Supporting Information for

Green emitting silicon nanoparticles as a fluorescent probe for highly sensitive crocin detection and pH sensing

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Reagents and materials

N-[3-(trimethoxysilyl)propyl]-ethylenediamine (DAMO), crocin, 4,6-diaminoresorcinol dihydrochloride, gallic acid, protocatechuic acid (PA), geniposide, magnolol, naringin, ferulic acid, urea, glucose, maltose, crocitin, L-methionine (L-Met), L-cysteine (L-Cys), L-arginine (L-Arg), L-threonine (L-Thr) and L-isoleucine (L-Ile) were purchased from Aladdin Reagent Co., Ltd. $NaH_2PO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ were purchased in Tianjin Fuchen Chemical Reagent Factory. Phosphate buffered saline solution (PBS) was prepared with 100 mM NaH_2PO_4-Na_2HPO_4. Cobalt chloride ($CoCl_2$), sodium chloride (NaCl), nickel chloride ($NiCl_2$), silver nitrate ($AgNO_3$), lead nitrate ($Pb(NO_3)_2$), sodium perchlorate ($NaClO_4$), potassium fluoride (KF), potassium oxalate ($K_2C_2O_4 \cdot H_2O$) and potassium iodide (KI) were obtained from Tianjin Kemio Chemical Reagent Co., Ltd. Anhydrous aluminum chloride ($AlCl_3$) was purchased from Tianjin FengChuan Chemical Reagent Technology Co., Ltd. Anhydrous ethanol was purchased from Zhengzhou Penny Chemical Reagent Co., Ltd. The reagents used in the high performance liquid chromatography (HPLC) experiment are chromatographic pure and purchased from Tianjin Siyou Chemical Co., Ltd. All other chemical reagents are analytical grade reagents, which can be directly used without further purification. Deionized water was used throughout the experiment.

Apparatus and characterization

The morphology and particle size of the SiNPs were characterized by JEOL JEM-2100F transmission electron microscopy (TEM). Fourier transform infrared spectroscopy (FT-IR) was recorded by a Bruker Tensor II spectrometer. X-ray photoelectron spectroscopy (XPS) was measured by an AXIS Supra photoelectron spectrometer. X-Ray Diffraction (XRD) pattern was obtained by D/max 82400 X-ray powder diffractometer (Rigaku, Japan) with Cu Kα radiation (λ= 0.154056 nm). Ultraviolet visible absorption spectrum (UV-Vis) was measured by ultraviolet visible spectrophotometer (Thermo evolution 260 bio). Time-dependent single photon counting was performed by FLS1000 steady-state/transient spectrometer (TCSPC) system was used to measure the fluorescence lifetime and quantum yield. Malvern Zetasizer Nano ZS90 nano particle size and Zeta potential analyzer were used to perform the measurements of zeta potential of the synthesized SiNPs. Fluorescence measurements were carried out using an F-7000 spectrofluorophotometer with both excitation and emission slits set at 5 nm, the excitation wavelength was 437 nm and emission wavelength was 513 nm. HPLC analysis was performed on a Thermo Scientific U-3000 chromatographic system.

Calculation of pK_a value of the SiNPs

The SiNPs are assumed to be monoacid. The SiNPs are all in the forms of molecule (HB) and ion (B^-) under high acidity and alkaline conditions, respectively. Firstly, a series of SiNPs solutions with different pH values (3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10) were prepared. Then, the FL intensity of the above solutions

was detected. A linear relationship between $lg\frac{I_{HB}^{0}-I}{I-I_{B^-}^{0}}$ and pH was observed.

$$pK_a = -lg\frac{I_{HB}^{0}-I}{I-I_{B^-}^{0}} + pH$$

I^0_{HB} represents the FL intensity of the SiNPs under high acidity conditions. $I^0_{B^-}$ represents the FL intensity of the SiNPs under high alkaline conditions. I represents the FL intensity of SiNPs under different pH conditions.

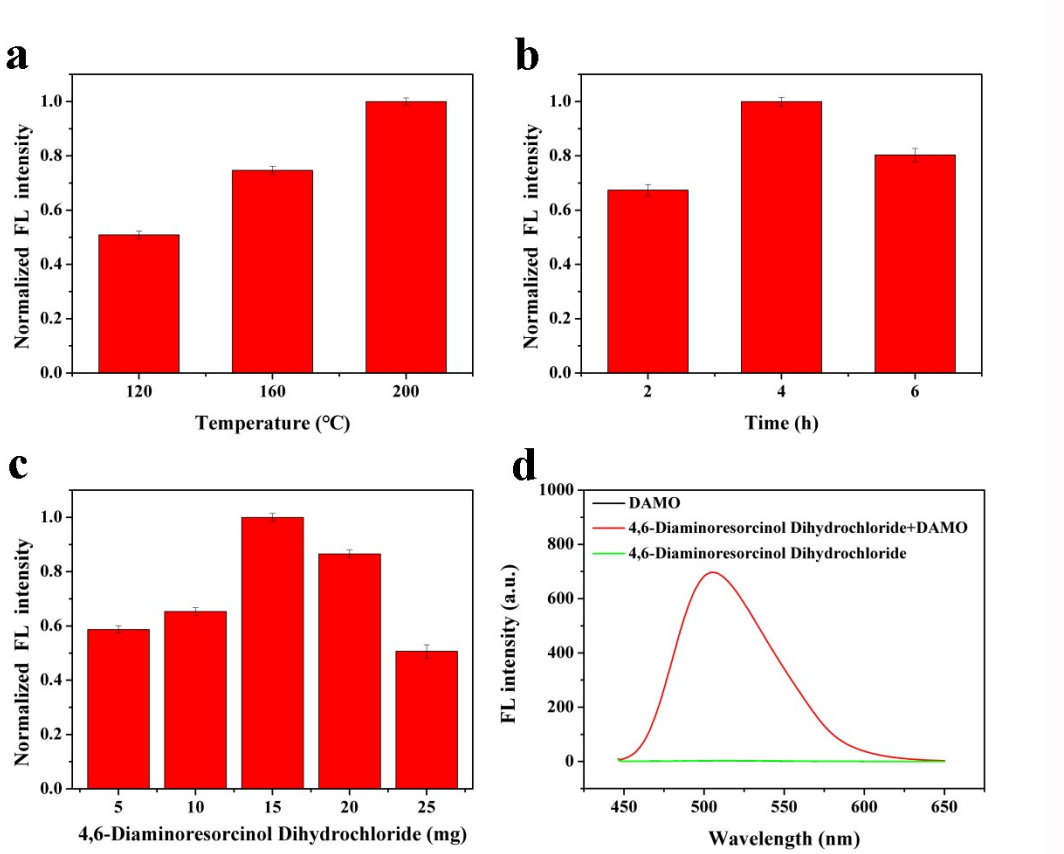
HPLC detection of gardenia yellow pigment

To validate the accuracy of the SiNPs-based fluorescence method for gardenia yellow pigment detection in traditional Chinese herb samples, HPLC analysis was performed. The separation was performed on a Venusil XBP-C_{18} column (4.6×250 mm, 5 μm). The conditions for detection of crocin by HPLC was as follows: mobile phase: acetonitrile (A) and water (B), elution mode: gradient elution (0~10 min: 22 ~ 30 A), flow rate: 1.0 mL/min, column temperature: 30 ℃, detection wavelength: 440 nm, injection volume: 5 μL. A series of crocin standard solutions of 0.03 mg/mL, 0.06 mg/mL, 0.120 mg/mL, 0.240 mg/mL and 0.480 mg/mL were prepared. The working curve was drawn with the concentration of crocin and chromatographic peak area. The gardenia yellow pigment content of three traditional Chinese herb samples was detected under the above detection conditions. And recovery experiments were also performed to further validate the accuracy of the HPLC method.

Preparation of fluorescent paper sensor

In order to detect crocin more conveniently, a paper sensor based on the SiNPs was established. The fabrication process of the paper sensor was as follows: Firstly,

the qualitative filter paper was immersed into SiNPs solution for 20 min, then it was taken out and dried in an oven at 50 ºC. After cooling to room temperature, the qualitative filter paper was cut into strips as fluorescent paper sensor. 10 μL of different concentrations of crocin solution was added to the obtained filter paper strips. After the solvent was naturally evaporated at room temperature, the filter paper strips were observed under sunlight and 365 nm ultraviolet lamp.



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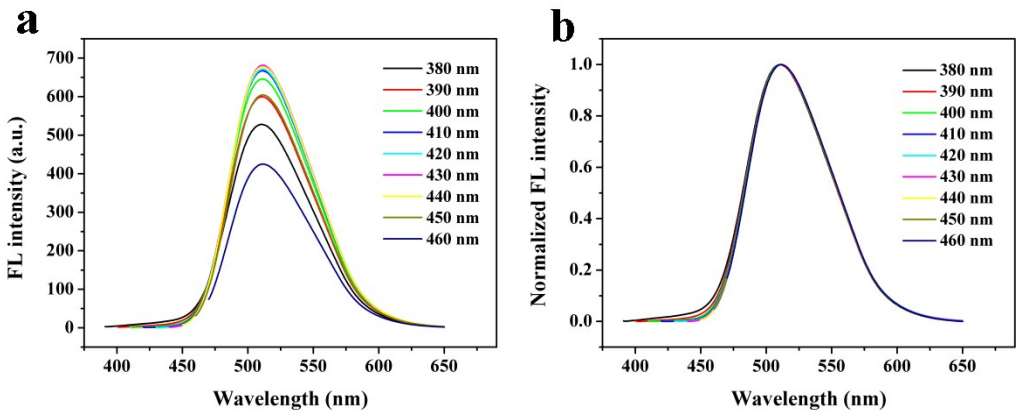
88 **Fig. S1** Normalized FL intensity of the SiNPs synthesized at different reaction

89 temperature (a), different reaction time (b) and different dosage of reducing agent (c).

90 The fluorescence emission spectra of the materials prepared by the reaction of only

91 DAMO, only 4,6-diaminoresorcinol dihydrochloride, DAMO+ 4,6-diaminoresorcinol

92 dihydrochloride under the same conditions (d).



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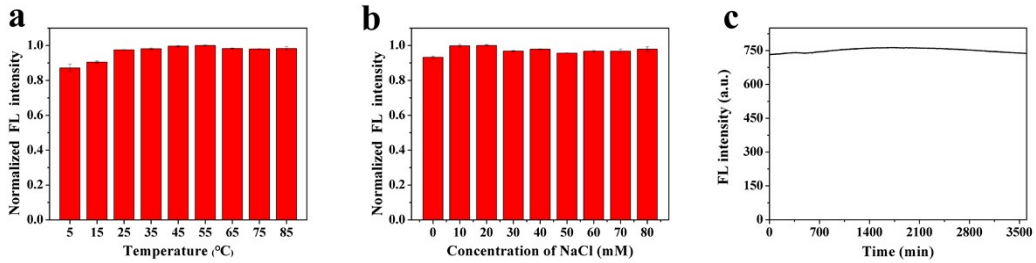
94 **Fig. S2** FL intensity (a), and normalized FL intensity (b) of the prepared SiNPs at

95 different excitation wavelengths.



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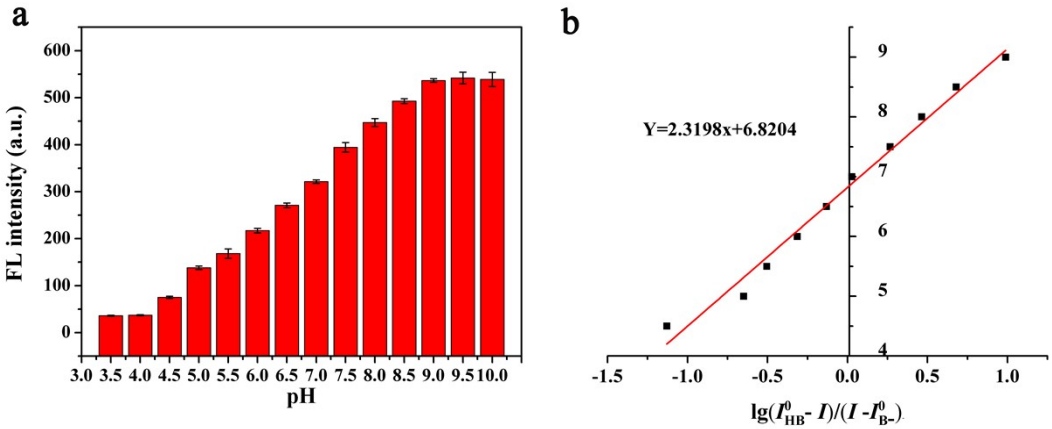
97 **Fig. S3** (a) Normalized FL intensity of the SiNPs after incubation at different
98 temperatures for 10 min; (b) Normalized FL intensity of the SiNPs in NaCl solution
99 of different concentrations; (c) The FL intensity variation tendency of the SiNPs as a
100 function of time under 437 nm light illumination. The error bar is the standard
101 deviation of three independent experiments.



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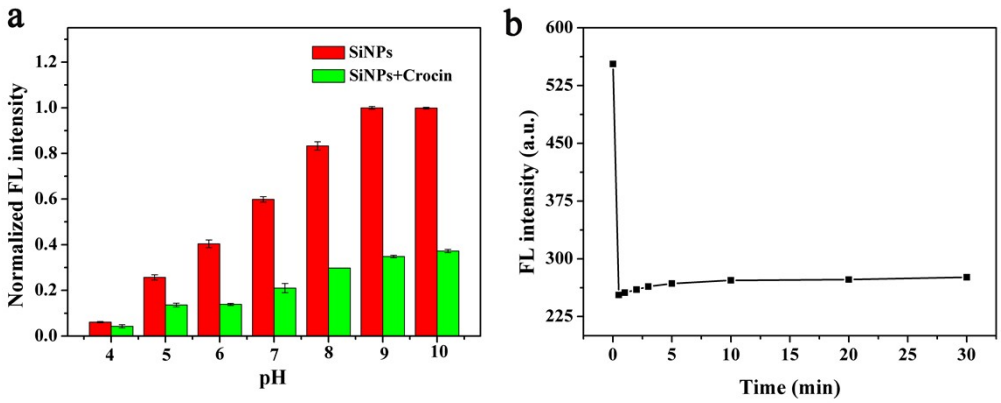
103 **Fig. S4** (a) FL intensity of the SiNPs incubated in 100 mM PBS with different pH

104 values. (b) $lg\frac{I_{HB}^{0}-I}{I-I_{B^-}^{0}}$ as a function of the pH.



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106 **Fig. S5** (a) Normalized FL intensity of the SiNPs (red bars) and the subsequent

107 addition of 10 μM crocin (green bars) at different pH values. (b) Time-dependent FL

108 intensity of the SiNPs with the addition of crocin (10 μM) at room temperature.

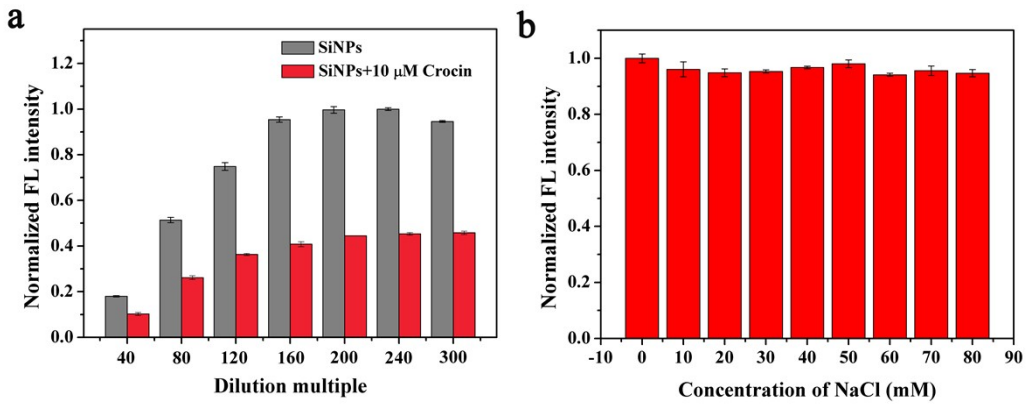
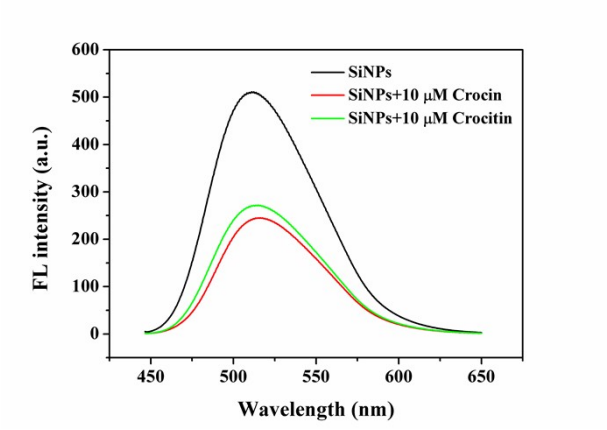


Fig. S6 (a) Normalized FL intensity of the SiNPs with different dilution multiple (gray bars) and the subsequent addition of 10 μM crocin (red bars). (b) Normalized FL intensity of the mixture of SiNPs and 10 μM crocin in the presence of different concentrations of NaCl.



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115 **Fig. S7** Fluorescence responses of the SiNPs upon addition of 10 μM crocin and

116 crocitin in a 100 mM pH 9.0 PBS solution, respectively.

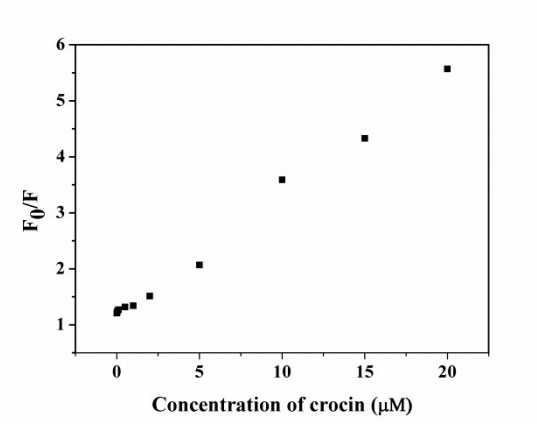


Fig. S8 F_0/F of the SiNPs as a function of the concentration of crocin.

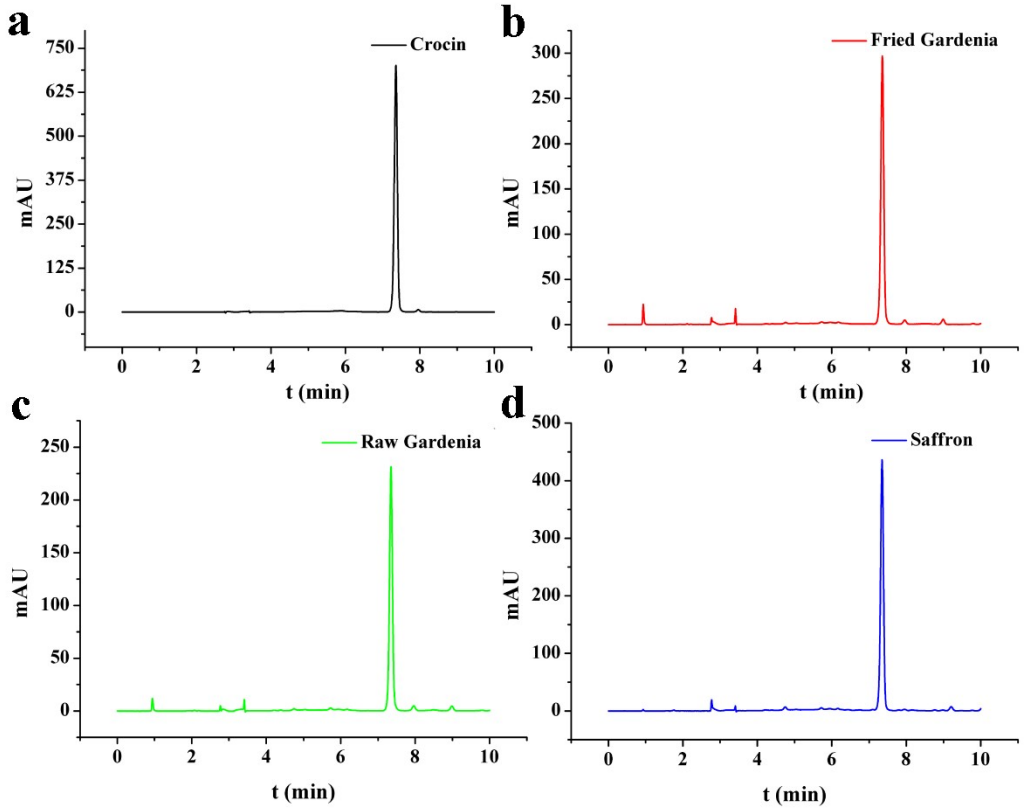
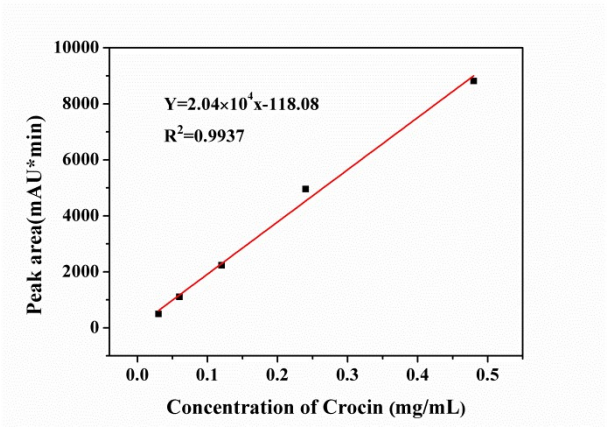


Fig. S9 HPLC chromatograms of crocin standard (a), raw gardenia (b) fried gardenia (c), and saffron (d); Detection conditions: mobile phase: acetonitrile (A) and water (B), elution mode: gradient elution (0 ~ 10 min: 22 ~ 30 A), flow rate: 1.0 mL/min, column temperature: 30 °C, detection wavelength: 440 nm).



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126 **Fig. S10** The linear relationship between peak area and crocin concentration in HPLC

127 method.

128 **Table S1** Comparison of methods for crocin detection.

Applied material	Method	Linear range	LOD	Ref.
-	RP-HPLC	0.86-27.54 mg·L^{-1}	0.42 mg·L^{-1}	6
-	HPLC- ESI-MS/MS	50-1000 ng/mL	0.02 μg/g	8
-	MEKC	5-100 μg·g^{-1}	0.2 μg·g^{-1}	9
Au	Electrochemical	0.99-9.09 μM	-	10
-	DLLME- UV-Vis	0.01-150 ng/mL	0.008 ng/mL	11
	DLLME-SFO- UV-Vis	0.01-150 ng/mL	0.005 ng/mL	
-	UV-Vis	5-100 mg·mL^{-1}	1.36 mg·mL^{-1}	12
SiNPs	Fluorescence	0.01-17 μM	3.3 nM	This work

129

Table S2 Influence of different crocin concentrations on fluorescence lifetime of SiNPs.

Concentration of crocin (μM)	Fluorescence lifetime (ns)
0	3.24
5	3.08
10	3.08
15	3.02

133 **Table S3** Determination of gardenia yellow pigment in raw gardenia, fried gardenia
134 and saffron by HPLC.

Sample	Original concentration (mg/mL)	Spiked concentration (mg/mL)	Measured concentration (mg/mL)	Recovery (%)	Average Recovery (%)	RSD (%, n=3)
Raw gardenia	0.066 (6.572 mg/g)	0.04600	0.11007	96.64	100.27	1.91
		0.04600	0.11169	100.17		
		0.04600	0.11195	100.73		
		0.04600	0.11257	102.08		
		0.04600	0.11232	101.54		
		0.04600	0.11184	100.48		
Fried gardenia	0.084 (8.371 mg/g)	0.08700	0.17017	99.96	100.13	0.19
		0.08700	0.17048	100.31		
		0.08700	0.17052	100.36		
		0.08700	0.17019	99.98		
		0.08700	0.17040	100.22		
		0.08700	0.17016	99.94		
Saffron	0.123 (122.764 mg/g)	0.11100	0.23408	100.38	100.06	0.26
		0.11100	0.23407	100.37		
		0.11100	0.23365	99.99		
		0.11100	0.23364	99.98		
		0.11100	0.23334	99.70		
		0.11100	0.23361	99.99		

135

Table S4 Determination of gardenia yellow pigment in raw gardenia, fried gardenia and saffron with different methods.

	Raw gardenia (mg/g)	Fried gardenia (mg/g)	Saffron (mg/g)
This work	6.534±0.226	8.420±0.295	122.727±1.018
HPLC	6.572±0.002	8.371±0.004	122.764±0.005