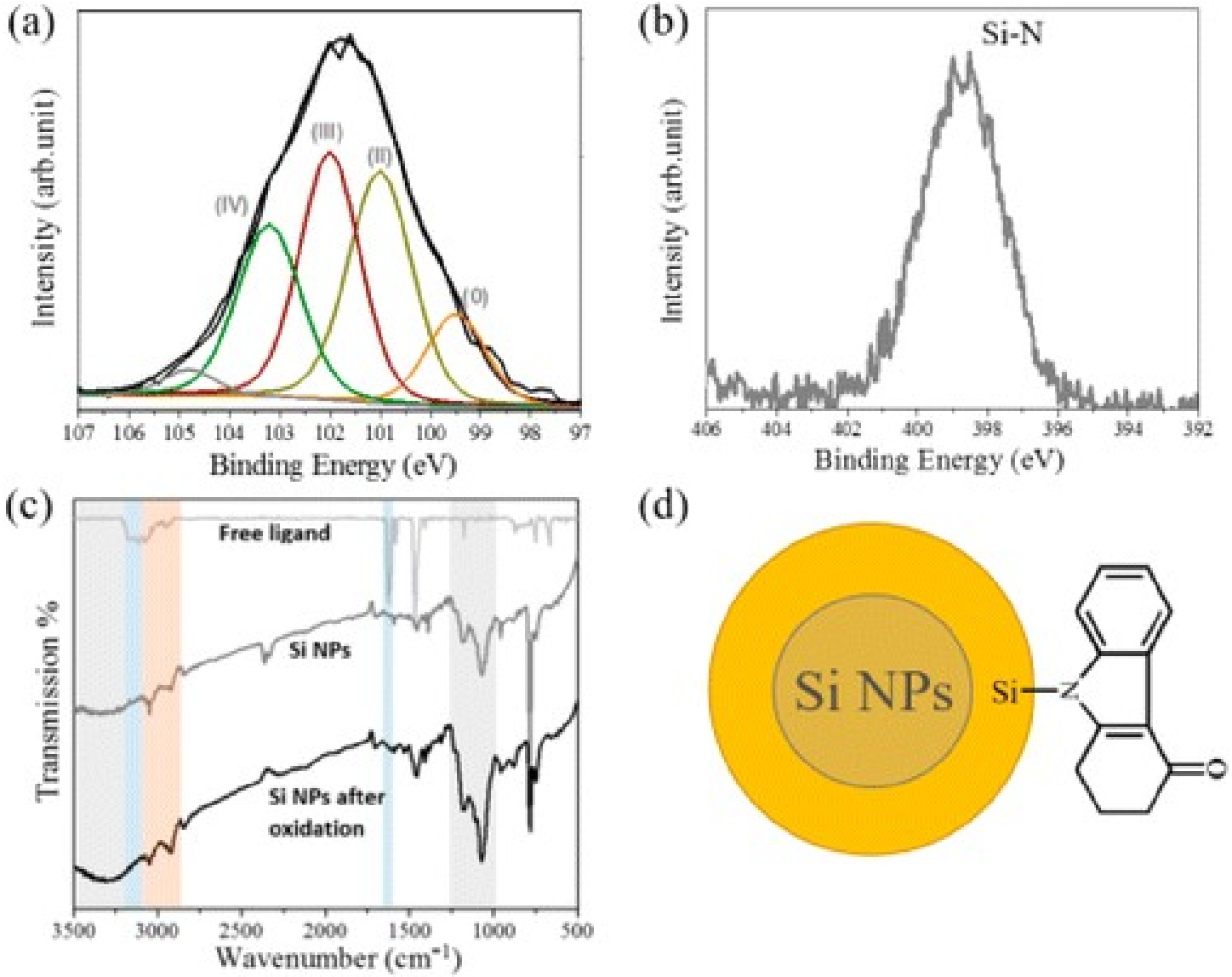


Figure 2. Characterization of the On-Si NPs. X-ray photoemission spectra of (a) Si 2p region and (b) N 1s region. (c) FTIR spectra of the On-Si NPs and On-ligands. (d) Structure model of the On-Si NPs.

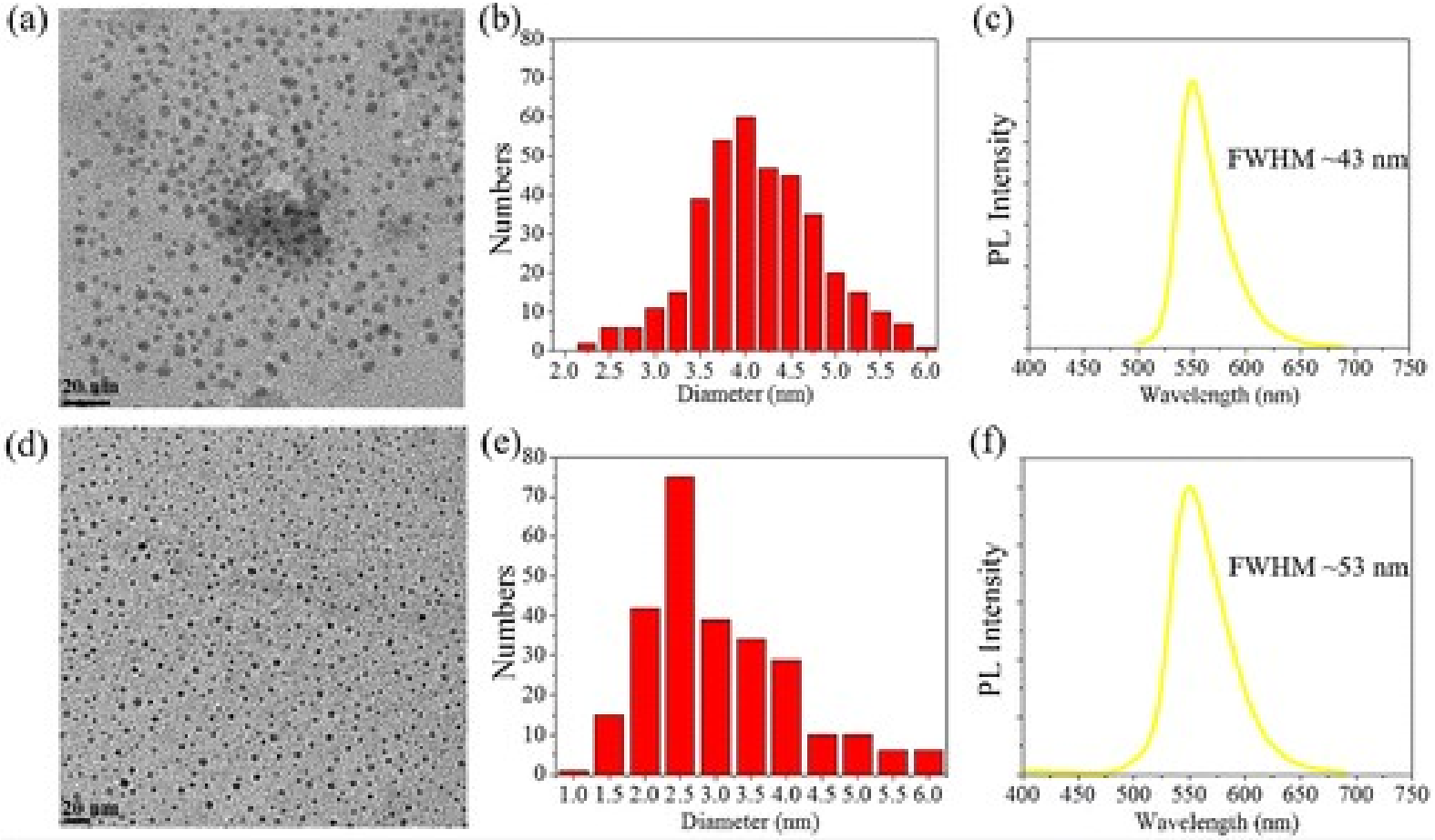


Figure 3. Si NPs of different sizes and their size-independent PL. (a and b) TEM graph and size distribution of Si NPs with average diameter of 4.1 nm. (c) PL spectrum of the 4.1 nm Si NPs. (d and e) TEM graph and size distribution of Si NPs with average diameter of 2.8 nm. (f) PL spectrum of the 2.8 nm Si NPs (scale bar in TEM images: 20 nm).

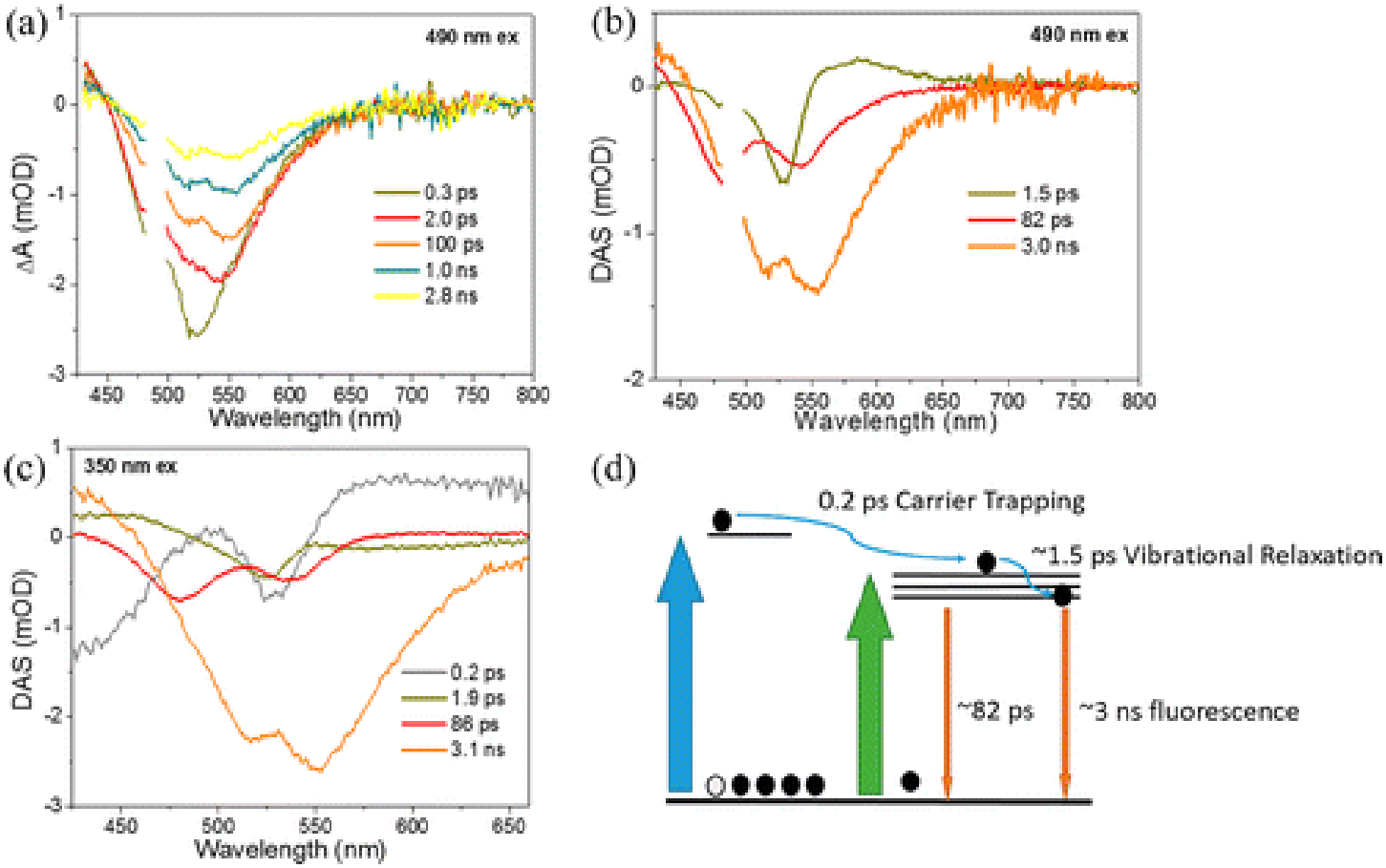


Figure 4. Femtosecond transient absorption study of the On-Si NPs. (a) Time evolution of transient absorption spectra (excitation at 490 nm). (b) Decay-associated spectra (DAS) obtained from the global analysis (excitation at 490 nm). (c) DAS obtained from the global analysis (excitation at 350 nm). (d) Energy diagram of the On-Si NPs.

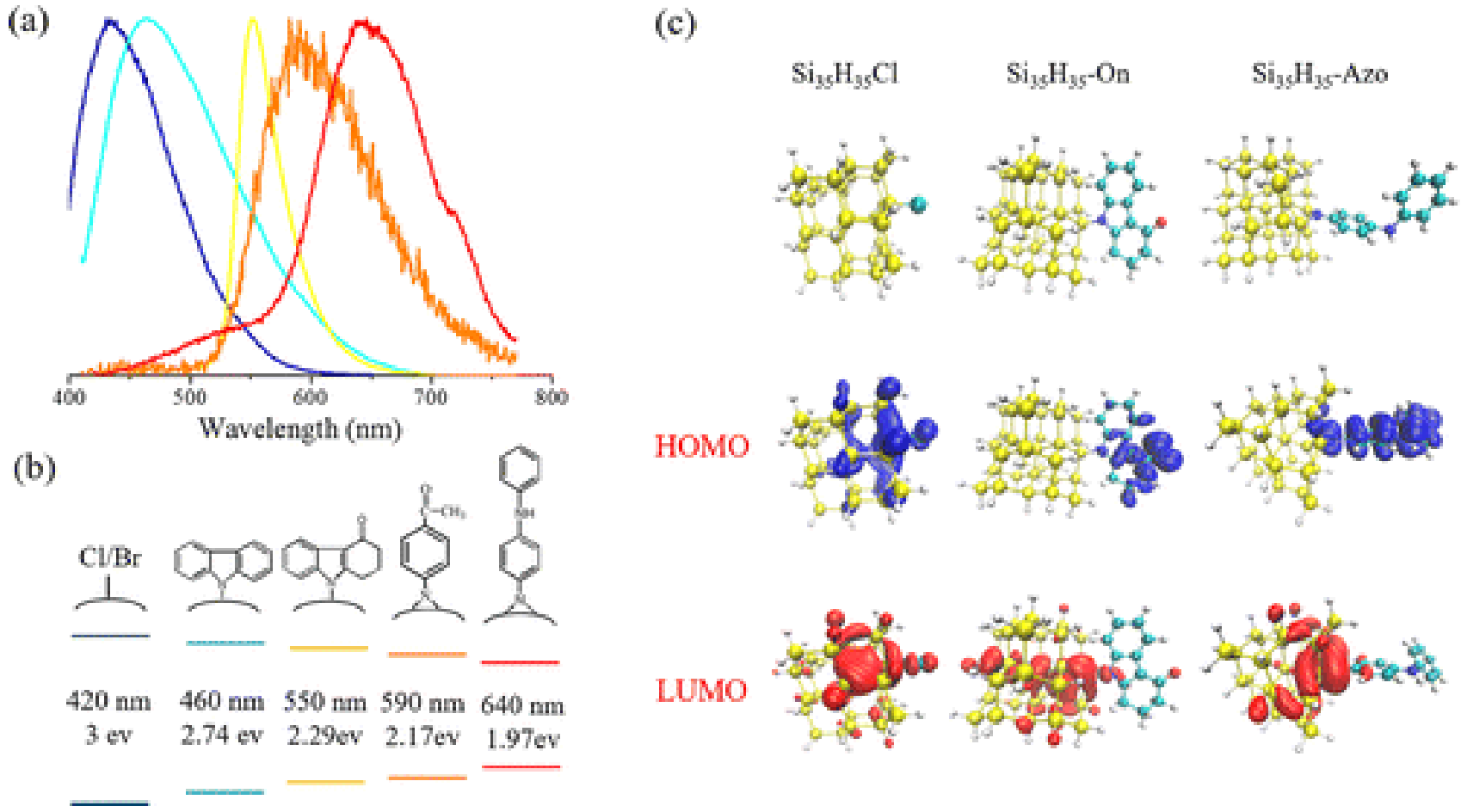


Figure 5. Ligand structure law on Si NPs' PL energy. (a) PL of Si NPs with different surface ligands excited at 400 nm (blue: chlorine; cyan: carbazole; yellow: On; orange: 4-aminoacetophenone; red: phenyl-1,4-phenylenediamine). (b) PL energies of various surface-modified Si NPs obtained from experiment. (c) Models of the nanoparticles with various ligands and HOMO and LUMO orbitals, respectively (left to right). (Azo stands for N-phenyl-1,4-phenylenediamine.)

Table 1. Calculated Band Gaps for $Si_{35}H_{35}R_1$ with Different Surface Ligands

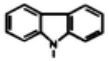
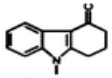
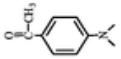
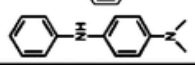
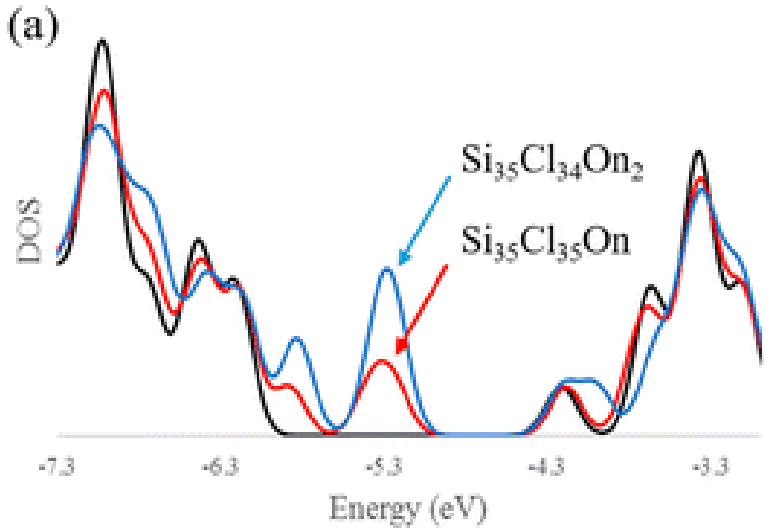
Entry	R_1	HOMO-LUMO Gap
1	-Cl	3.38 ev
2		2.59 ev
3		2.46 ev
4		2.37 ev
5		1.88 ev

Table 2. Calculated HOMO, LUMO, and Energy Band Gap (eV) for $Si_{35}Cl_{34}R_1R_2$

entry	$-R_1$	$-R_2$	HOMO–LUMO	HOMO	LUMO
1	–Cl	–Cl	1.99	–6.20	–4.21
2	–On	–Cl	1.06	–5.24	–4.18
3	–On	–On	1	–5.20	–4.20



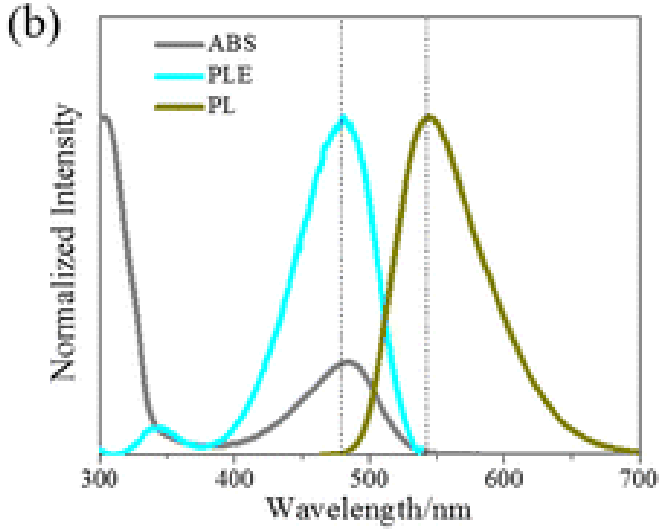


Figure 6. Influence of ligand amount on the optical properties of Si NPs. (a) Calculated electron density distribution of the HOMO and LUMO of the Si NPs with different amounts of On-ligand. (b) PL, PLE, and absorption spectra of the green-yellow-emitting On-Si NPs obtained by reducing the amount of added surface ligand during reaction.

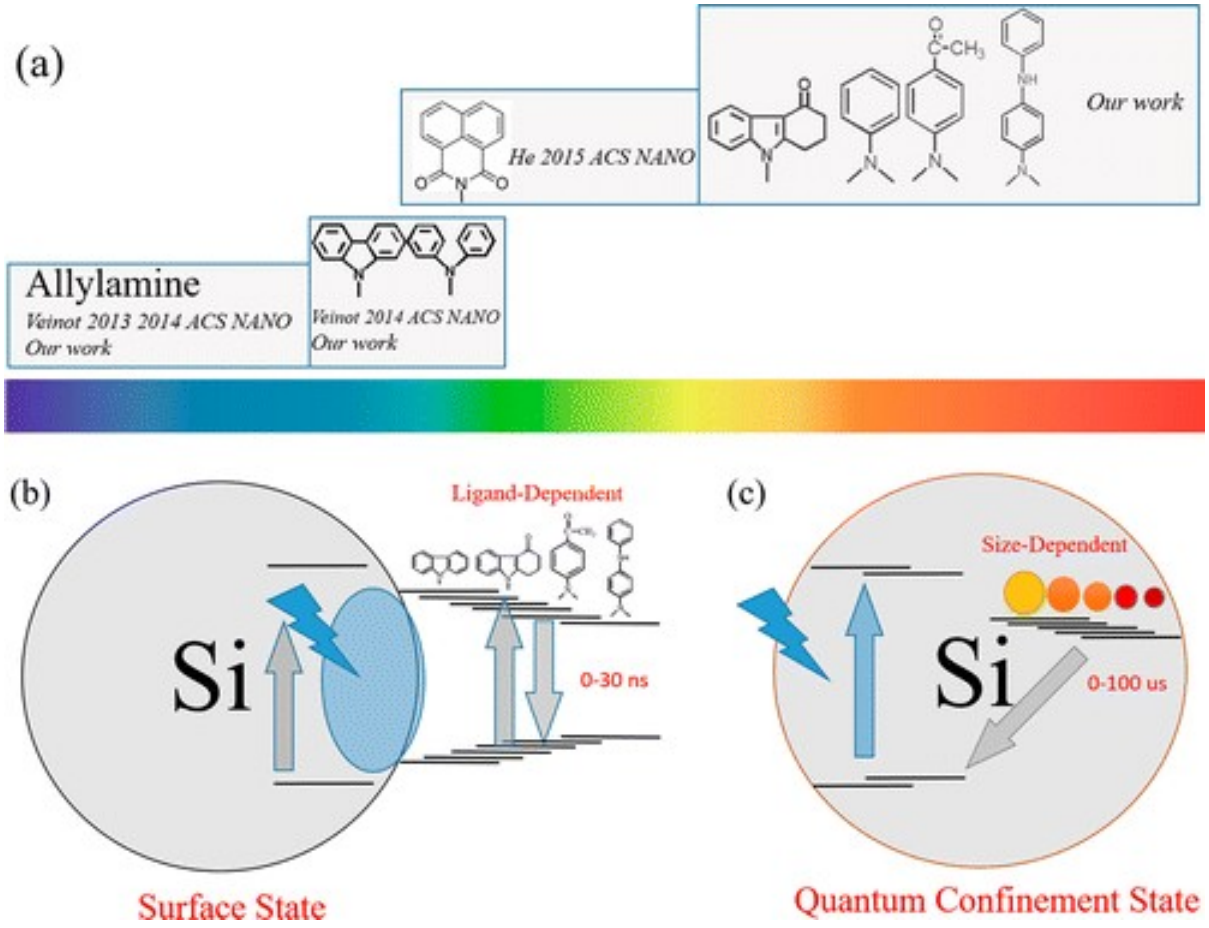


Figure 7. PL mechanism of surface nitrogen-capped Si NPs. (a) Spectral tunability of surface nitrogen-capped Si NPs from different fabrication methods that follow the ligand structure law. (b) Scheme of the surface PL from surface nitrogen-capped Si NPs. (c) Scheme of the quantum confinement PL from conventional Si quantum dots, as a contrast.

Summary

- Ultrabright yellow-emitting Si NPs with a QY up to 90% and a narrow PL bandwidth (~40 nm) have been obtained.

- The PL performance of Si NPs after surface modification can compete with commercial dyes and typical quantum dots.

- The influences of particle size and ligand on the Si NPs' PL have been comprehensively studied, which demonstrate that the structure of ligands is critical for the PL from the surface.

- A general ligand structure based PL energy law for surface nitrogen-capped Si NPs has been obtained both experimentally and theoretically.

Future direction

Transient absorption studies on the doped trap states.