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A ratiometric fluorescence method based on silicon nanoparticles/o-phenylenediamine/MnO_2 nanosheets system for vitamin C detection

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Reagents

(3-aminopropyl) triethoxy silane (APTES), guanine and copper sulfate pentahydrate ($CuSO_4·5H_2O$) were purchased from Anhui Zesheng Technology Co., LTD. Hydrogen peroxide (H_2O_2, 30%) was purchased from Yantai Shuangshuang Chemical Co., LTD. Manganese chloride ($MnCl_2·4H_2O$) was purchased from Shanghai Haohong Biomedical Technology Co., LTD. Glutathione (GSH) was purchased from Shanghai Maclin Biochemical Technology Co., LTD. Glycine (Gly), alanine (Ala), L-Cysteine (L-Cys), L-glutamic acid (L-Glu), L-histidine (L-His), L-tryptophan (L-Trp), ascorbic acid (VC), glucose, fructose, threonine (Thr), serine (Ser), methionine (Met), lysine (Lys), tyrosine (Tyr), o-phenylenediamine (OPD), dopamine hydrochloride (DA) and tetramethylammonium hydroxide (TMA) were purchased from Aladdin Biochemical Technology Co., LTD. Sodium hydrogen phosphate ($Na_2HPO_4·12H_2O$), sodium dihydrogen phosphate ($NaH_2PO_4·2H_2O$) and ferrous sulfate ($FeSO_4$) were purchased from Tianjin Fuchen Chemical Reagent Factory. Potassium bromide (KBr) and oxalic acid were purchased from Tianjin Fengchuan Chemical Reagent Technology Co., LTD. Sodium chloride (NaCl), citric acid and urea were purchased from Zhengzhou Paini Chemical Reagent Factory. Zinc sulfate ($ZnSO_4$) was purchased from Luoyang Haohua Chemical Reagent Co., LTD. Lead nitrate ($Pb(NO_3)_2$) and barium chloride ($BaCl_2$) were purchased from Beijing Red Star Chemical Plant. Silver nitrate ($AgNO_3$), aluminum nitrate ($Al(NO_3)_3$), calcium chloride ($CaCl_3$) and magnesium nitrate ($Mg(NO_3)_2$) were purchased from Tianjin Kemiou Chemical Reagent Co., LTD. Cadmium sulfate ($CdSO_4·8H_2O$) was purchased from Tianjin Damao Chemical Reagent Factory. Cobalt sulfate

($CoSO_4 \cdot 7H_2O$) was purchased from Tianjin Kaitong Chemical Reagent Co., LTD. Nickel chloride ($NiCl_2 \cdot 6H_2O$) was purchased from Chengdu Kelon Chemical Reagent Factory. Mercury nitrate ($Hg(NO_3)_2$) was purchased from Jiaxing Chemical Reagent Co., LTD. Vitamin C tablets, chewable vitamin C tablets and vitamin C injections were purchased from local pharmacies. Ultrapure water was used throughout the experiment.

Apparatus

American FEI Tecnai F20 transmission electron microscopy (TEM) was used to observe the morphology of SiNPs and MnO_2 nanosheets. Germany Bruker D8 Advance powder X-ray diffractometer (PXRD) was used to determine the crystalline structure of SiNPs. Ultraviolet-2600i ultraviolet-visible (UV-Vis) spectrophotometer was used to investigate the optical properties of SiNPs and the detection mechanism of the method. Both the Shimadzu/Krayos AXIS Ultra DLD photoelectron spectrometer (XPS) in Japan and the Thermo Scientific Nicolet 6700 Fourier Transform Infrared spectrometer (FT-IR) were used to analyze the chemical bond formation of SiNPs. The Edinburgh FLS1000 steady state/transient fluorescence spectrometer was used to analyze the fluorescence lifetime of SiNPs under different conditions. The F-7000 fluorescence spectrometer was used to measure the fluorescence spectra under different experimental conditions. Shanghai TF-FD-1 freeze-drying oven was used for freeze-drying SiNPs solution.

Pretreatment and detection of actual samples

Vitamin C tablets, chewable vitamin C tablets and vitamin C injection were

selected as the actual samples in this experiment. These samples were pretreated as follows: After 20 vitamin C tablets and 10 chewable vitamin C tablets were weighed separately, the two tablets were ground into a powder. 0.01g vitamin C tablet powder was dissolved in 5.0 mL ultra-pure water. 0.04g vitamin C chewable tablet powder was dissolved in 5.0 mL ultra-pure water. After the sample solution was filtered by 0.22 μm filter membrane, the filtrate was diluted with ultra-pure water to a certain volume for use. After vitamin C injection was centrifuged (15000 rpm, 10 min), 10 μL of supernatant was taken into the centrifuge tube, which was diluted to 5 mL with ultra-pure water for subsequent use. A certain volume of sample diluent was added to the SiNPs/OPD/MnO_2 probe solution in place of VC standard solution. The contents of VC in the actual samples were calculated by the FL intensity ratio (F_{560}/F_{465}) of the ratiometric fluorescent probe and the fitted working curve.

Measurement of relative fluorescence QY

Using quinine sulfate (QY: 55%) as a reference, the fluorescence emission spectra of SiNPs and quinine sulfate with different absorbance were measured at the same excitation wavelength. The relative fluorescence QY of SiNPs was calculated by Equation S1. In addition, the absorbance of both was less than 0.10 to ensure the accuracy of the results.

$$\varphi = \varphi_1 \times \frac{A_1}{I_1} \times \frac{I}{A} \times \frac{n^2}{n_1^2} \qquad \text{Equation S1}$$

In Equation S1, φ and φ_1 were the relative fluorescence QY of SiNPs and quinine sulfate, respectively. A and A_1 were absorbance of SiNPs and quinine sulfate, respectively. I and I_1 were the integrated fluorescence emission peak intensities of

SiNPs and quinine sulfate, respectively. n and n_1 were the solvent refractive indices of SiNPs and quinine sulfate, respectively.

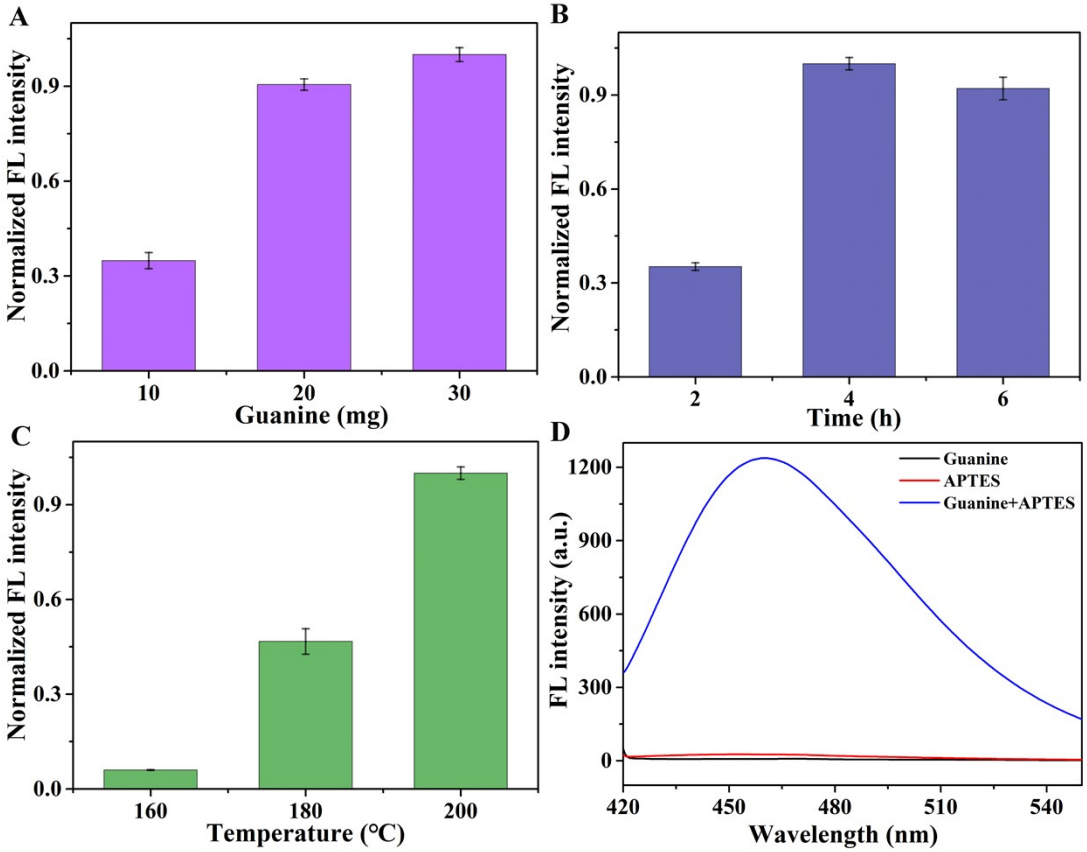

Fig. S1. (A) Normalized FL intensity of SiNPs under different dosage of guanine; (B) Normalized FL intensity of SiNPs at different reaction time; (C) Normalized FL intensity of SiNPs at different reaction temperature; (D) Fluorescence emission spectra of APTES, guanine and APTES + guanine after reaction at 200 ℃ for 4 h. The volume of SiNPs was 50 μL. The total volume of solution was 2 mL.

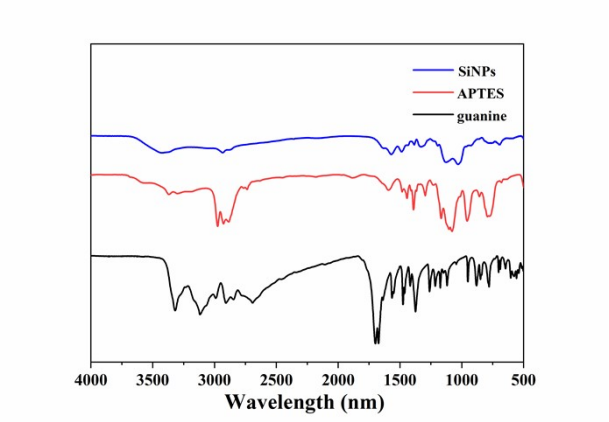

Fig. S2. FT-IR spectra of SiNPs, APTES and guanine.

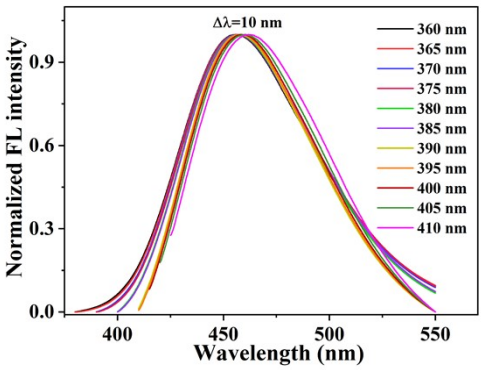

Fig. S~~2~~3. Fluorescence emission spectra of SiNPs at different excitation wavelengths (360~410 nm). The volume of SiNPs was 50 μL. The total volume of solution was 2 mL.

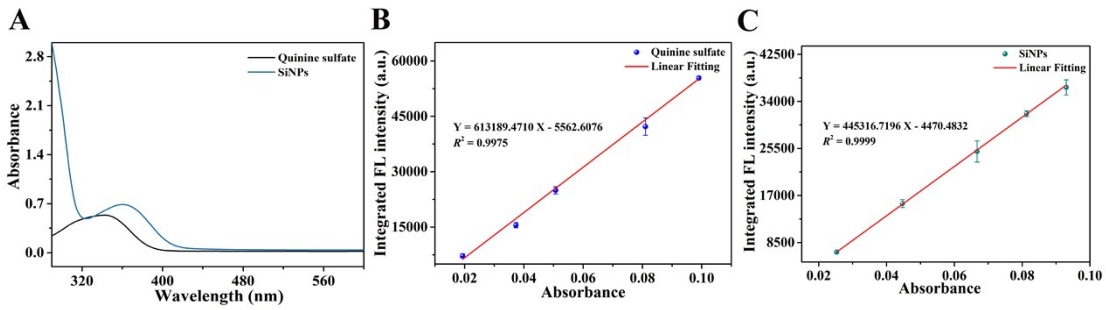

Fig. S34. (A) UV-Vis absorption spectra of SiNPs and quinine sulfate; (B) Plots of integrated FL intensity of quinine sulfate as a function of optical absorbance; (C) Plots of integrated FL intensity of SiNPs as a function of optical absorbance. The error bar is the standard deviation of three parallel tests. The volume of SiNPs was 50 μL. The total volume of solution was 2 mL.

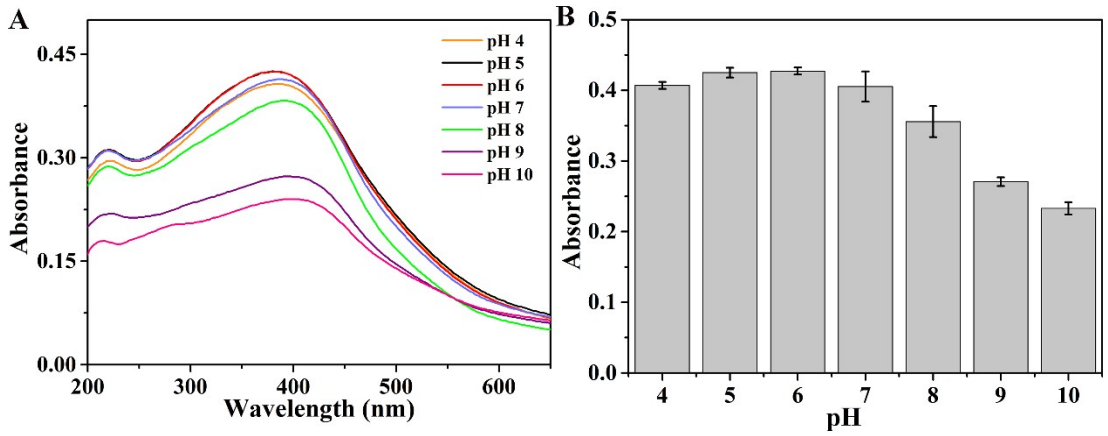

Fig. S45. (A) UV-Vis absorption spectra of MnO_2 nanosheets at different pH; (B) Absorbance of MnO_2 nanosheets at 380 nm at different pH. The volume of MnO_2 nanosheets was 20 μL. The total volume of solution was 2 mL.

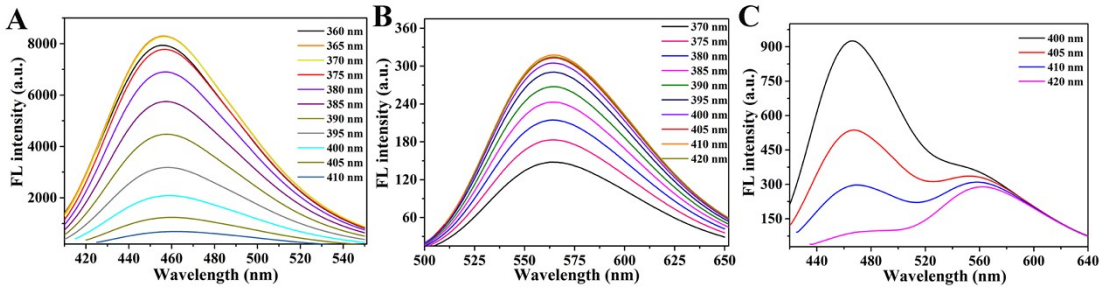

Fig. S~~5~~6. Fluorescence emission spectra of (A) SiNPs, (B) oxOPD and (C) SiNPs/OPD/MnO_2 at different excitation wavelengths. The total volume of SiNPs/OPD/MnO_2 probe solution was 2 mL (The volume of SiNPs was 50 μL. The volume of MnO_2 nanosheets was 20 μL. The concentration of OPD was 100 μM.).

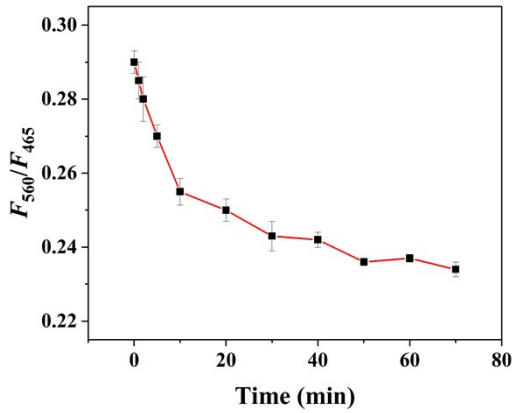

Fig. S7. The FL intensity ratio (F_{560}/F_{465}) of SiNPs/OPD/MnO_2 probe after incubation with 30 μM VC for different time (0-70 min). The total volume of SiNPs/OPD/MnO_2 probe solution was 2 mL (The volume of SiNPs was 50 μL. The volume of MnO_2 nanosheets was 20 μL. The concentration of OPD was 100 μM.).

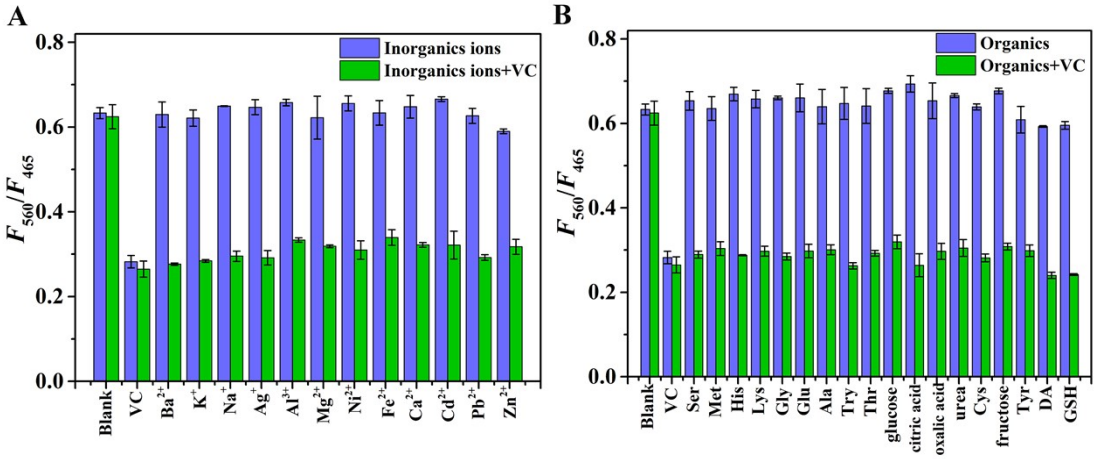

Fig. S~~6~~8. (A) FL intensity ratio (F_{560}/F_{465}) of ~~the~~ SiNPs/OPD/MnO_2 probe after addition of inorganic ions (purple bar) and the subsequent addition of 30 μM VC (green bar); (B) FL intensity ratio (F_{560}/F_{465}) of ~~the~~ SiNPs/OPD/MnO_2 probe after addition of organic substances (purple bar) and the subsequent addition of 30 μM VC (green bar). The concentration of K^+, Na^+, Cd^{2+} and urea was 100 μM, respectively. The concentration of Ag^+, citric acid and cysteine was 50 μM, respectively. The concentration of Fe^{2+}, glutathione and tyrosine was 10 μM, respectively. The dopamine concentration was 5 μM. The concentration of other interferences was 200 μM. The total volume of SiNPs/OPD/MnO_2 probe solution was 2 mL (The volume of SiNPs was 50 μL. The volume of MnO_2 nanosheets was 20 μL. The concentration of OPD was 100 μM.).

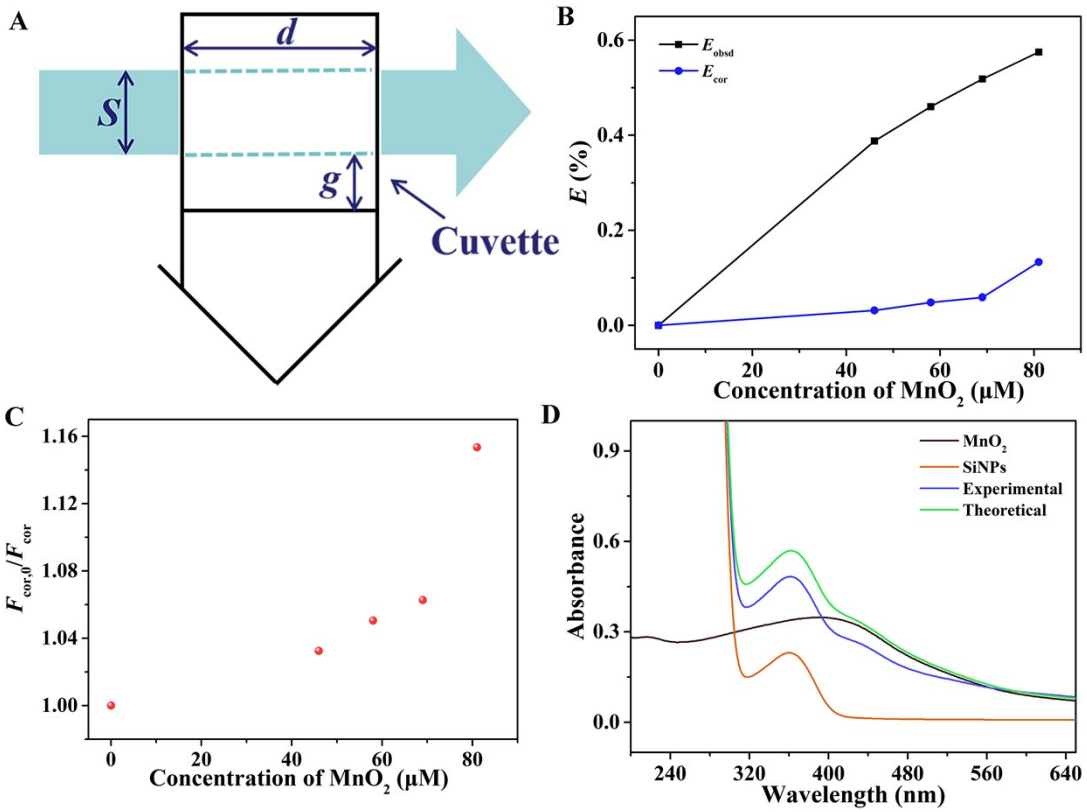

Fig. S~~7~~9. (A) The parameters used in equation (1). *g* was the distance between the edge of the excited beam and the edge of the cubed (*g*=0.25 cm); *d* was the width of the cubed (*d*=1.00 cm); *s* was the thickness of the excited beam (*s*=0.50 cm). (B) Inhibition efficiency of the measured (E_{obsd}) and corrected (E_{cor}) FL intensity of SiNPs at 465 nm.

(C) Influence of MnO_2 nanosheets concentrations on the corrected FL intensity ratio ($F_{cor,0}/F_{cor}$) of SiNPs. (D) UV-Vis spectra of SiNPs, MnO_2 nanosheets, and the theoretical and experimental UV-Vis spectra of the mixture of SiNPs and MnO_2 nanosheets. The volume of SiNPs was 50 μL. The volume of MnO_2 nanosheets was 20 μL. The total volume of solution was 2 mL.

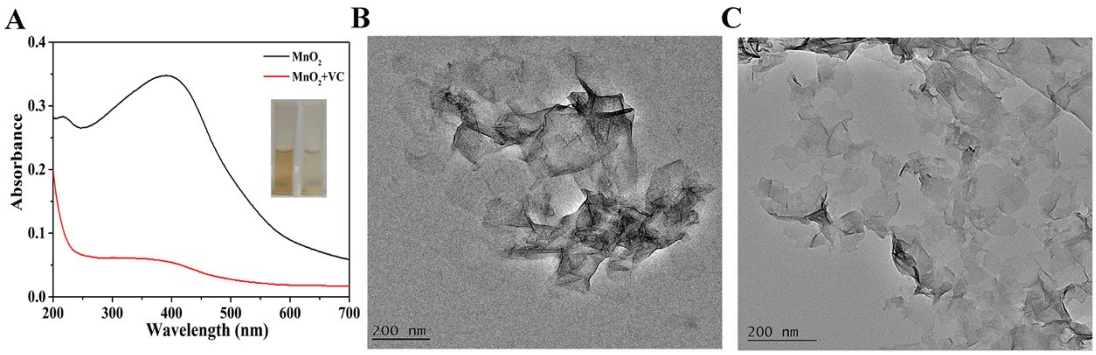

Fig. S~~8~~10. (A) UV-Vis absorption spectra of MnO_2 nanosheets and the mixture of MnO_2 nanosheets and VC (the inset illustration was pictures of MnO_2 nanosheets solution without (left) and with VC (right) in daylight); (B) TEM image of MnO_2 nanosheets; (C) TEM image of the mixture of MnO_2 nanosheets and VC. The volume of MnO_2 nanosheets was 20 μL. The total volume of solution was 2 mL.

Table S1 Parameters for calculation of the fluorescence QY of SiNPs.

	Quinine sulfate	SiNPs
Abs	0.019、0.037、0.051、0.081、0.099	0.025、0.045、0.067、0.081、0.093
Integrated FL intensity	7215.06、15538.71、24973.28、42241.13、55393.46	6788.29、15538.71、24958.58、31801.53、36535.18
Lope	613189.47	445316.72
QY (%)	55.00	39.94

Table S2 Comparison of ratiometric fluorescence methods for VC detection.

Material	Method	Linear range	LOD	Ref.
AuNCs-PbS-QDs	fluorescence	3-40 μM	1.5 μM	37
molybdenum disulfide quantum dots	fluorescence	0.5-40 μM	0.2 μM	38
RhB@Tb-MOFs	fluorescence	10-100 μM	2.54 μM	39
carbon dots/ polydopamine	fluorescence	0.5-30 μM	0.28 μM	40
SiNPs@OPD/MnO_2	fluorescence	0.5~40 μM	0.42 μM	This work

Table S23 Effect of MnO_2 nanosheets and VC on the fluorescence lifetime (τ) of SiNPs.

Sample	τ（ns）
SiNPs	10.01
SiNPs+MnO_2	9.93
SiNPs+MnO_2+VC	9.66

Table S~~3~~4 Parameters for the calculation of IFE proportion.

MnO_2 nanosheets (μM)	A_{ex} [a]	A_{em} [b]	CF [c]	F_{obsd} [d]	F_{cor} [e]	E_{obsd} [f]	E_{cor} [g]	$F_{cor,0}/F_{cor}$
0	0.0510	0.0020	1.06	1495.7	1585.3	0.00	0.00	1.00
46	0.2980	0.1713	1.68	915.6	1535.3	0.39	0.03	1.03
58	0.3590	0.2130	1.87	807.3	1509.0	0.46	0.05	1.05
69	0.4280	0.2440	2.07	720.4	1491.8	0.52	0.06	1.06
81	0.4317	0.2793	2.16	635.6	1374.3	0.58	0.13	1.15

[a]: The absorbance of SiNPs with MnO_2 nanosheets at excitation wavelength (λ=405 nm);

[b]: The absorbance of SiNPs with MnO_2 nanosheets at emission wavelength (λ=465 nm);

[c]: The correction factor ($CF=F_{cor}/F_{obsd}$) should be less than 3 to ensure the accuracy of the results;

[d]: The measured FL intensity of SiNPs with MnO_2 nanosheets at 465 nm;

[e]: The corrected FL intensity of SiNPs with MnO_2 nanosheets at 465 nm after IFE deduction;

[f]: The experimental value of quenching efficiency was calculated by $1-F_{obsd}/F_{obsd,0}$ ($F_{obsd,0}$ was the measured FL intensity of SiNPs in the absence of MnO_2 nanosheets);

[g]: The corrected value of quenching efficiency was calculated by $1-F_{cor}/F_{cor,0}$ ($F_{cor,0}$ was the corrected FL intensity of SiNPs in the absence of MnO_2 nanosheets).