Novel water-dispersible silicon nanoparticles as fluorescent and colorimetric dual-mode probe for emodin detection

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**Reagents and materials**

(3-aminopropyl)triethoxysilane (APTES), ferulic acid, emodin, gallic acid, protocatechuic acid (PA), quercetin, chrysophanol, baicalin, berberine, physcion, and polygonin were obtained from Aladdin Chemical Co. Ltd. NaH$_2$PO$_4$·2H$_2$O and Na$_2$HPO$_4$·12H$_2$O were purchased from Tianjin Fuchen Chemical Reagent Factory. Phosphate buffered saline solution (PBS) was prepared with 10 mM NaH$_2$PO$_4$-Na$_2$HPO$_4$. Sodium chloride (NaCl), sodium sulfate (Na$_2$SO$_4$), sodium nitrate (NaNO$_3$), sodium hypochlorite (NaClO), potassium fluoride (KF), potassium bromide (KBr), silver nitrate (AgNO$_3$), aluminium chloride (AlCl$_3$), magnesium chloride (MgCl$_2$), barium chloride (BaCl$_2$), chromium trichloride (CrCl$_3$), nickel chloride (NiCl$_2$) and ferrous chloride (FeCl$_2$) were received from Tianjin Kemiou Chemical Reagent Co., Ltd. Potassium dichromate (K$_2$Cr$_2$O$_7$) was purchased from Shanghai Lingfeng Chemical Co. Ltd. All reagents were analytical grade and used without further purification. Deionized water was used throughout the experiment.

**Apparatus and characterization**

Transmission electron microscopy (TEM) image of the SiNPs were obtained using a Tecnai G2F30 instrument. A drop of the SiNPs solution was placed on a copper grid coated with a thin layer of amorphous carbon film and dried at room temperature for the TEM analysis. Powder X-ray diffraction (PXRD) patterns were performed on a D/max 82400 X-ray powder diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 0.154056 nm). Fourier transform infrared spectrum (FT-IR) was conducted on a Bruker Tensor II spectrometer using KBr pellets. X-ray photoelectron spectroscopy (XPS)
measurement was performed using an AXIS Supra photoelectron spectrometer. UV-Vis absorption spectra were recorded by an EVOLUTION 260 BIO UV-Vis spectrophotometer. The fluorescence lifetime and quantum yield of the SiNPs were measured by Edinburgh FLS1000 steady/transient fluorescence spectrometer. Fluorescence measurements were carried out using an F-7000 spectrofluorophotometer with both excitation and emission slits set at 5 nm. The excitation wavelength was set at 409 nm. Absorption and emission measurements were conducted in 1 cm × 1 cm quartz cuvette.

Pretreatment process of the practical samples of traditional Chinese herbs

The extraction process of emodin from Rheum officinale was as follows: Take 0.1 g of Rheum officinale powder, 25 mL chloroform and 20 mL 2.5mol/L sulfuric acid solution into a round-bottom flask, weighed, and then refluxed at 80 °C for 2 hours. After cooling to room temperature, the resulted solution was weighed again and then the weight loss was complemented with chloroform. 10 mL of the chloroform layer was evaporated and dried. The obtained residue was dissolved by 10 mL methanol and the solution was filtered. Finally, the filtrate was taken for testing.

The extraction process of Polygonum cuspidatum was similar to that of Rheum officinale. The details were as follows: Take 0.15 g of Polygonum cuspidatum powder and 25 mL of methanol solution into a round-bottom flask, weighed, and then refluxed at 75 °C for 1 hours. After cooling to room temperature, the resulted solution was weighed again and then the weight loss was complemented with methanol. The resulted solution was filtered and 5 mL of filtrate was evaporated and dried. The obtained
residue was dissolved by 10 mL of 8% hydrochloric acid solution. 2 mL of the above solution was mixed with 10 mL chloroform. The mixture solution was then refluxed at 90 °C for 1 hours. The acid layer was washed with chloroform (3×10 mL) and the resulted solution was combined with chloroform layer. Excess solvent was removed by evaporation. The obtained residue was dissolved by 10 mL methanol and the solution was filtered. Finally, the filtrate was taken for testing.
Figure S1 Normalized FL intensity of the SiNPs synthesized at different reaction temperature (A), different reaction time (B) and different weight of ferulic acid (C); The fluorescence emission spectra of the materials prepared by the reaction of only APTES, only ferulic acid, and APTES+ferulic acid under the same conditions (D).
**Figure S2** FL intensity of the prepared SiNPs at different excitation wavelengths.
Figure S3 The fluorescence emission spectra of the SiNPs under different temperature (A), pH (B) and concentration of NaCl (C).
Figure S4 (A) Normalized FL intensity of the SiNPs (black bars) and the subsequent addition of 20 μM emodin (red bars) at different pH values. (B) Time-dependent FL intensity of the SiNPs with the addition of emodin (20 μM) at room temperature.
Figure S5 (A) Photographs of the mixture solution of SiNPs mixed with 20 μM emodin or other different interfering substances (from left to right: 1. emodin, 2. gallic acid, 3. PA, 4. quercetin, 5. chrysophanol, 6. baicalin, 7. berberine, 8. physcion, and 9. polygonin); (B) Photographs of the mixture solution of SiNPs, mixed with 20 μM emodin and other interfering substances (from left to right: 1. blank, 2. gallic acid, 3. PA, 4. quercetin, 5. chrysophanol, 6. baicalin, 7. berberine, 8. physcion, and 9. polygonin). The concentration of emodin was 20 μM; the concentration of each interfering substance was 40 μM.
Figure S6 Zeta potentials of the SiNPs, emodin and the mixtures of the SiNPs and emodin in a pH 7.0 PBS solution.
Figure S7 Optimized structures of APTES (A), ferulic acid (B), emodin (C) and the corresponding HB complexes and their relative Gibbs free energies. Distances were in Å. The Gibbs free energies of A, B and C were set to 0.0 kcal/mol as references.
Figure S8 Time-resolved decay curves of the SiNPs in the absence and presence of emodin.
Figure S9 $F_0/F$ of the SiNPs as a function of the concentration of emodin.
**Figure S10** High performance liquid chromatography of (A) Polygonum cuspidatum, emodin and methanol blank solvent; (B) Rheum officinale, emodin and methanol blank solvent (Detection conditions: mobile phase: methanol~0.1% phosphoric acid water (85:15), flow rate: 1.0 mL/min, column temperature: 30 °C, detection wavelength: 254 nm).
Table S1 Influence of different emodin concentrations on fluorescence lifetime of the SiNPs.

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<thead>
<tr>
<th>Concentration of emodin (µM)</th>
<th>Fluorescence lifetime (ns)</th>
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<tbody>
<tr>
<td>0</td>
<td>8.83</td>
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<tr>
<td>5</td>
<td>8.93</td>
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<td>20</td>
<td>8.86</td>
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<td>50</td>
<td>8.82</td>
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Table S2 Determination of emodin in Rheum officinale and Polygonum cuspidatum with different methods.

<table>
<thead>
<tr>
<th></th>
<th>Rheum officinale (mg/g)</th>
<th>Polygonum cuspidatum (mg/g)</th>
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<tbody>
<tr>
<td>This work</td>
<td>9.83±0.12</td>
<td>4.40±0.07</td>
</tr>
<tr>
<td>HPLC</td>
<td>9.68±0.11</td>
<td>4.76±0.01</td>
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