In Situ Rapid Growth of Fluorescent Silicon Nanoparticles under Room Temperature and Atmospheric Pressure

Yiling Zhong, Bin Song, Fei Peng, Yanyan Wu, Sicong Wu, Yuanyuan Su and Yao He*

Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Institute of Functional Nano & Soft Materials (FUNSOM), and Collaborative Innovation Center of Suzhou Nano Science and Technology (NANO-CIC), Soochow University, Suzhou, Jiangsu 215123, China
E-mail: yaohe@suda.edu.cn

Supporting Information

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Video S1 shows the experimental reaction procedure. (3-Aminopropyl)trimethoxysilane ($C_6H_{17}NO_3Si$) molecules are readily reacted with Cy7 molecules (a typical kind of organic dyes) under normal temperature and pressure, yielding fluorescent SiNPs in a glass bottle. As shown in Video S1, Cy7 organic dye solution with 1 mL is dropped into 1 mL $C_6H_{17}NO_3Si$ solution under normal temperature and pressure. Relatively strong fluorescence is observed within 3-min reaction. Fluorescent intensity is gradually enhanced accompanied with increase of reaction time. Significantly, distinct orange fluorescence is observed during 10-min reaction. As the reaction proceeds, the orange fluorescence is further enhanced. Finally, highly fluorescent SiNPs are readily achieved after 30-min reaction under room temperature and atmospheric pressure, exhibiting strong orange fluorescence under UV irradiation.

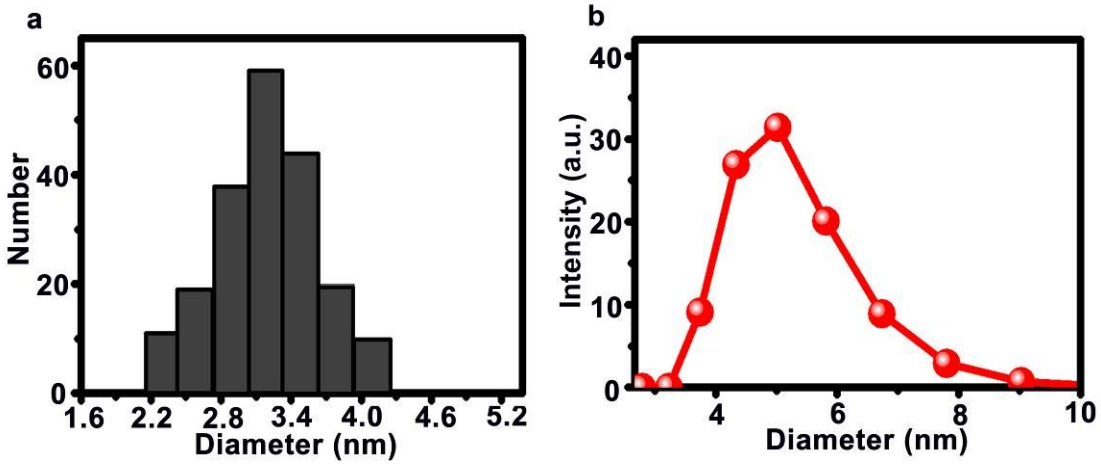

Fig. S1 (a) The TEM diameter distribution, and (b) DLS of the as-prepared SiNPs. The diameter distribution, calculated by measuring more than 200 particles, shows an average diameter of 3.1 ± 0.36 nm. The diameter measured by DLS confirms the small size of the as-prepared SiNPs with a hydrodynamic diameter of ~5.0 nm. The slightly different diameters measured by TEM and DLS are due to various tested conditions in TEM and DLS characterizations.

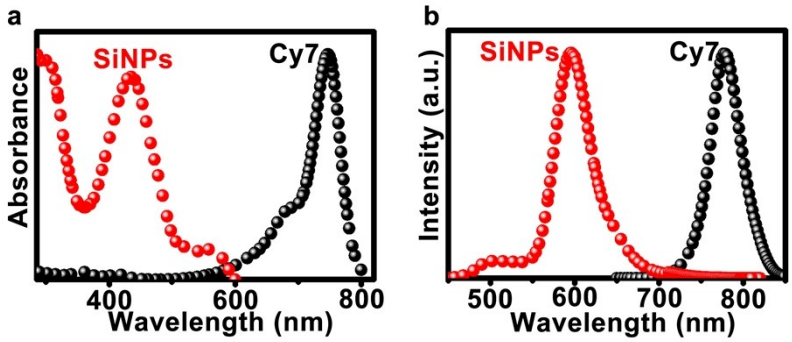

Fig. S2 Optical properties of SiNPs. (a) Absorption and (b) photoluminescence (UV-PL) spectrum of the as-prepared SiNPs, and Cy7. Excitation wavelengths for the as-prepared SiNPs, and Cy7 are 420, and 747 nm, respectively.

Fig. S2 exhibits the normalized UV-PL spectrum of the resultant SiNPs, indicating that the SiNPs possess good optical properties with clearly resolved absorption peak and symmetrical PL peak. In comparison to organic dye Cy7 (maximum emission wavelength (λ_{max}= 774 nm) and absorption peak (747 nm)), the as-prepared SiNPs exhibit distinctly shorter λ_{max} (600 nm) and absorption peak (435 nm).

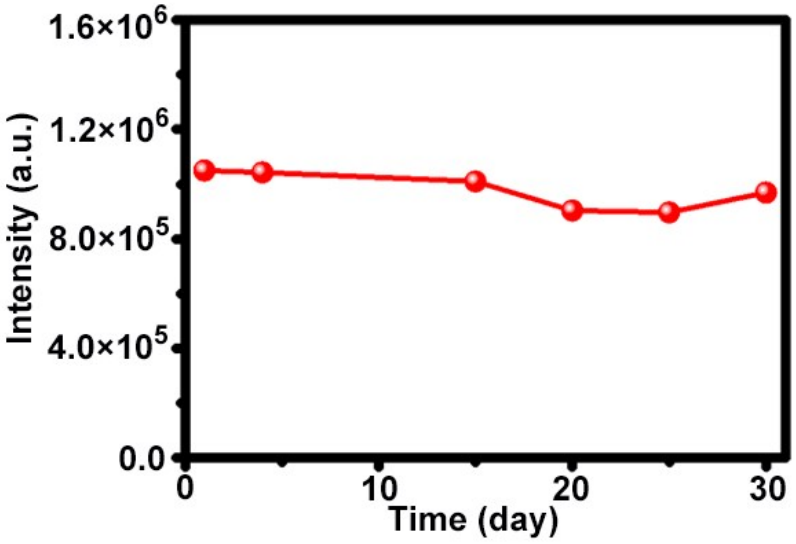

Fig. S3 Temporal evolution of fluorescence of the as-prepared SiNPs during one-month storage. The as-prepared SiNPs possess robust storage stability and maintain strong and stable fluorescence for one month when stored in ambient environment. The corresponding PL intensity shows a minimal loss (< 14 %) during 1 month, which is attributed to the protection from the possible surface ligands (e.g., -NH_2 and -COOH), as well as the unique PL properties of SiNPs, similar to previous reports.[1-6]

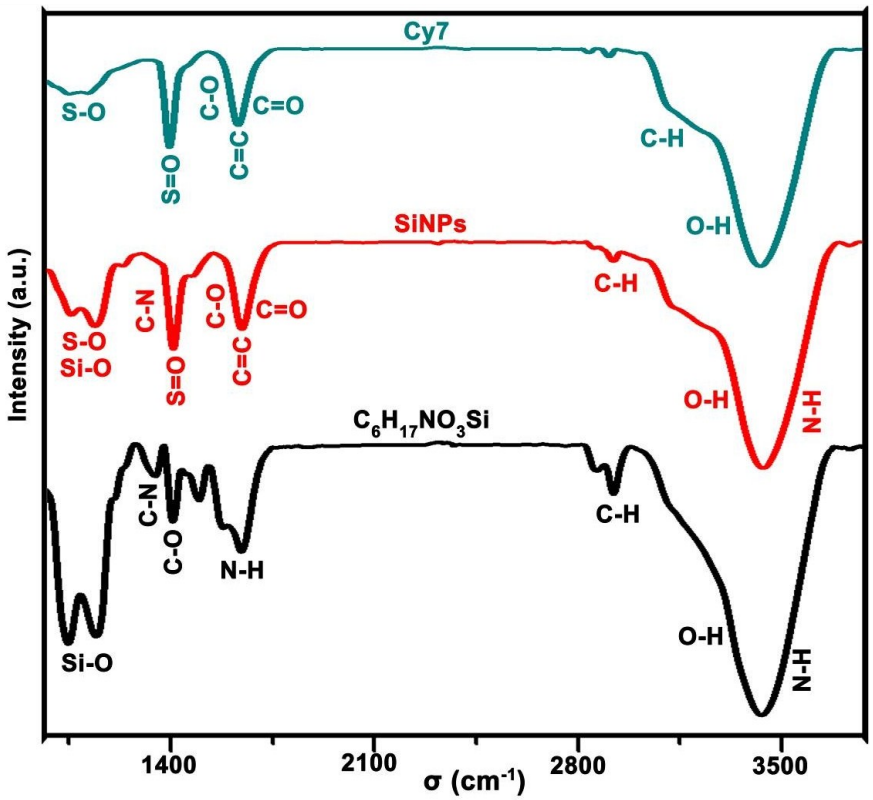

Fig. S4 FTIR spectra of the as-prepared SiNPs, Cy7, and $C_6H_{17}NO_3Si$, exhibiting several distinct absorption peaks in the range of 950-3800 cm^{-1}. Typically, for the Cy7 (cyan line), the characteristic FTIR absorbance peaks at 1060, 1370-1410, 1390-1440, 1618-1647, 1600-1680, 2850-2980, and 3000 cm^{-1} are assigned to S-O vibration, S=O vibration, C-O vibration, C=C stretching vibration, C=O stretching vibration, C-H stretching vibration, O-H vibration, respectively. For the $C_6H_{17}NO_3Si$ (black line), the strong FTIR absorbance peaks at 1080, 1380, 1390-1440, 1580, 2850-3000, 3000 and 3400 cm^{-1} are assigned to the vibrational stretch of Si-O bonding, C-N vibration, C-O vibration, N-H bending vibrations, C-H stretching vibration, O-H vibration and the N-H stretching vibration, respectively. For the resultant SiNPs (red line), the strong FTIR absorbance peaks at 1060, 1080, 1380, 1370-1410, 1390-1440, 1618-1647, 1600-1680, 2850-3000, 3000, and 3400 cm^{-1} are assigned to S-O vibration, Si-O vibration, C-N vibration, S=O vibration, C-O vibration, C=C stretching vibrations, C=O stretching vibration, C-H stretching vibration, O-H vibration, and N-H stretching vibration, respectively.[1-14]

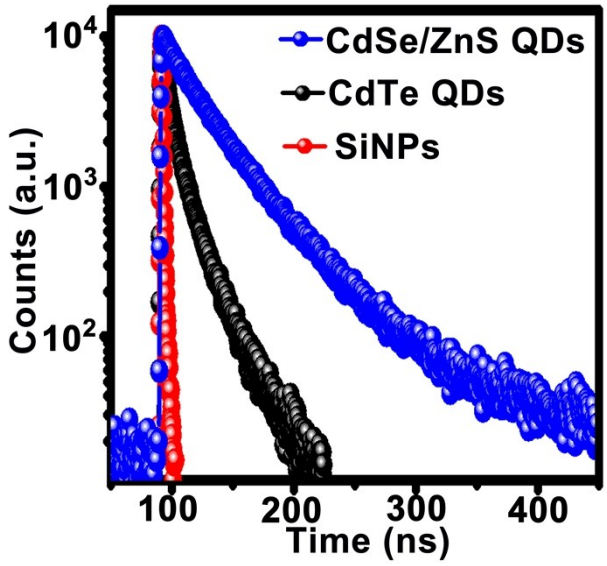

Fig. S5 Fluorescence decays of CdTe and CdSe/ZnS QDs, as well as the as-prepared SiNPs.

PL decay of CdTe QDs, CdSe/ZnS QDs, and three-color SiNPs is determined, as displayed in Fig. S5 and Table 1. Typically, the PL decay curves of CdTe and CdSe/ZnS QDs are well fit to a third-order exponential decay. The decay times of components of CdTe QDs are 9.219, 2, and 27.039 ns, respectively, with a calculated average lifetime of 19.68 ns. In comparison to CdTe QDs, CdSe/ZnS QDs exhibit distinctly longer fluorescent lifetime (i.e., the decay times of components are 10.182, 31.399 and 62.747 ns, respectively, with a calculated average lifetime of 45.59 ns). In striking contrast, the fluorescent lifetime of the as-prepared SiNPs is extremely short, ranging at ~1 ns level. Typically, the calculated average lifetime of the resultant SiNPs is 1.01 ns.

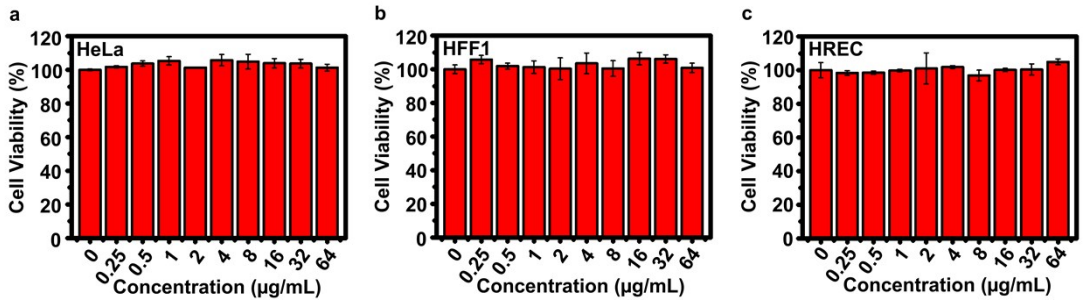

Fig. S6 Cytotoxicity assessment of the as-prepared SiNPs. (a-c) Cell viability of HeLa cells (a), human neonatal foreskin fibroblast cells (HFF1, (b)), and human retinal endothelial cells (HREC, (c)) incubated with the SiNPs for 5 h, respectively. The cell viability is calculated as percentage from the viability of the control (untreated) cells. The viability of the control cells is considered 100%. The results are means ± SD from three independent experiments.

In order to use nanomaterials in biological applications, we need to systematically evaluate the cytotoxicity to cells (cancer cells or non cancer cells) of nanomaterials. In 2013, Leong et al. investigated zinc oxide nanomaterials (ZnO NMs) effect on human neonatal foreskin fibroblast cells (BJ WT).[15] The authors revealed that upon 50 μM of ZnO NMs treatment for 5 h, no significant cell number attrition of BJ WT was observed. However, when the cells were treated by 200 μM (~ 16 μg/mL) of ZnO NMs for 5 h, their cell viability decreased to less than 60%. In our case, we interrogate in vitro toxicity of the resultant SiNPs with different concentrations (e.g., 0.25, 0.5, 1, 2, 4, 8, 16, 32, and 64 μg/mL) using established MTT assay. Fig. S6 shows that the cell viability of cancer cells (i.e., HeLa cells) and non cancer cells (i.e., HFF1 and HREC) all maintains above 90% during 5-h incubation with SiNPs, whose concentration ranges from 0.25 μg/mL to 64 μg/mL. These data suggest negligible cytotoxicity of the SiNPs, which is due to favorable biocompatibility of silicon and well consistent with previous reports.[1-6]

Materials and Devices

Reagent. (3-Aminopropyl)trimethoxysilance (97%) was purchased from Sigma-Aldrich. CdSe/ZnS QDs were purchased from Wuhan jiayuan Co., Ltd (China). Cy3, Cy5, and Cy7 were purchased from Fanbo biochemical Co., Ltd (China). All chemicals were used without additional purification. All solutions were prepared using Milli-Q water (millipore) as the solvent.

Characterization. Ultra-High Intensity UV-A Lamp (MAXIMA^{TM} ML-3500S/FA, 365 nm) was made by SPECTRONICS, USA. The Ultra-High Intensity UV-A Lamp with a spot reflector has a nominal steady-state UV-A intensity of 50,000 $\mu W/cm^2$ at 15 inches (38 cm). The SiNPs were characterized by UV-vis absorption, photoluminescence (PL), transmission electronic microscopy (TEM), high-resolution TEM (HRTEM), and Fourier-transform infrared (FTIR) spectroscopy. Optical measurements were performed at room temperature under ambient air conditions. UV-vis absorption spectra were recorded with a Perkin Elmer Lambda 750 UV-vis-infrared spectrophotometer. Photo-luminescence (PL) measurements were performed using a HORIBA JOBIN YVON FLUOROMAX-4 spectrofluorimeter. The PLQY of samples was estimated using Rhodamine B (QY=99%) in ethanol as a reference standard, which was freshly prepared to reduce the measurement error,[2-4,16,17] respectively. TEM and HRTEM samples were prepared by dispersing the sample onto carbon-coated copper grids with the excess solvent evaporated. The TEM/HRTEM overview images were recorded using Philips CM 200electron microscope operated at 200 kV. For FTIR measurements, KBr was pressed into a slice, onto which the SiNPs sample was dropped. The solvent in the sample was adequately evaporated by irradiation (>30 min) with high-power incandescent lamp. FTIR spectrum was record on a Bruker HYPERION FTIR spectrometer and cumulated 32 scans at a resolution of 4 cm^{-1}.

To compare theses decays we calculated the average PL times (τ_{av}) that describe the mean time taken for a photon to be emitted using the following equation:

$$\tau = \frac{\Sigma a_i \tau_i^2}{\Sigma a_i \tau_i} \quad (1)$$

The partial factors a_i and partial lifetimes τ_i were estimated from a fit of an i-exponential function of the form $I_{PL}(t) \propto \Sigma a_i \exp(-t/\tau_i)$ to the experimental PL decay curves (Table 1). Here, I_{PL} is PL intensity, t denotes time, and a_i represents a weighting of the various decay time components τ_i (Table 1 and Fig. S5).[18-20]

Methods

Synthesis of fluorescent SiNPs. The SiNPs precursor solution was prepared by adding 10 mL of (3-Aminopropyl)trimethoxysilane (concentration: 1.027 g/mL) to 10 mL Cy7 aqueous solution (concentration: 50 μg/mL) in a common glass bottle with volume of 60 mL. ~3 mg fluorescent SiNPs were readily achieved in ~60 min via one-step reaction at room temperature (20-25 ^{o}C) and atmospheric pressure. We can readily deduce that the process can in principle be scaled up to produce any desirable amount of SiNPs by using appropriately larger amount of reactants. To ensure an objective and real-time investigation and comparison of optical properties and morphologies of samples, the samples solution was directly extracted respectively from the same reaction solution at different reaction time (e.g., 3, 10, 30, and 60 min) for optical (e.g., UV-PL, photographs, and lifetime measurement, etc.) and TEM characterization. For cytotoxicity assessment and storage stability, the resultant SiNPs aqueous sample was further purified by dialysis (MWCO: 500, Viskase) extensively against Milli-Q water to remove (3-aminopropyl)trimethoxysilane and Cy7 molecules. The residual (3-aminopropyl)trimethoxysilane molecules and Cy7 were fully filtrated because their molecular weight is much smaller than 0.5 KDa. The SiNPs molecular weight larger than 0.5 KDa was diluted by certain of Milli-Q water. Such purified SiNPs aqueous solution could be dried to produce solid-state SiNPs sample.

Optical measurements, TEM, and DLS characterizations of the prepared SiNPs. Optical measurements were performed at room temperature under ambient air

conditions. UV-vis absorption spectra were recorded with a Perkin Elmer Lambda 750 UV-vis-infrared spectrophotometer. 600 μL solution of the prepared SiNPs sample was transferred into an exclusive Quanrtz cuvette for UV spectra measurements. Photoluminescence (PL) measurements were performed using a HORIBA JOBIN YVON FLUOROMAX-4 spectrofluorimeter. 3 mL solution of the prepared SiNPs sample was transferred into an exclusive Quanrtz cuvette for PL spectra measurements. TEM and HRTEM samples were prepared by dispersing the sample onto carbon-coated copper grids with the excess solvent evaporated. The TEM/HRTEM overview images were recorded using Philips CM 200 electron microscope operated at 200 KV. Light-scattering analysis was performed using a DynaPro Dynamic Light Scatterer (DLS), which was made by Malvern Corp, U. K. (ZEN3690). 1 mL SiNPs sample was transferred into an exclusive vitreous for DLS measurements. Experiment parameters were as follow, Scan times: 100; Dispersant: Water; Temperature: 25 ^{o}C; Viscosity: 0.8872 cP; RI: 1.330; Dielectric constant: 78.5.

Photostability comparison of FITC, CdTe QDs, CdSe/ZnS QDs and SiNPs, and fluorescent lifetime measurement of CdTe QDs, CdSe/ZnS QDs and SiNPs. CdTe QDs were prepared based on our previous reports.[17] Particularly, to guarantee the reliable comparison, the photoluminescence intensity of FITC, CdTe QDs, CdSe/ ZnS QDs, and SiNPs was adjusted to the same value. The four samples were continuously irradiated for different time intervals using an ultra-high intensity UV-A lamp (MAXIMA^{TM} ML-3500S/FA, 365 nm). Ensemble fluorescence lifetime measurements were performed on Fluorescence Spectrometer (HORIBA Jobin Yvon, French) using the time-correlated single-photon counting (TCSPC) technique.

MTT assay of cell viability. Colorimetric 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT, Sigma-Aldrich) assay, recognized as an established method, was employed for assessment of cytotoxicity in our experiment. In brief, Cells (e.g., HeLa cells, human neonatal foreskin fibroblast cells (HFF1), and human retinal endothelial cells (HREC)) dispersed in 96-well cell-culture plate at 1.5×10^4 / well were cultured at 37 ^{o}C for 12 h under 5% CO_2. Thereafter, SiNPs of serial

concentrations (0.25, 0.5, 1, 2, 4, 8, 16, 32, 64 μg/mL) were added into the each cell and co-incubated with Cells for 5 h. Then 20 μL stock MTT (5 mg mL^{-1}) was added to each well, and cells were cultured at 37 ^{o}C for 4 h. Afterwards, the cells were lysed by 10% acidified sodium dodecyl sulfate (10% SDS), whose cell viability was further determined based on measurement of the absorbance at 570 nm using the microplate reader (Bio-Rad 680, U.S.A.). To ensure reproducibility, three independent experiments were performed and all measurements were carried out in triplicate.

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