Supporting Information

Salicylideneanilines Encapsulated Mesoporous Silica Functionalized Gold Nanoparticles: A Low Temperature Calibrated Fluorescent Thermometer

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S1. Experimental section.

1.1 Reagent and chemicals:
Tetraethyl orthosilicate (TEOS), 1, 4-bis(triethoxysily)propane tetrasulfide (TESPTS), 4-aminobenzoic acid, and salicylaldehyde were procured from Chemical Reagent Company. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Mv = 5800) was purchased from Aldrich. All of the reagents and solvents were of analytical reagent grade and used as received.

1.2 Preparation of 4-(2-hydroxybenzylideneamino)benzoic acid (HBA).
4-(2-hydroxybenzylideneamino)benzoic acid (HBA) were prepared according to a reported process with some modifications. [1] Briefly, 5.42 g (0.0396 mol) of 4-aminobenzoic acid was dissolved in 120 mL of ethanol, and 4.83 g (0.0396 mol) of salicylaldehyde in 80 mL of ethanol was added rapidly under magnetically stirring. After several minutes, the final yellow product started to precipitate. The mixture was totally stirred 2 h at room temperature, and the precipitated solid was isolated by filtration through a glass frit. The product was washed with ethanol and dried in a vacuum oven at 313 K. 8.5 g (0.0353 mol, 89%) of yellow 4-(2-hydroxybenzyli-deneamino)benzoic acid was obtained. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 12.79 (br s, 1H), 8.98 (s, 1H), 8.01 (d, 2H), 7.68 (d, 1H), 7.47 (d, 2H), 7.42 (d, 1H), 6.99 (m, 2H). FTIR (KBr, cm^{-1}): ν = 1679 cm^{-1} (C=O aryl acid band), 1600 cm^{-1} (C=C aromatic valence), 1569 cm^{-1} (C=C aromatic valence), 1287 cm^{-1} (C-O band), 860 cm^{-1} (aromatic 1, 4-disubstitution), 751 cm^{-1} (aromatic 1, 2-disubstitution).

1.3 Preparation of gold nanoparticles intercalated into the walls of mesoporous silica (GMS).
Gold Nanoparticles intercalated into the walls of mesoporous silica (GMS) was prepared following the previously reported method. [2] In a typical procedure, GMS was synthesized by dissolving 10 g of P123 in 375 ml of a 2M HCl solution, subsequently, a mixture of 20.8 g of tetreaethyl orthosilicate (TEOS) and 0.4 g 1, 4-bis(triethoxysily)propane tetrasulfide was quickly added with vigorous magnetic stirring, then the pre-designated amounts of aqueous $HAuCl_4$ solution were added dropwise. The solution was stirred for 24 h at 313 K and then aged for 72 h at 373 K. The solid was filtered off, washed with water for three times and with ethanol for two times, dried at 373 K for 24 h and calcined at 773 K for 5 h.

1.4 In vitro cytotoxicity assay (MTT Assay).[3]
The assay was performed in triplicate in the following manner. MEF (mouse embryo fibroblast) cells were grown in 96-well plates at a density of approximately 10 000 cells per well and exposed to tested materials or other agents (final volume 0.2 ml per well). At the indicated times, 10 µl of 5 mg ml^{-1} MTT solution in PBS was added to each well and incubated for 4 hours. After removal of the medium, 150 µl of DMSO was added to each well to dissolve the formazan crystals. The absorbance at 540 nm was determined using a Biokinetics plate reader (Bio-Tek Instruments, Inc., Winooski, VT, USA). Triplicate wells were assayed for each condition and the standard deviation was determined. The relative cell viability was expressed as a percentage relative to the untreated control cells.

S2. Scherrer sizes of gold nanoparticles.
From the x-ray diffraction (XRD) pattern of GMS given in Figure S2, the mean size of the gold nanoparticle crystallites can be calculated from the Scherrer formula: $t = 0.9\lambda/B\cos(\theta)$. Where t is the average crystallite size (nm), λ is the wavelength of the x-ray source ($\lambda_{Cu\text{-}K\alpha}$ = 0.15418 nm), B is the full-width half-maximum (FWHM) of the diffraction peak, θ is the diffraction angle. From the Scherrer formula, the average size of gold nanoparticles can be calculated using the FWHM of the most intense (111) peak. For GMS, the average crystallite size was calculated to be 2.3 nm respectively.

S3. Quantum yield of HBA-GMS at different temperatures.[4]

Quantum yield of HBA-GMS at room temperature was measured on a spectrofluorometer equipped with an integrating sphere. Quantum yield of HBA-GMS at the low temperatures was determined by comparison with that at room temperature (*rt*), using the following equation:

$$\phi_x = \phi_{rt} \frac{\int f_x(\lambda) d\lambda}{\int f_{rt}(\lambda) d\lambda}$$

where ϕ_x, ϕ_{rt} is the fluorescence quantum yield at *x* K and *rt* respectively, and $f_x(\lambda)$, $f_{rt}(\lambda)$ is the fluorescence spectrum at *x* K and *rt*, respectively. This equation was based on the following assumptions: (1) The sample is excited at the same wavelength and with the same intensity both at a low and the room temperature, and (2) the absorbance at the excited wavelength was the same at both of the temperatures. HBA-GMS showed temperature-dependant luminescence with a very high quantum yield (Table S1) over a wide temperature range (8 to 298 K). This intense thermosensitive emission over a wide range conquers the limitation that high temperatures induced a low signal/noise ratio, thus suggesting that HBA-GMS was an excellent candidate for a reliable and absolute luminescent temperature sensor.

Table S1 Quantum yields of HBA-GMS at different temperatures.

T(K)	8	25	40	55	70	85	100	115	140	165	190	215	265	298
ϕ	0.76	0.72	0.69	0.66	0.62	0.59	0.56	0.52	0.46	0.39	0.33	0.28	0.22	0.20

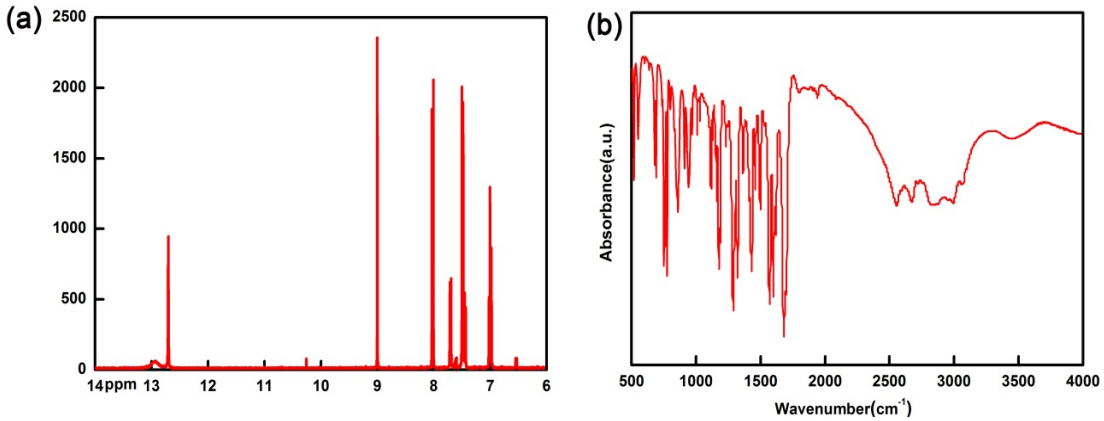

Figure S1. (a) 1H NMR spectrum of 4-(2-hydroxybenzylideneamino)benzoic acid (HBA). (b) FTIR spectra of HBA.

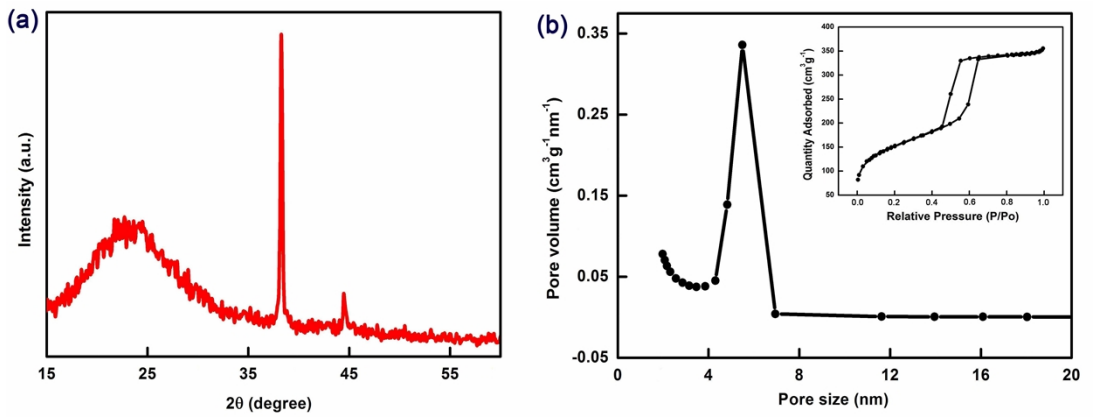

Figure S2. (a) XRD patterns of GMS. (b) Pore size distribution of GMS, which is calculated by Barrett-Joyner-Halenda (BJH) method according to the absorption branch of nitrogen adsorption/desorption isotherms.[5] Inset: The nitrogen adsorption/desorption isotherms at 77 K.

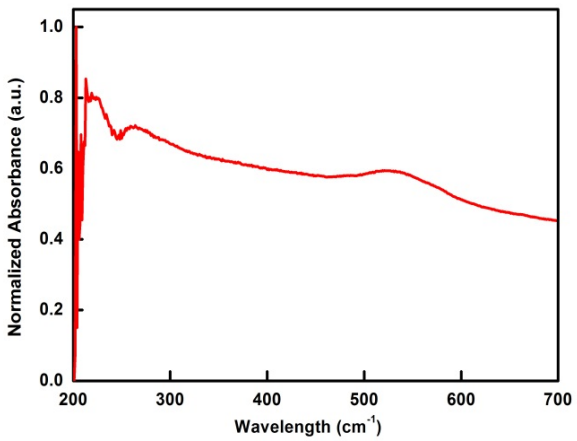

Figure S3. Absorption spectra of GMS at 298 K.

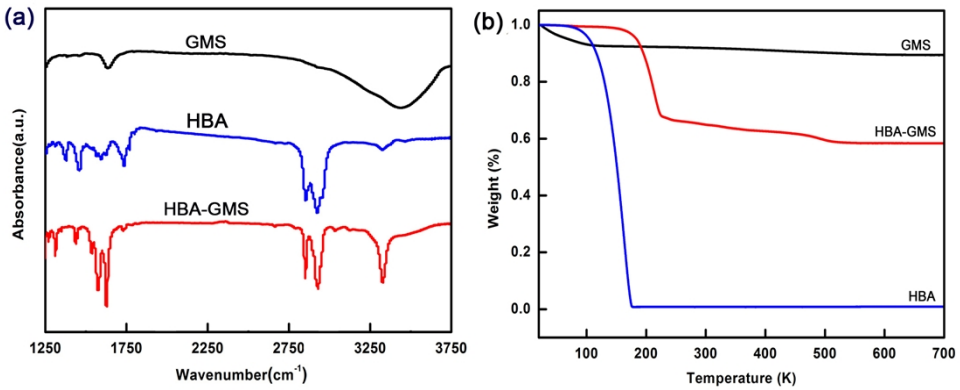

Figure S4. (a) FTIR spectra of GMS, HBA, and HBA-GMS. (b) Thermogravimetric Analysis (TGA) under air of GMS, HBA, and HBA-GMS. 2 mg HBA is mixed with 3 mg of GMS in aqueous solution at pH 7. The solution is stirred overnight and then the material is recovered by filtration on a Millipore system. The weight percentage of HBA is ~28 wt% for HBA-GMS.

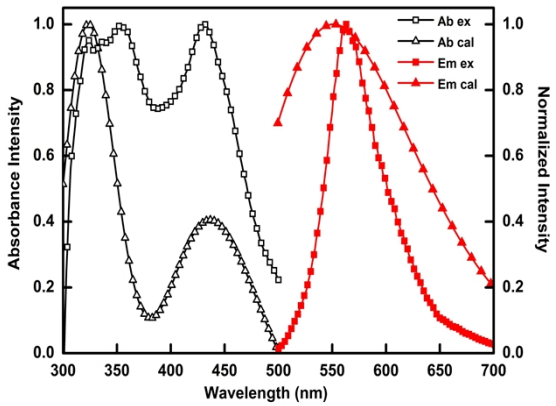

Figure S5. Measured absorption (hollow square) and emission (solid square) spectra of HBA; The calculated absorption (hollow triangle) and emission (solid triangle) spectra of HBA.

References

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