Supporting Information

Fabricating Highly-Luminescent Solid-Hybrids based on Silicon Nanoparticles: A Simple, Versatile and Green Method

Jingchun Huang[1], *Qi Li*[1], *Zhengzhong Shao*[1]*

[1]State Key Laboratory of Molecular Engineering of Polymers, Advanced Material Laboratory, Department of Macromolecular Science, Fudan University, Shanghai 200438, P. R. China

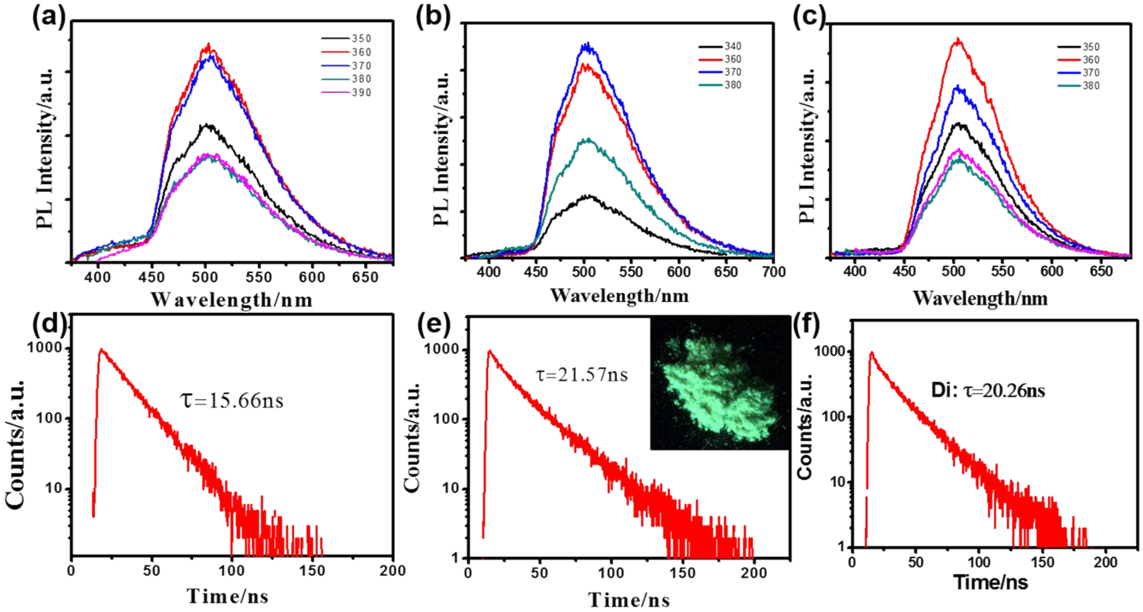

Figure S1. PL and TCSPC spectra of diphenylamine modified Si NPs(a and d) and their corresponding phosphors (b and e) and the phosphors(c and f) after 6 months storage.

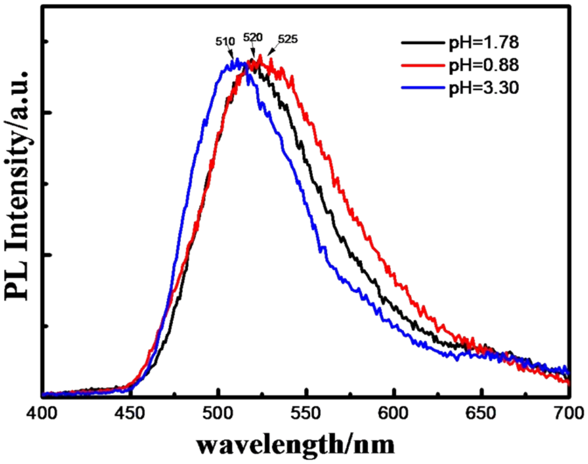

Figure S2. PL spectra of phosphors made by 4 - methoxy diphenylamine modified Si NPs under different pH.

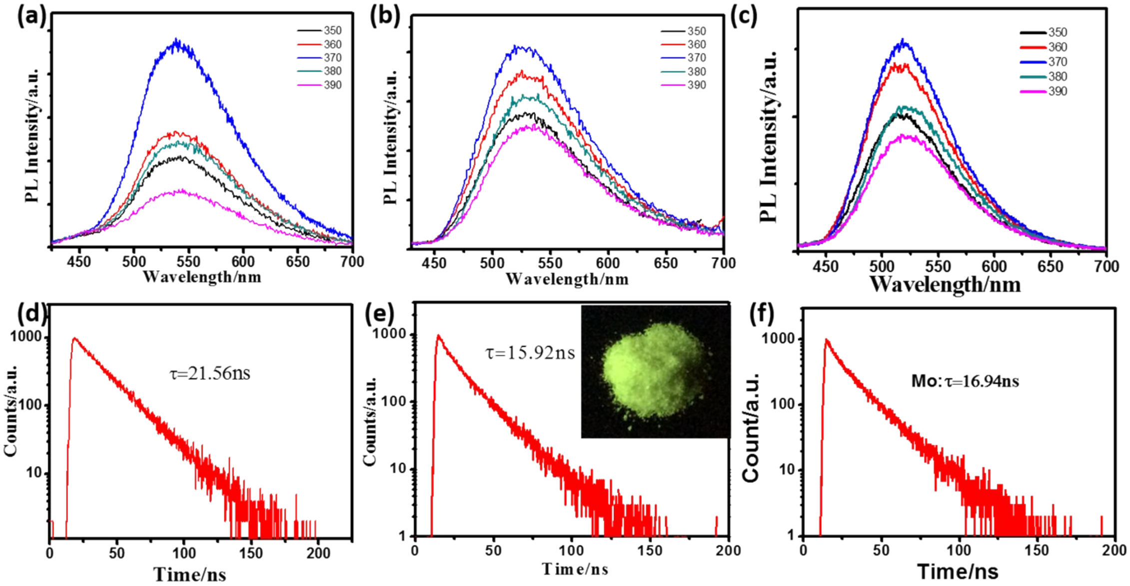

Figure S3. PL and TCSPC spectra of 4 - methoxy diphenylamine modified Si NPs(a and d) and their corresponding phosphors (b and e) and the phosphors(c and f) after 6 months storage.

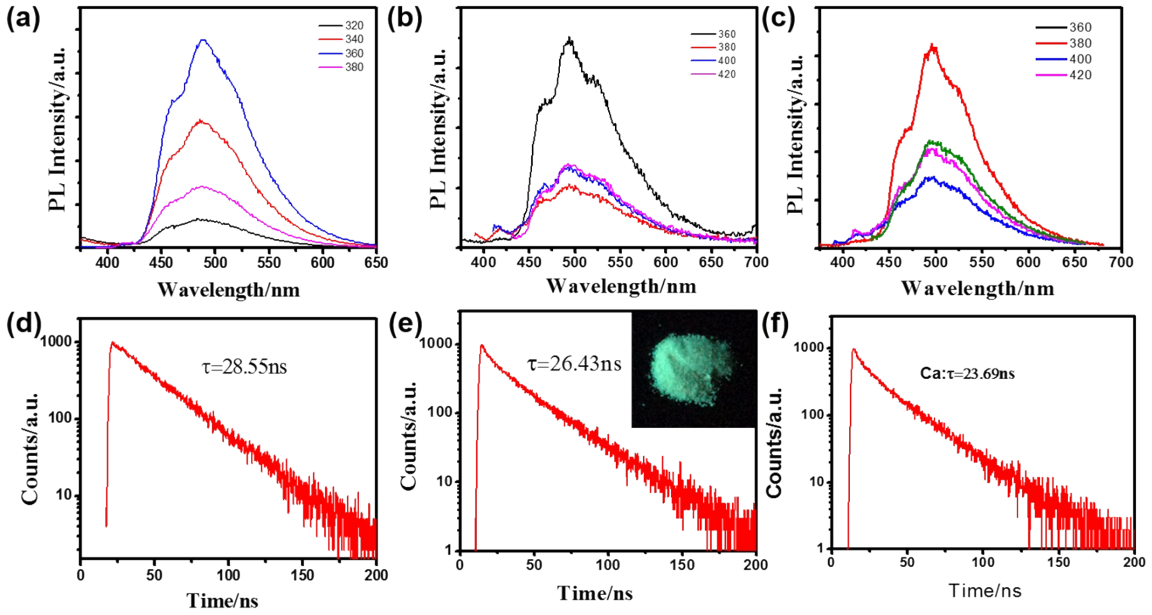

Figure S4. PL and TCSPC spectra of carbazole modified Si NPs(a and d) and their corresponding phosphors (b and e) and the phosphors(c and f) after 5 months storage.

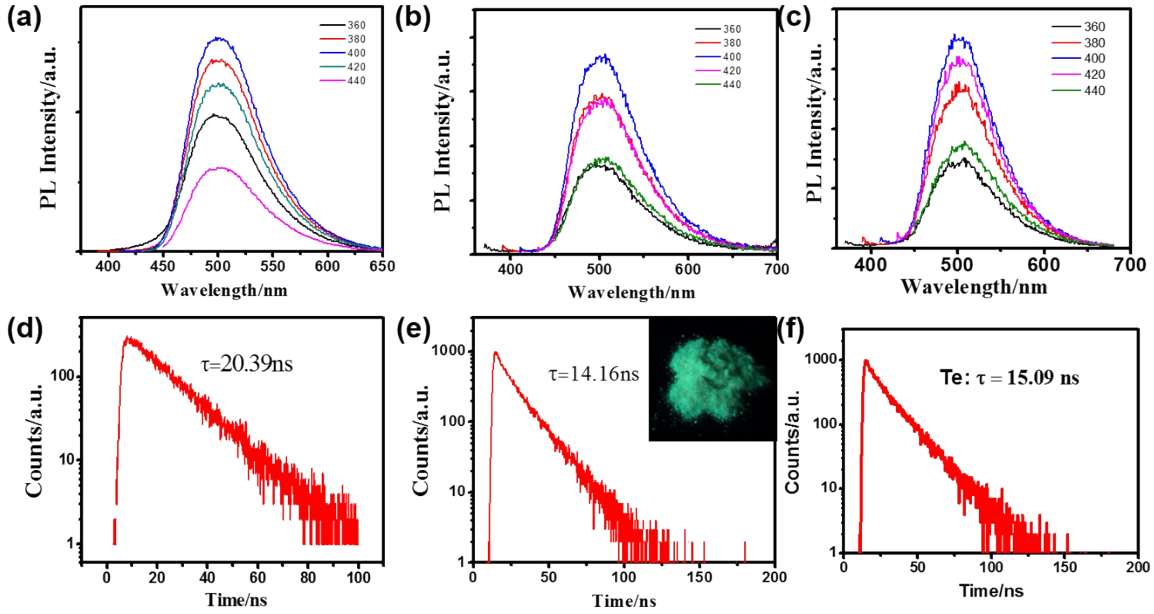

Figure S5. PL and TCSPC spectra of 1,2,3,4-Tetrahydrocarbazole modified Si NPs(a and d) and their corresponding phosphors (b and e) and the phosphors(c and f) after 5 months storage.

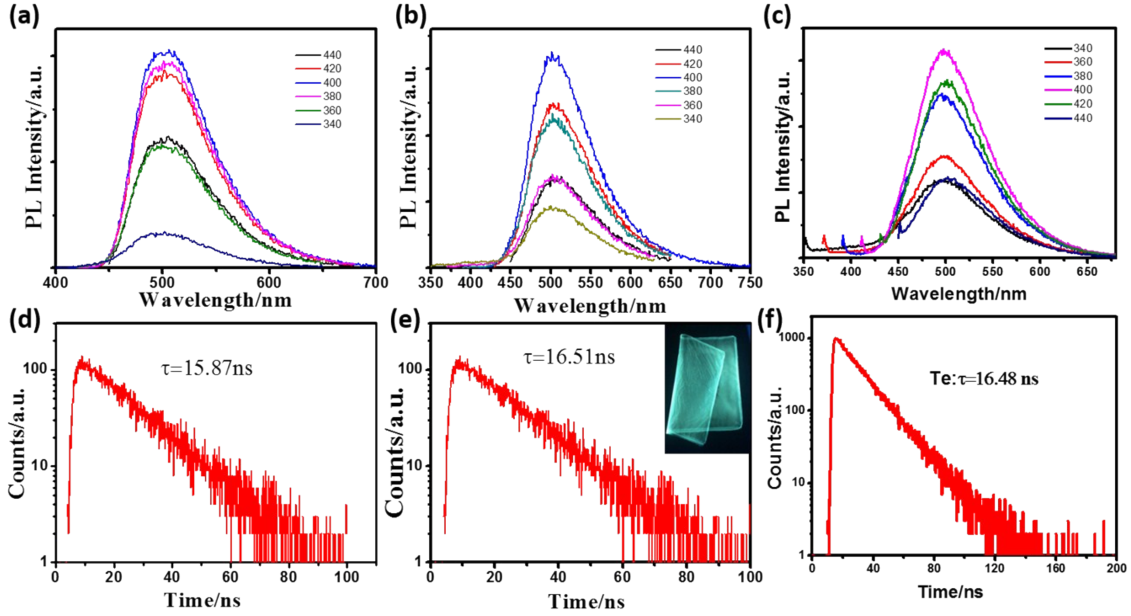

Figure S6 PL and TCSPC spectra of 1,2,3,4-Tetrahydrocarbazole modified Si NPs(a and d) and their corresponding PVA film (b and e) and the film(c and f) after 9 months storage.

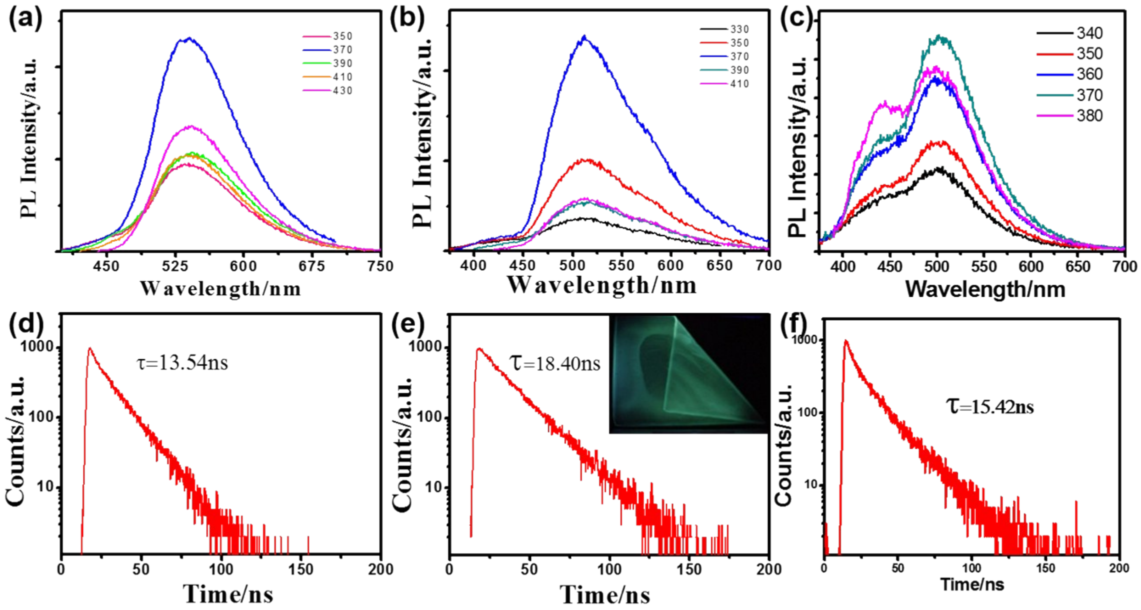

Figure S7 PL and TCSPC spectra of 4 - methoxy diphenylamine modified Si NPs (a and d) and their corresponding PVA film (b and e) and the film(c and f) after 7 months storage.

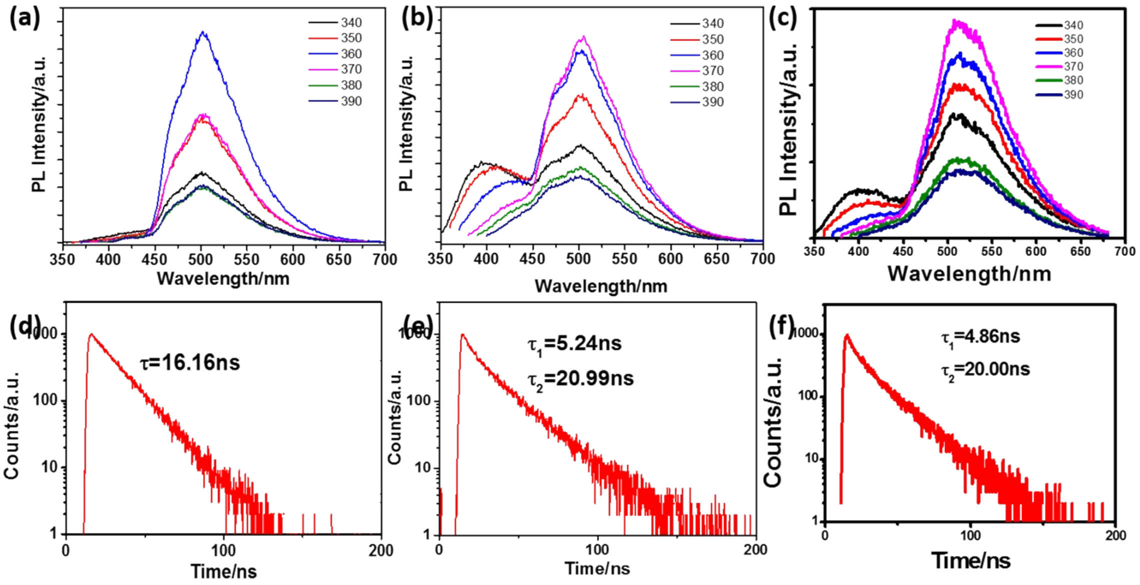

Figure S8 PL and TCSPC spectra of diphenylamine modified Si NPs (a and d) and their corresponding gelatin film (b and e) and the film(c and f) after 2 months storage.

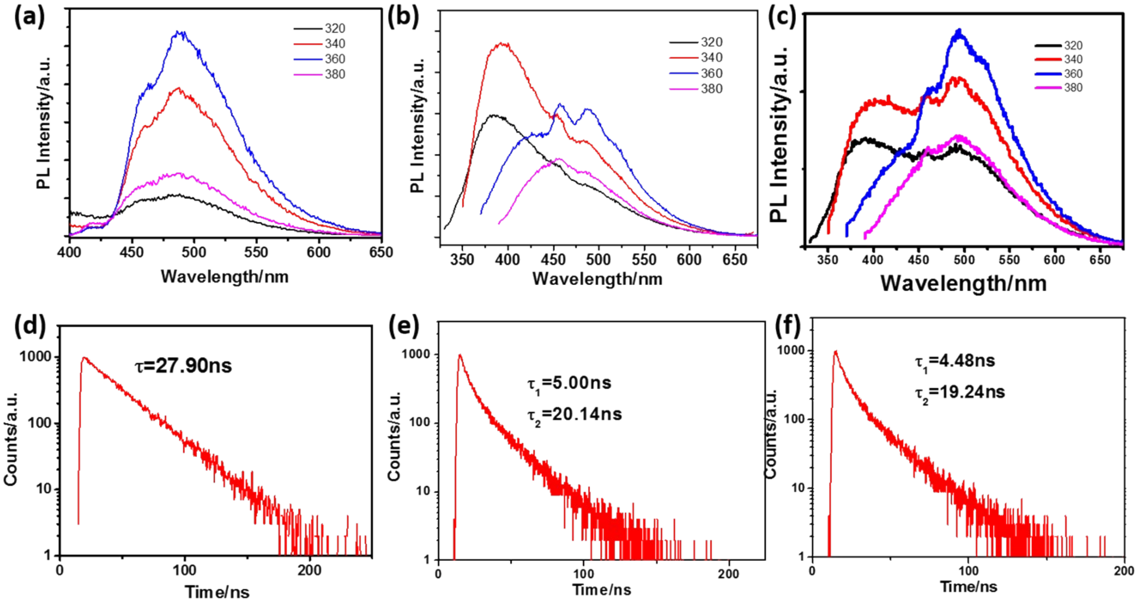

Figure S9 PL and TCSPC spectra of carbazole modified Si NPs (a and d) and their corresponding gelatin film (b and e) and the film(c and f) after 2 months storage.

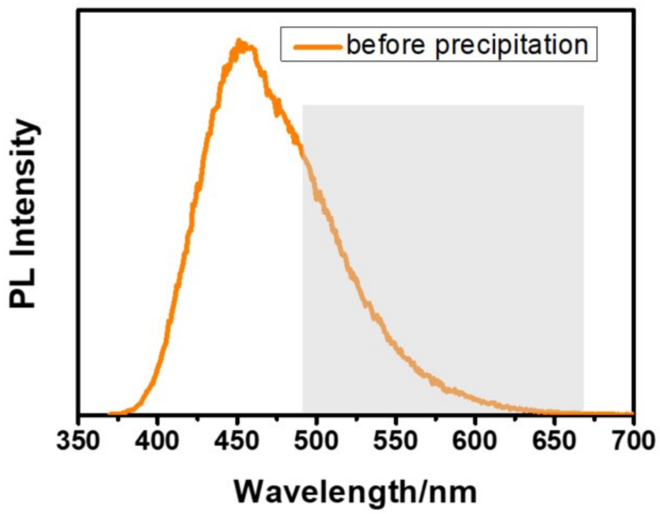

Figure S10. PL properties of Mo-Si NPs before alkali-treatment. Excited at 360 nm. The long tail (shadow region) is arising from the yellow emitting part which can be separated from precipitation under high pH.

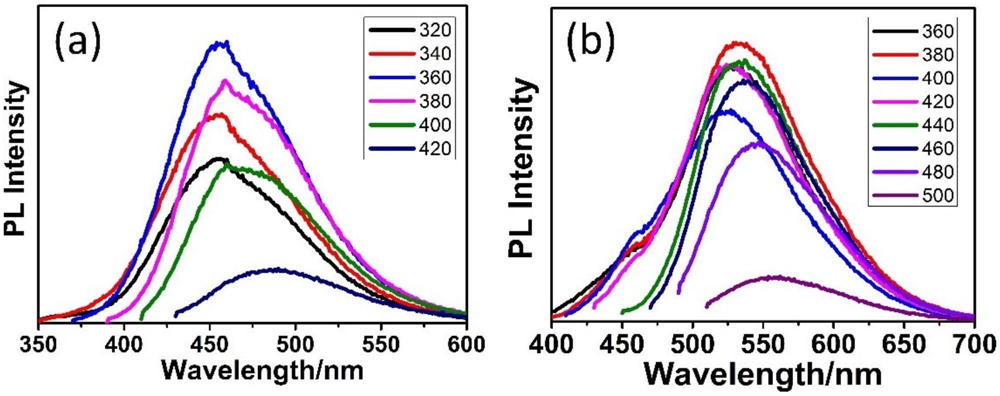

Figure S11. PL properties of the two kinds of Mo-Si NPs separated by alkali-treatment. (a)Liquid supernatant under pH=10; (b) Precipitation under pH=10 and re-dissolved in acid.

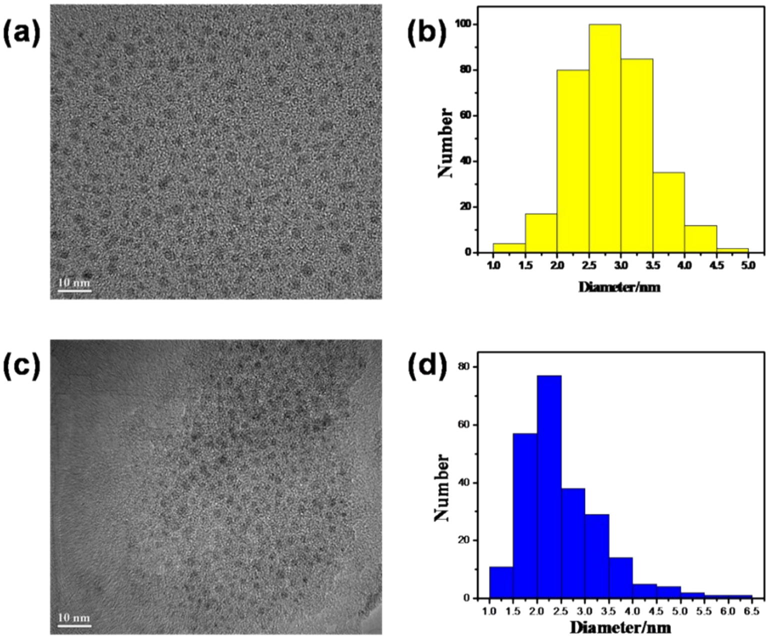

Figure S12. FETEM pictures of yellow-emitting Si NPs (a) and blue-emitting Si NPs(c). Size distribution of particle size from a survey of (b) 700 yellow-emitting Si NPs and (d) 293 blue-emitting Si NPs.

Note: In our experiment, the original samples after synthesis are actually a mixture of Si NPs with slightly different sizes and surfaces which show a broad PL (Figure S 10). Under the pH of 10, part of the Si NPs can be precipitated out and we found that this part show a yellow PL after re-dissolved in water and acid again. We provided more characterization to investigate the difference of the two parts of Si NPs in here. Firstly, we did a statistical analysis of the NP size towards these two kinds of Si NPs (Figure S12). The size of yellow ones is almost the same as the blue ones. The mean diameter of the yellow one is 2.8±0.6 nm and the blue one is 2.5±0.8nm. More importantly, based on X-ray photoelectron spectroscopy (XPS), the surface of the yellow Si NPs is more oxidized comparing to the blue ones (Figure S13). In contrast with the blue-emitting Si NPs, more Si-X(X=Si, N, Cl) bonds on the surface of the yellow ones were oxidized into Si-O-Si or Si=O.

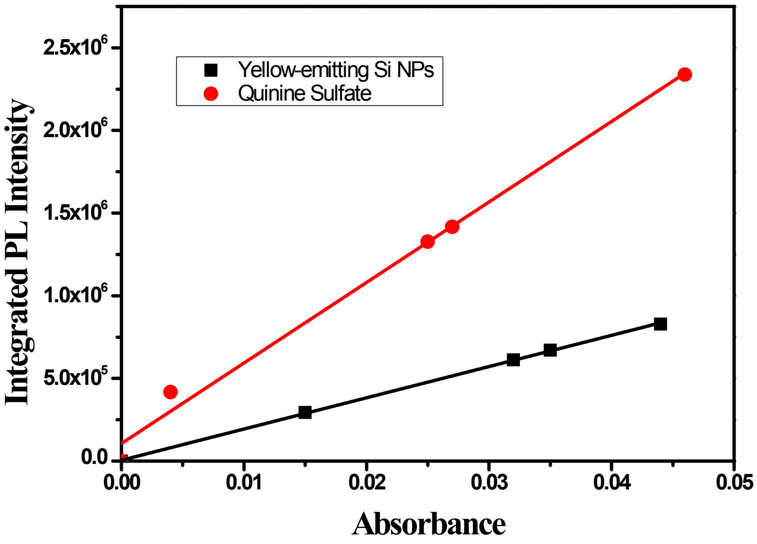

Figure S13. PLQYs measurements of the yellow-emitting Si NPs. A typical example of integrated PL intensity dependence on the absorbance for Si NPs (black) and Quinine sulfate (red) in 0.1 M H_2SO_4. The solid lines represent the fitting results for each set of data. PLQYs of Si NPs was calculated by using the equation: φx=φst(Kx/Kst)(ηx/ηst)^2, Where φ is the QY, K is the slope determined by the curves and η is the refractive index. The subscript “st” refers to the standards and “x” refers to the unknown samples. For these aqueous solutions, ηx/ηst=1.

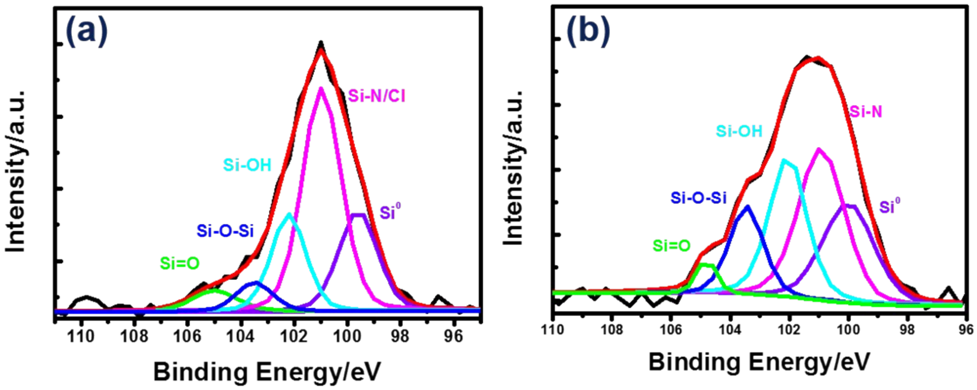

Figure 14. X-ray photoelectron spectra (XPS) of the Si 2p spectral regions of (a) blue-emitting Si NPs and (b)yellow-emitting Si NPs.Compostional information was obtanied from the X-ray photoelectron spectrum(XPS).The high-resolution Si 2p region is dominated by five peaks concentered at 96.5 eV to 106 eV.On the whole, the yellow-emitting Si NPs represents more surface oxidation than the blue one.

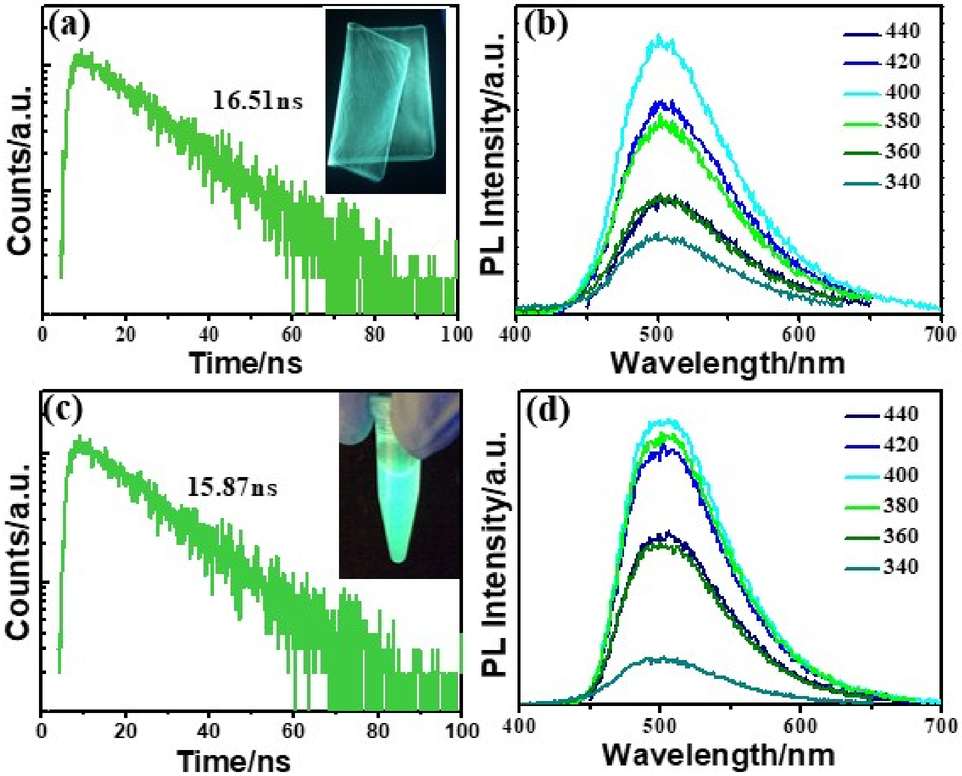

Figure S15. (a) and (b) are the TCSPC and PL spectra of Te-Si NP/Clay/PVA films. (c) and (d) are the the TCSPC and PL spectra of Te-Si NPs in solution.

Table S1. Comparison of the PLQY of different Si NPs and phophors tested by Integrating method and Refernce method.

Si NPs	**State**	**Integrating sphere**	**Reference method**
Ca- Si NPs	colloidal	80%	82%
	powder	98%	/
Te-Si NPs	colloid	53%	38%
	powder	41%	/
Di- Si NPs	colloid	74%	50%
	powder	72%	/
Mo- Si NPs	colloid	17%	24%
	powder	44%	/

Table S2. Comparison of emission wavelength and FLT of different phosphors and emitting films before and after different time's storage.

SAMPLES	STATE	EMISSION WAVELENGTH	FLT
Ca phosphors	5 month before	494nm	26.43ns
	5 month after	495 nm	23.69 ns
Te phosphors	5 month before	506 nm	14.16 ns
	5 month after	496 nm	15.09 ns
Di phosphors	5 month before	501 nm	21.57 ns
	5 month after	504 nm	20.26 ns
Mo phosphors	6 month before	519 nm	15.92 ns
	6 month after	518 nm	16.94 ns
Ca gelatin film	2 month before	485 nm	15.00 ns
	2 month after	494 nm	14.53 ns
Te PVA film	9 month before	501 nm	16.51 ns
	9 month after	497 nm	16.48 ns
Di gelatin film	2 month before	505 nm	18.51 ns
	2 month after	507 nm	17.47 ns
Mo PVA film	7 month before	512 nm	18.40 ns
	7 month after	502 nm	15.42 ns