Supplementary Information

Modulated Fluorescence Properties in Fluorophore-contained Gold Nanorod@mSiO$_2$

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Experimental section

Materials

Chloroauric acid ($HAuCl_4{\cdot}3H_2O$), cetyltrimethyl ammonium bromide (CTAB), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$) and L-ascorbic acid (AA), were purchased from Fluka. Tetraethyoxysilane (TEOS), hydrochloric acid (HCl) solution and ammonium nitrate (NH_4NO_3) were obtained from Shanghai Chemical Reagents Company. Doxorubicin hydrochloride (DOX) was obtained from Huafeng United Technology Company (Beijing, P.R. China). Rhodamine 6G (R6G) was obtained from Acros Organics, hematoporphyrin dihydrochloride (HP) and fluorescein isothiocyanate (FITC) were obtained from Alfa Aesar. All the above chemicals were used without additional purification. Milli-Q water was used in all the experimental process.

Supplementary figures

Table S1 Particle size and size distribution of GNR and GNR@mSiO$_2$ with different thickness.

Sample	Hydrodynamic diameter / nm[a]	Size analyzed from TEM / nm
GNR	81.4	(54.0 ± 5.0) × (13.0 ± 1.5)
GNR@mSiO$_2$-14	113.2	(81.8 ± 5.0) × (40.8 ± 2.0)
GNR@mSiO$_2$-20	140.9	(94.4 ± 5.0) × (53.4 ± 2.5)
GNR@mSiO$_2$-29	188.9	(112.2 ± 5.0) × (71.2 ± 5.0)

a The diameter was determined at 25 ^{o}C by DLS.

Table S2 The quantum yield and enhancement factor for GNR@mSiO$_2$-20-DOX/HP.

Sample	QY[a]	Solvent	λ_{ex} / nm	FIEF[b]	QYEF[c]
pure DOX	3.3%	Water	480		
GNR@mSiO$_2$-20-DOX	8.0%	Water	480	2.5	2.4
pure HP	0.71%	Water	369		
GNR@mSiO$_2$-20-HP	1.8%	Water	369	2.8	2.5

a QY, quantum yield was determined by the equation (1).

b FIEF, fluorescence intensity enhancement factor.

c QYEF, quantum yield enhancement factor.

The quantum yield of Rhodamine 6G (R6G) in ethanol solution is 94.0% when excited at 488 nm. We used this sample as the control. DOX-, HP- loaded GNR@mSiO$_2$-20 at the concentration ratio of 200:1, GNR@mSiO$_2$-20 and pure DOX/ HP aqueous solution were prepared to measure the UV-vis spectra and fluorescence spectra. The concentration of all fluorophore was 0.833 μg/ mL. The relative fluorescence quantum yield of GNR@mSiO$_2$-fluorophores (Table S3) was calculated through the absorbance at the excitation and the intensity of luminescence emission by using the equation (1) [1-3].

$$QY_S = QY_R \frac{I_S A_R n_S^2}{I_R A_S n_R^2} \quad (1)$$

QY: Quantum yield, S: sample, R: standard substance, I: Intensity of luminescence emission, A: absorbance at the excitation, n: refractive index, n_{H2O}=1.33, $n_{ethanol}$= 1.36.

Table S3 The average length, width, aspect ratio and LSPRW of gold nanorods in Figure S2(a).

Sample	Average length/ nm	Average width/ nm	Aspect ratio	LSPRW/ nm
GNR-2.5	43.6 ± 5.5	17.4 ± 2.0	2.5 ± 0.5	731
GNR-2.9	45.8 ± 6.5	15.6 ± 2.5	2.9 ± 1.0	746
GNR-3.8	50.4 ± 5.5	13.5 ± 1.0	3.8 ± 1.0	786
GNR-4.0	55.8 ± 5.5	14.0 ± 1.5	4.0 ± 0.5	821
GNR-4.2	54.0 ± 5.0	13.0 ± 1.5	4.2 ± 0.5	843
GNR-4.6	60.7 ± 8.5	13.4 ± 1.5	4.6 ± 1.0	891

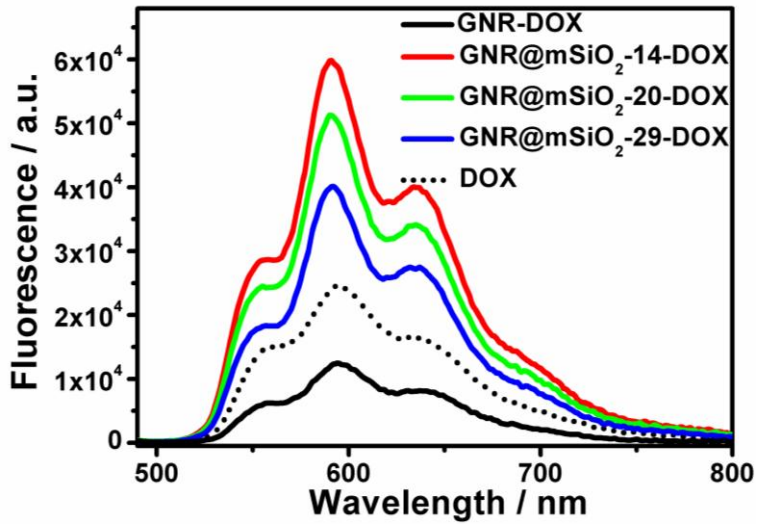

Figure S1. Stimulated at 480 nm, the fluorescence spectra of pure DOX, GNR-DOX and GNR@mSiO$_2$-DOX with different thicknesses at the concentration ratio of 100: 1.

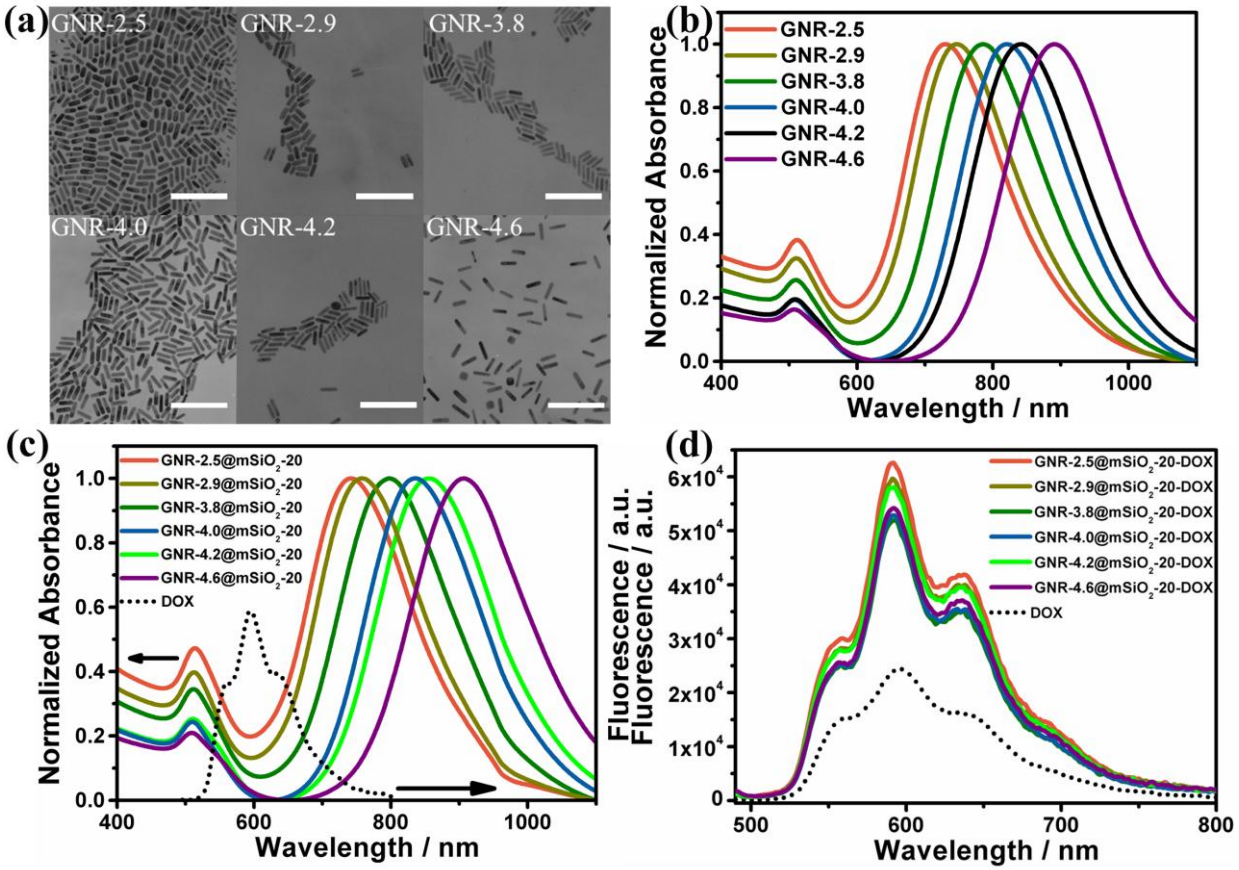

Figure S2. (a) Representative TEM images of GNRs with different aspect ratios, all scale bars represented 200 nm. (b) The UV-vis spectra of corresponding GNRs. (c) The absorption for GNR@mSiO$_2$-20 with different aspect ratios (solid line), the fluorescence spectra for pure DOX (dot line). (d) Stimulated at 480 nm, the fluorescence spectra of same thickness for different aspect ratios GNR@mSiO$_2$-20-DOX at the concentration ratio of 200: 1.

Figure S2a showed the representative TEM images of GNR-Y (Y meant the aspect ratio). Their shape also underwent a gradual transformation from peanuts to rods. As the average aspect ratio increased from 2.5 to 4.6, the LSPRW shifted from 731 to 891 nm (Figure S2b and Table S2). After coating ~20 nm mesoporous silica, the LSPRW of GNR-2.5 red shifted from 731 nm to 742 nm. In addition, the LSPRWs for GNR@mSiO_2-20 with the aspect ratio of 2.9, 3.8, 4.0, 4.2 and 4.6 were 757 nm, 797 nm, 835 nm, 859 nm and 907 nm, respectively (Figure S2c).

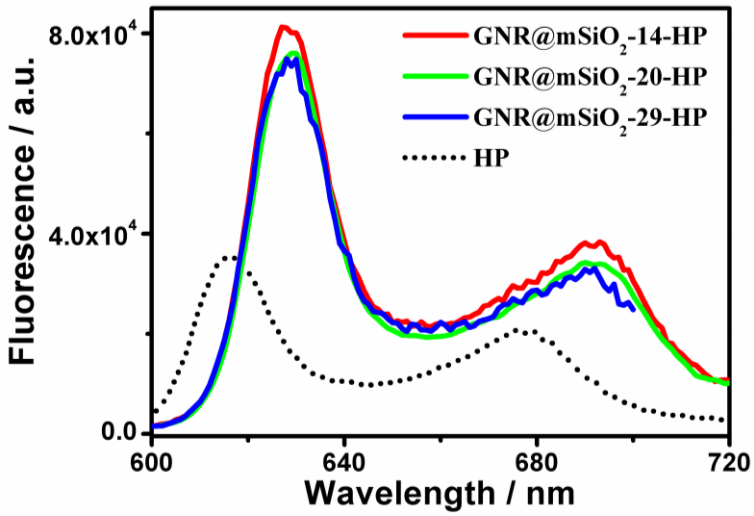

Figure S3. Stimulated at 369 nm, the fluorescence spectra of pure HP and GNR@mSiO_2-HP with different thicknesses at the concentration ratio of 100: 1.

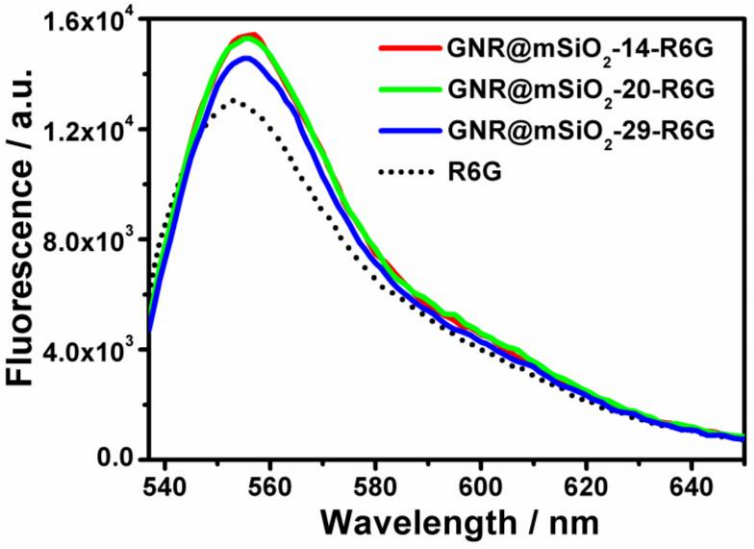

Figure S4. Stimulated at 527 nm, the fluorescence spectra of pure R6G and GNR@mSiO_2-R6G with different thicknesses at the concentration ratio of 100: 1.

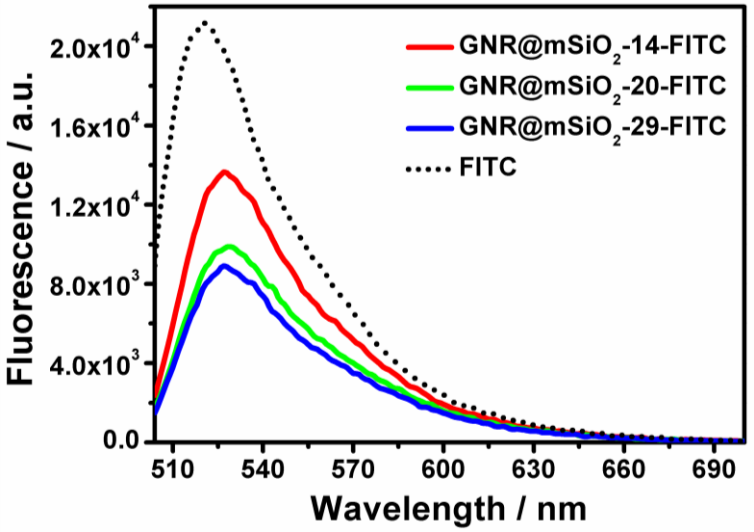

Figure S5. Stimulated at 494 nm, the fluorescence spectra of pure FITC and GNR@mSiO_2-FITC with different thicknesses at the concentration ratio of 100: 1.

References:

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