Electronic Supplementary Material (ESI) for Analytical Methods.

Green synthesis of yellow-green emissive silicon nanoparticles and their application for the sensitive fluorescence detection of bilirubin

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Reagents and materials

3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (AEEA, 95%) and bilirubin (97%) were purchased from Energy Chemical Co., Ltd. 2-aminophenylboronic acid hydrochloride (95%), fructose (99%), glucose (98%), lactose (98%), vitamin C (Vc, 99%), urea (99%), uric acid (98%), creatine (99%), cholesterol (95%), guanine (98%), adenine (98%), cytosine (99%), thymine (98%), hemoglobin (90%), glutathione (98%), lysine (Lys, 98%), cysteine (Cys, 99%), histidine (His, 99%), alanine (Ala, 99%) and arginine (Arg, 98%) were obtained from Aladdin Reagents Co., Ltd. $Na_2HPO_4 \cdot 12\ H_2O$ (99%) and $NaH_2PO_4 \cdot 2\ H_2O$ (99%) were purchased from Tianjin Fuchen Chemical Reagent Factory. Phosphate buffer solution (PBS) was prepared with 10 mM NaH_2PO_4-Na_2HPO_4. Sodium hydroxide (NaOH, 96%), potassium chloride (KCl, 99.5%), calcium chloride ($CaCl_2$, 96%), sodium chloride (NaCl, 99.5%), magnesium nitrate ($Mg(NO_3)_2$, 99%), aluminum nitrate ($Al(NO_3)_3$, 99%), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99%), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99%) and copper sulfate ($CuSO_4 \cdot 5H_2O$, 98%) were bought from Tianjin Kemiou Chemical Reagent Co., Ltd. Fetal bovine serum (FBS, special grade) was purchased from Beijing Wobison Technology Co., Ltd. All of the chemicals used were analytical reagent grade or above and did not require further purification. Deionized water was used throughout the experiment.

Apparatus

Transmission electron microscopy (TEM) images of SiNPs were obtained using a Tecnai G2F30 instrument. A drop of SiNPs solution was dropped on a copper grid

and dried at room temperature for TEM analysis. X-ray photoelectron spectroscopy (XPS) was measured by AXIS Supra photoelectron spectrometer. X-ray powder diffraction (PXRD) analysis was recorded on the Bruker D8 Advance X-ray diffractometer. Fluorescence lifetimes of SiNPs and the mixture of SiNPs and bilirubin, and the quantum yield of SiNPs were recorded on the Edinburgh FLS1000 Steady/Transient fluorescence spectrometer. Fourier transform infrared spectra (FT-IR) were performed using KBr pellets on the Bruker Tensor II spectrometer. Fluorescence measurements were performed using an F-7000 fluorescence spectrophotometer with the excitation and emission slits set to 5 nm and 10 nm, respectively. Absorption and emission measurements were made in a 1 cm × 1 cm quartz cuvette. UV-Vis absorption spectra were measured using the EVOLUTION 260 BIO UV-Vis spectra photometer. The zeta potentials were measured using the Zeta potential analyzer.

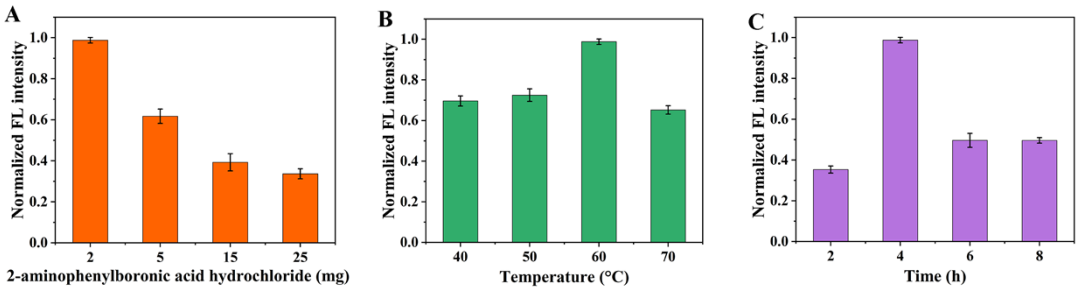

Figure S1 Normalized FL intensity of SiNPs synthesized at different weight of 2-aminophenylboronic acid hydrochloride (A), different reaction temperature (B) and different reaction time (C).

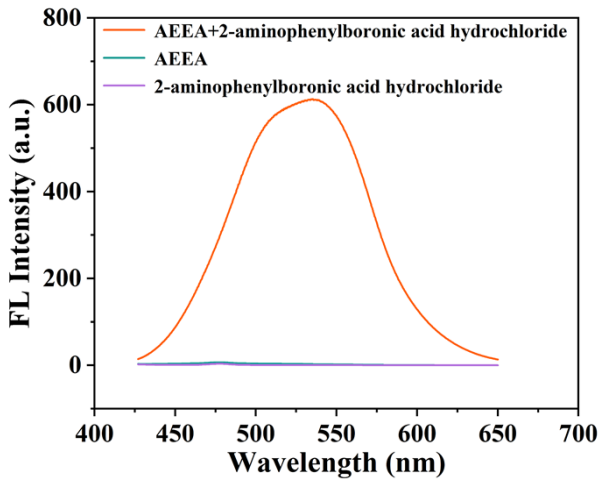

Figure S2 The fluorescence emission spectra of the products prepared by the reaction of only AEEA, only 2-aminophenylboronic acid hydrochloride, and AEEA+2-aminophenylboronic acid hydrochloride under the same conditions.

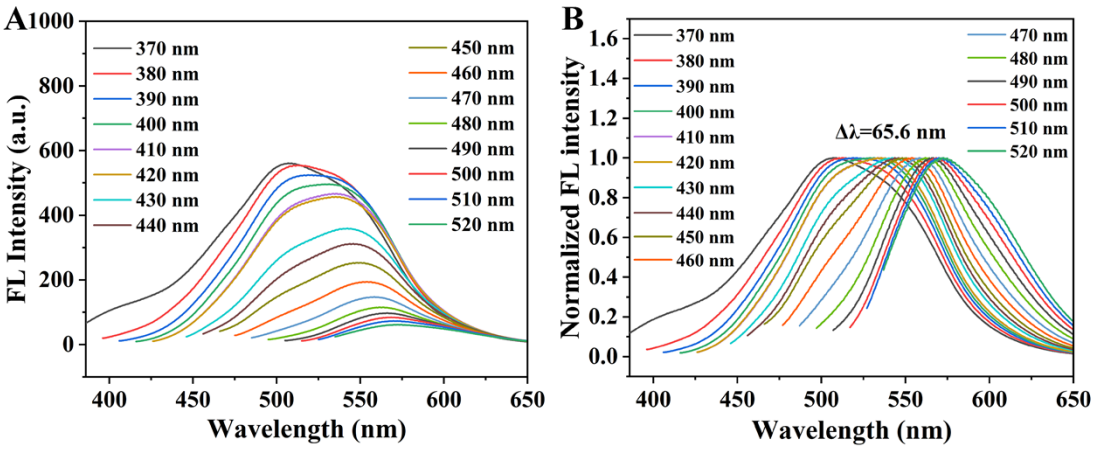

Figure S3 FL intensity (A) and normalized FL intensity (B) of the prepared SiNPs at different excitation wavelengths.

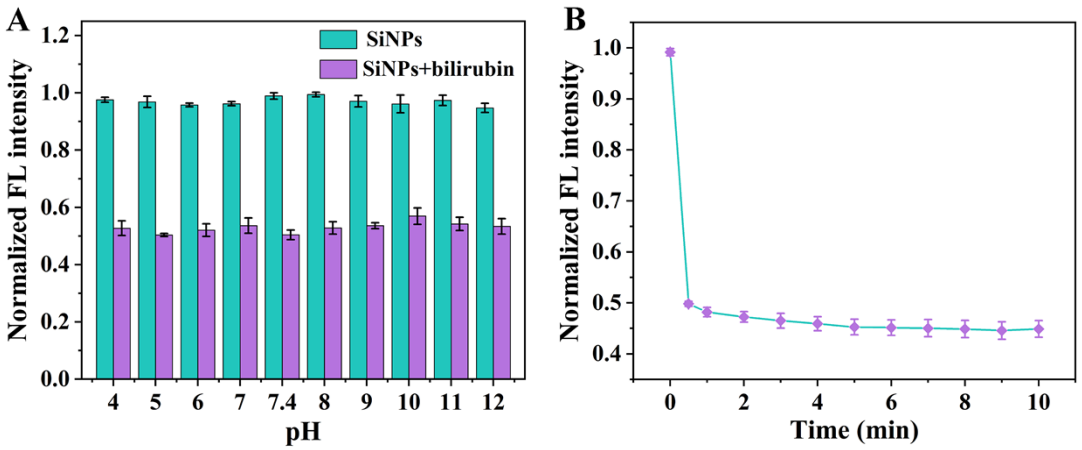

Figure S4 (A) Normalized FL intensity of SiNPs and SiNPs+bilirubin (20 μM) at different pH values. (B) Time-dependent normalized FL intensity of SiNPs with the addition of bilirubin (20 μM).

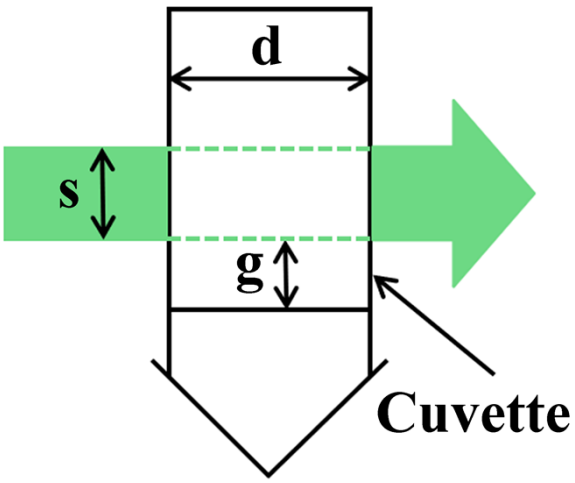

Figure S5 The parameters used in equation (1).

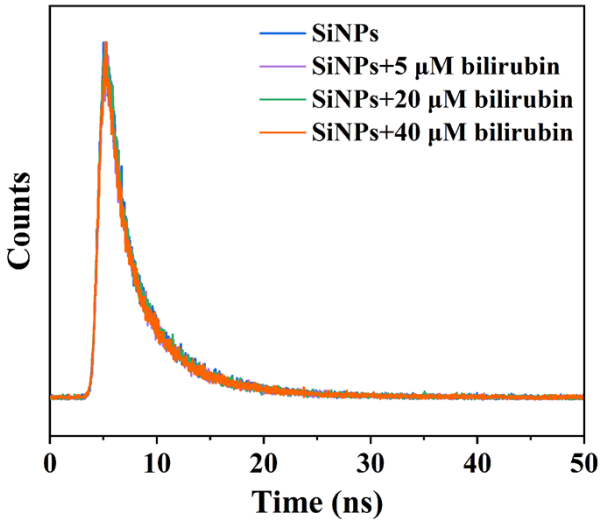

Figure S6 Fluorescence decay curves of SiNPs and the mixture of SiNPs and bilirubin (5, 20 and 40 μM).

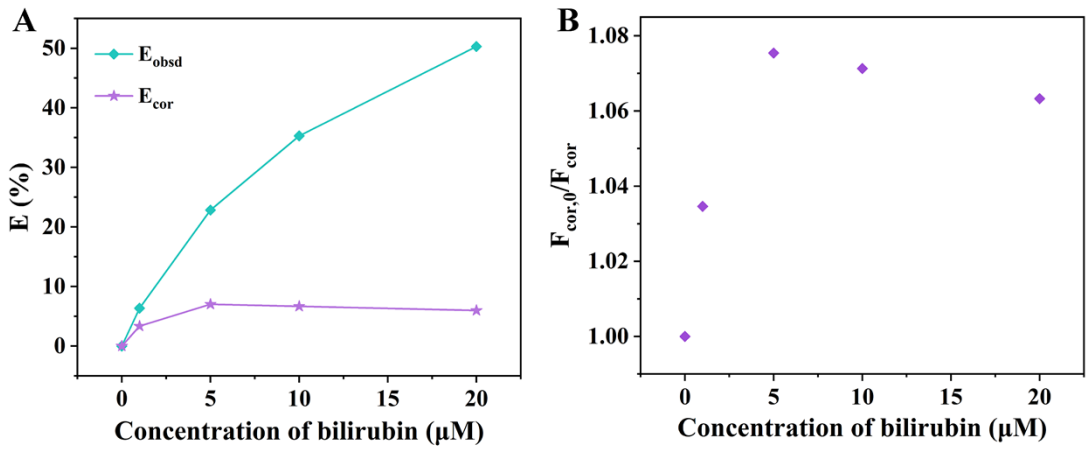

Figure S7 (A) Suppressed efficiency (E, %) of observed (blue line, E_{obsd}) and corrected (purple line, E_{cor}) FL intensity. (B) Influence of bilirubin concentrations on the corrected FL intensity ratio ($F_{cor,0}/F_{cor}$) of SiNPs.

Table S1 Parameters used to calculate IFE of bilirubin on the fluorescence of SiNPs.

Concentration (μM)	A_{ex}[a]	A_{em}[b]	CF[c]	F_{obsd}[d]	F_{cor}[e]	E_{obsd}[f]	E_{cor}[g]
0.00	0.24	0.07	1.41	385.57	543.65	0.00	0.00
1.00	0.26	0.07	1.44	361.03	519.88	0.06	0.04
5.00	0.41	0.08	1.69	297.47	502.72	0.23	0.08
10.00	0.60	0.08	2.02	249.50	503.99	0.35	0.07
20.00	0.94	0.10	2.74	187.77	514.48	0.51	0.05

[a]A_{ex} and [b]A_{em} are the absorbance of SiNPs upon addition of bilirubin at 410 and 536 nm, respectively.

[c]Corrected factor (CF) is calculated as F_{cor}/F_{obsd}.

[d]F_{obsd} is the measured FL intensity of SiNPs upon addition of bilirubin at 536 nm.

[e]F_{cor} is the corrected FL intensity with Eq. (1) by removing IFE from the measured FL intensity (F_{obsd}).

[f]E_{obsd} =1-$F_{obsd}/F_{obsd,0}$, in which $F_{obsd,0}$ is the observed FL intensities of SiNPs in the absence of bilirubin.

[g]E_{cor}=1-$F_{cor}/F_{cor,0}$, in which $F_{cor,0}$ is the corrected FL intensities of SiNPs in the absence of bilirubin.

Table S2 Influence of different concentrations of bilirubin on the fluorescence lifetime of SiNPs.

Concentration (μM)	Fluorescence lifetime (ns)
0.00	4.20
5.00	4.21
20.00	4.16
40.00	4.04