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Dispersity, mesoporous structure and particle size modulation of hollow mesoporous silica nanoparticles with excellent adsorption performance

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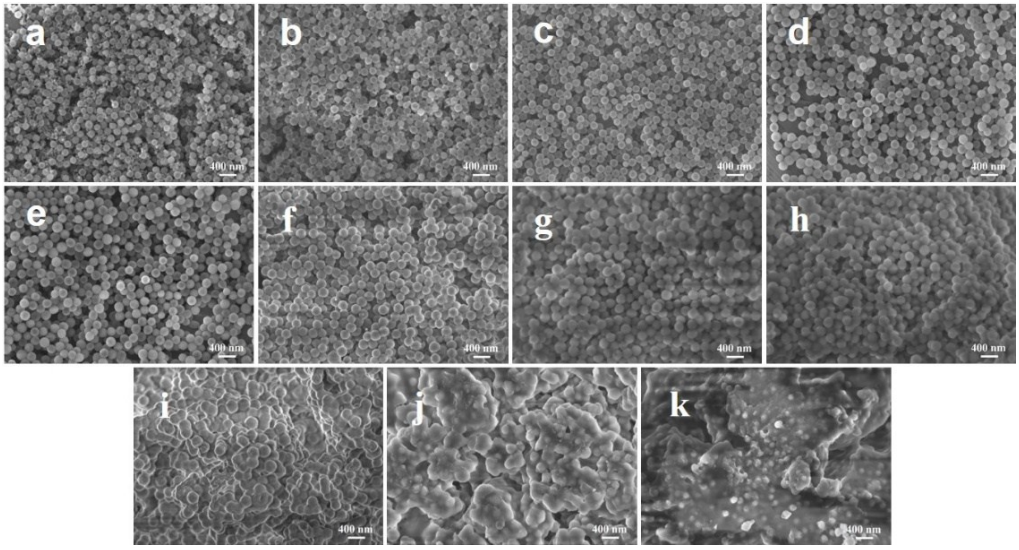

Figure S1 Low magnification SEM images of HMSNs-as-C_n (a: $C_{1.00}$, b: $C_{1.25}$, c: $C_{1.50}$, d: $C_{1.75}$, e: $C_{2.00}$, f: $C_{2.25}$, g: $C_{2.50}$, h: $C_{2.75}$, i: $C_{3.00}$, j: $C_{3.25}$ and k: $C_{3.50}$) obtained with the volume of core-etching agent as 100 mL and etching time as 0.5 h.

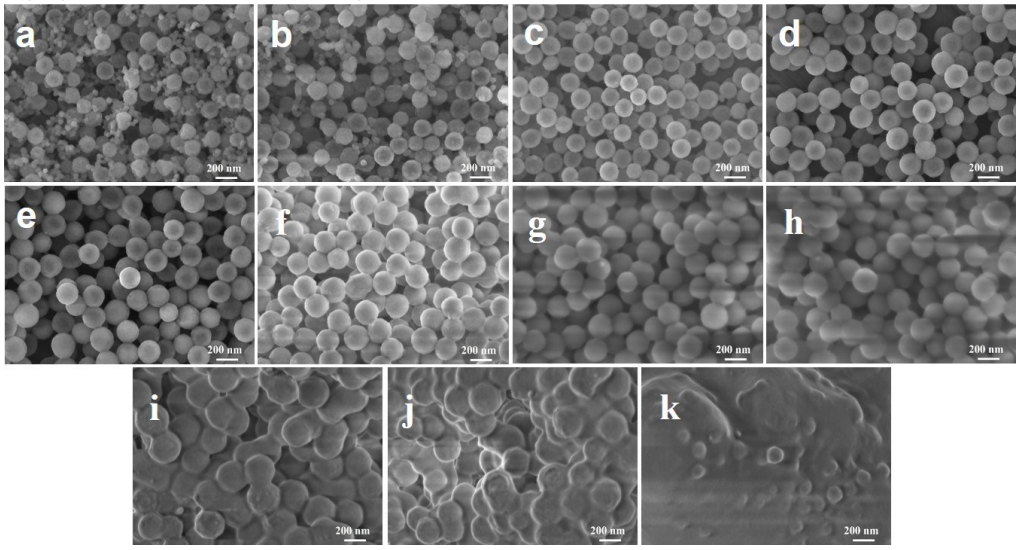

Figure S2 High magnification SEM images of HMSNs-as-C_n (a: $C_{1.00}$, b: $C_{1.25}$, c: $C_{1.50}$, d: $C_{1.75}$, e: $C_{2.00}$, f: $C_{2.25}$, g: $C_{2.50}$, h: $C_{2.75}$, i: $C_{3.00}$, j: $C_{3.25}$ and k: $C_{3.50}$) obtained with the volume of core-etching agent as 100 mL and etching time as 0.5 h.

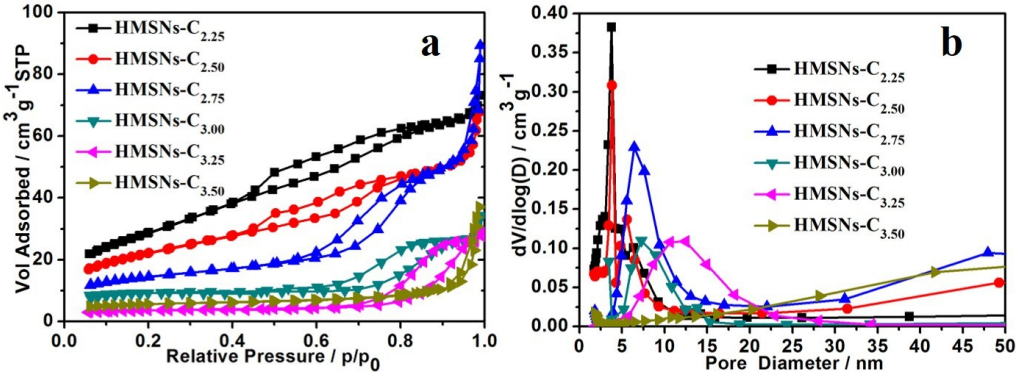

Figure S3 N_2 adsorption-desorption isotherms (a) and their corresponding pore size distributions (b) of HMSNs-C_n ($C_{2.25} \leq C_n \leq C_{3.50}$) obtained with the volume of core-etching agent as 100 mL and etching time as 0.5 h.

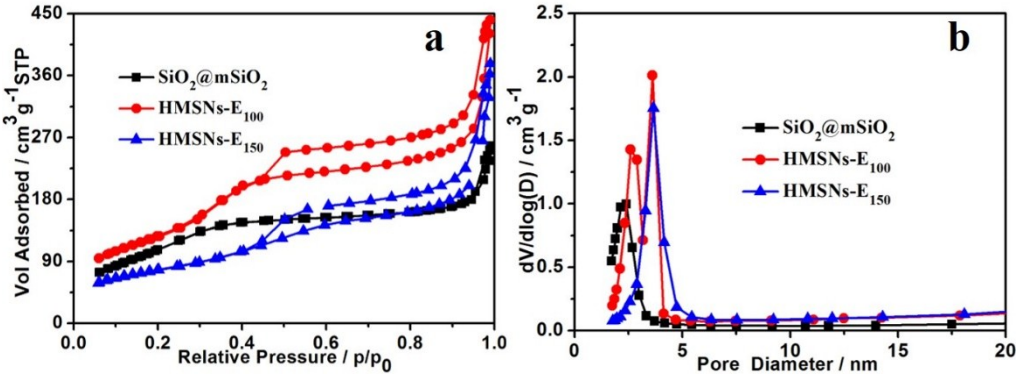

Figure S4 N_2 adsorption-desorption isotherms (a) and their corresponding pore size distributions (b) of SiO_2@mSiO_2, HMSNs-E_{100} and HMSNs-E_{150} obtained with the volume of C_{18}TMS as 1.50 mL and etching time as 0.5 h.

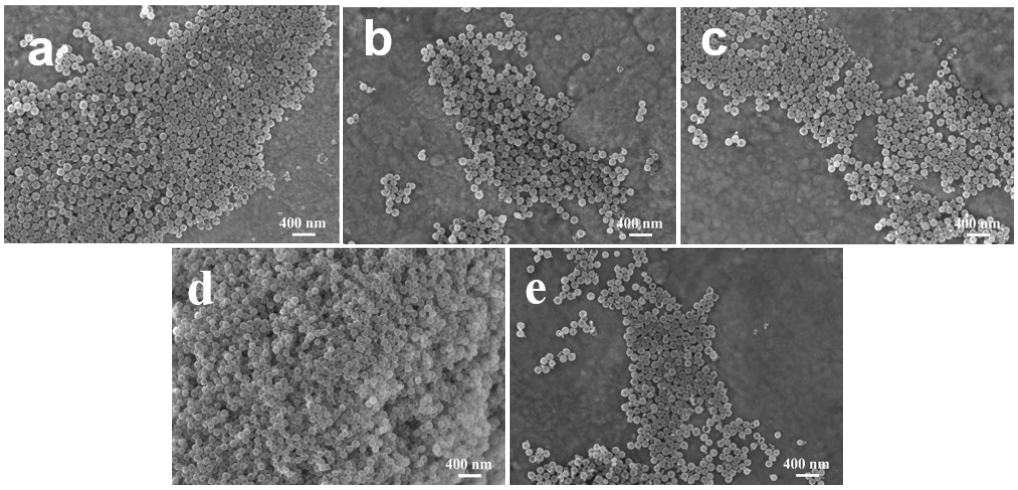

Figure S5 Low magnification SEM images of HMSNs-T_n (a: $T_{0.5}$, b: $T_{1.5}$, c: $T_{2.5}$, d: $T_{3.5}$ and e: $T_{4.5}$) obtained with the volume of C_{18}TMS and core-etching agent as 1.50 and 150 mL, respectively.

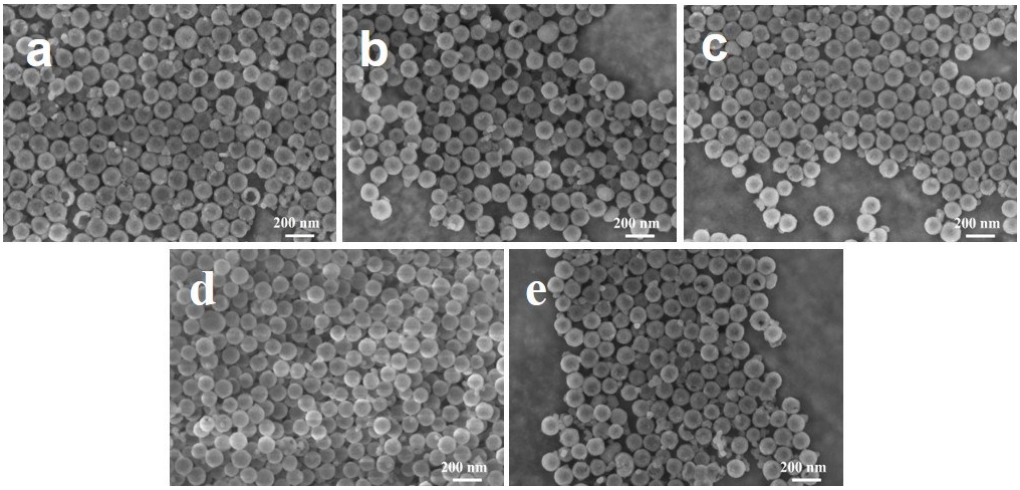

Figure S6 High magnification SEM images of HMSNs-T_n (a: $T_{0.5}$, b: $T_{1.5}$, c: $T_{2.5}$, d: $T_{3.5}$ and e: $T_{4.5}$) obtained with the volume of C_{18}TMS and core-etching agent as 1.50 and 150 mL, respectively.

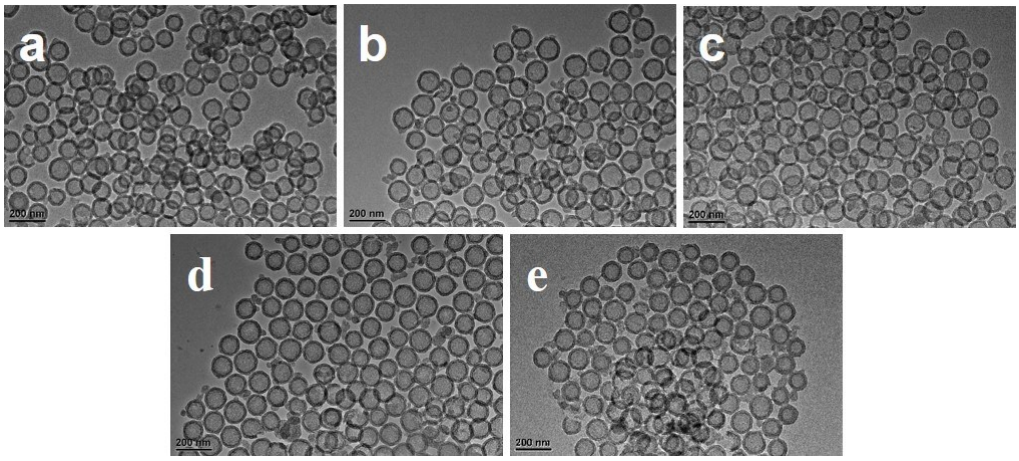

Figure S7 Low magnification TEM images of HMSNs-T_n (a: $T_{0.5}$, b: $T_{1.5}$, c: $T_{2.5}$, d: $T_{3.5}$ and e: $T_{4.5}$) obtained with the volume of C_{18}TMS and core-etching agent as 1.50 and 150 mL, respectively.

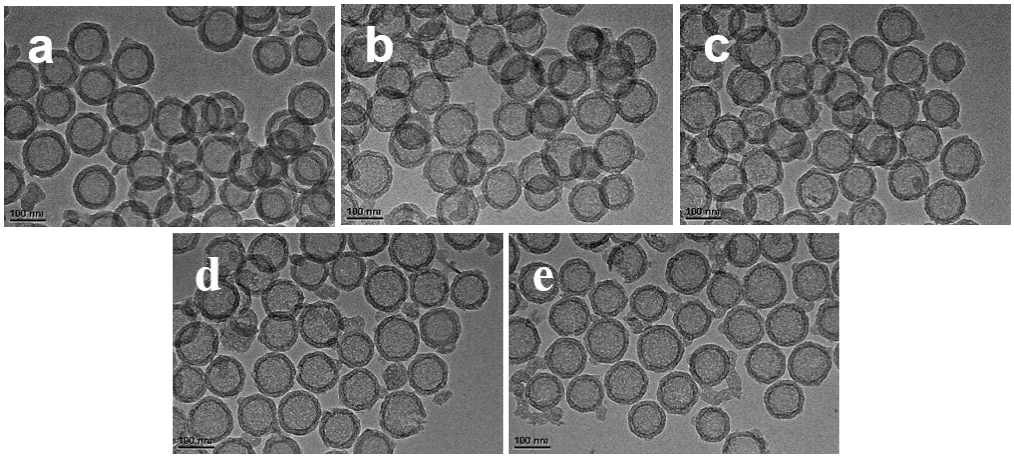

Figure S8 High magnification TEM images of HMSNs-T_n (a: $T_{0.5}$, b: $T_{1.5}$, c: $T_{2.5}$, d: $T_{3.5}$ and e: $T_{4.5}$) obtained with the volume of C_{18}TMS and core-etching agent as 1.50 and 150 mL, respectively.

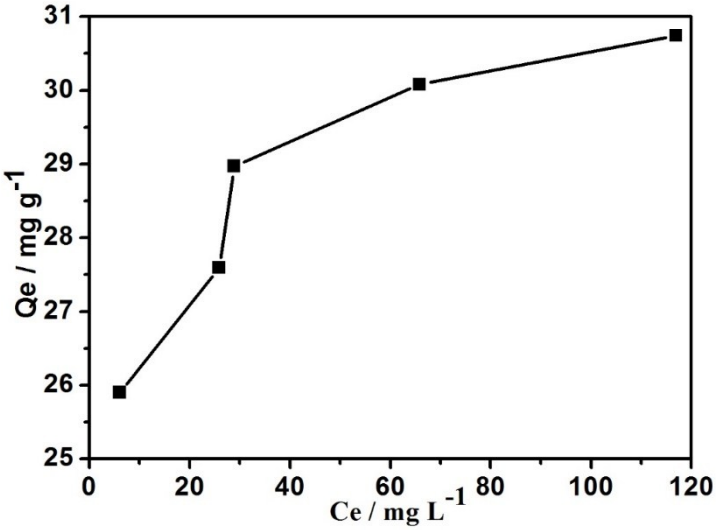

Figure S9 The adsorption isotherm of MB on HMSNs-$T_{1.5}$.

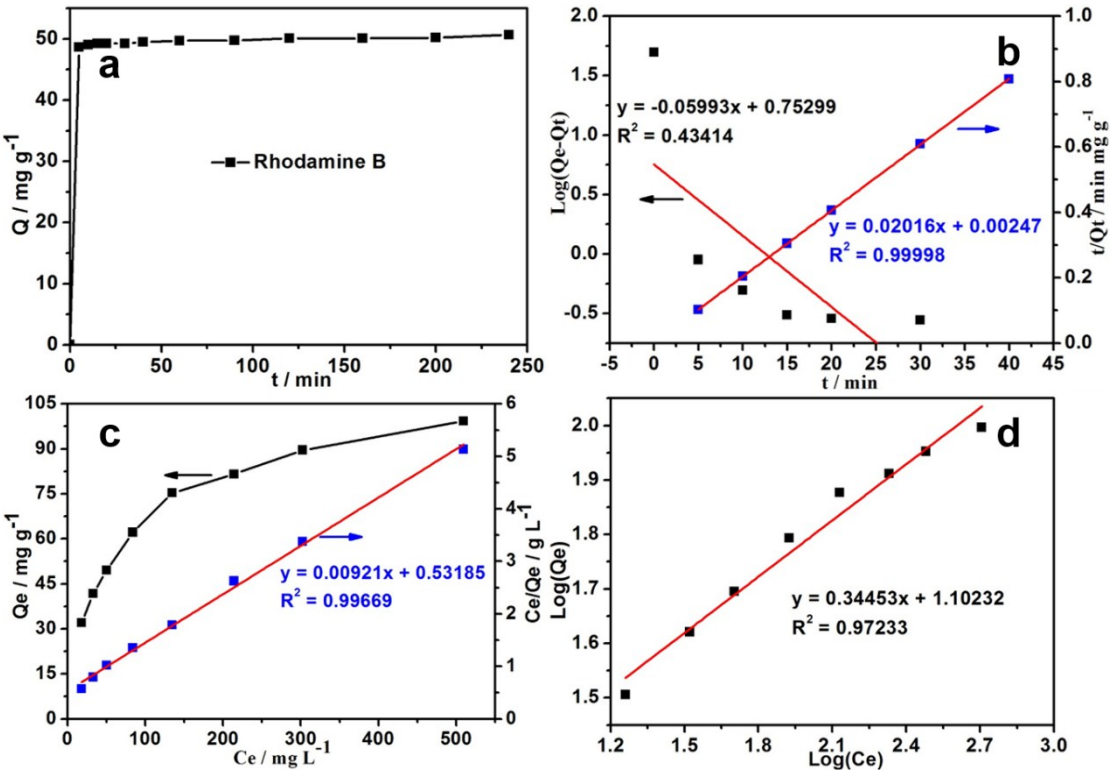

Figure S10 The adsorption kinetic curve of Rhodamine B (RB) on HMSNs-$T_{1.5}$ (a), kinetic data of RB adsorption on HMSNs-$T_{1.5}$ evaluated using pseudo-first-order model and pseudo-second-order model (b), adsorption isotherm and Langmuir isotherm of RB on HMSNs-$T_{1.5}$ (c) and Freundlich isotherm of RB on HMSNs-$T_{1.5}$ (d).

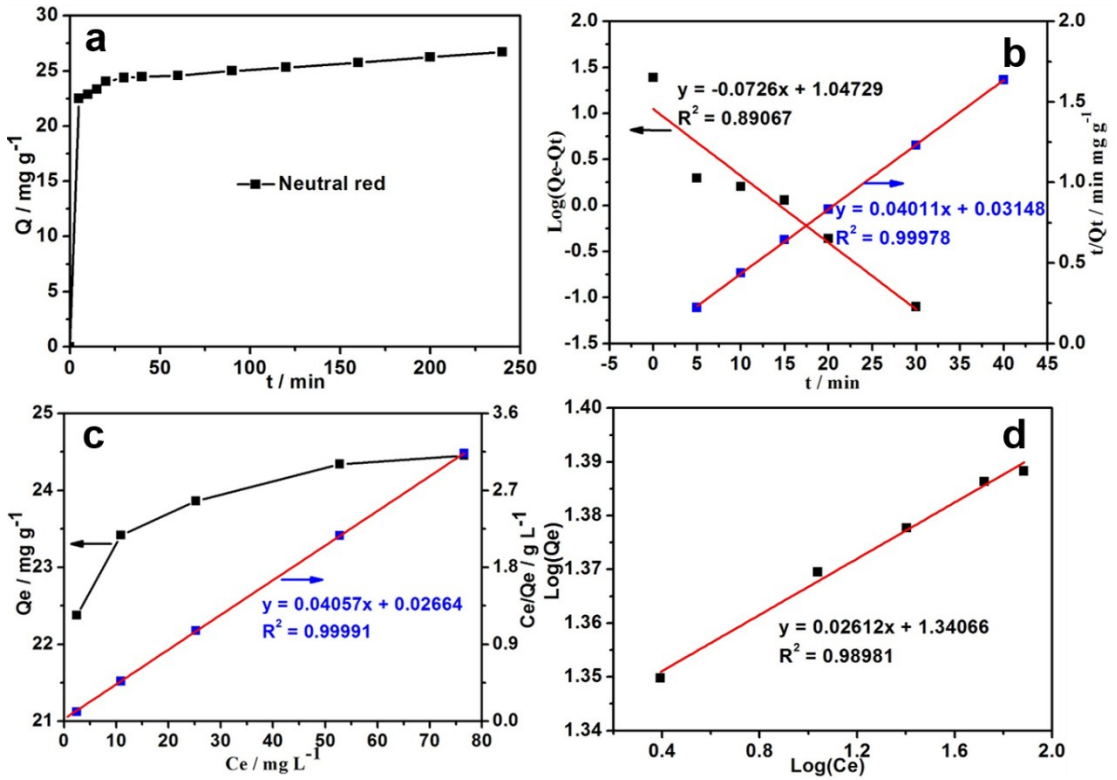

Figure S11 The adsorption kinetic curve of Neutral red (NR)on HMSNs-$T_{1.5}$ (a), kinetic data of NR adsorption on HMSNs-$T_{1.5}$ evaluated using pseudo-first-order model and pseudo-second-order model (b), adsorption isotherm and Langmuir isotherm of NR on HMSNs-$T_{1.5}$ (c) and Freundlich isotherm of NR on HMSNs-$T_{1.5}$ (d).

Table S1 Comparison between the reported representative synthetic methods for preparing HMSNs and our method.

Method	Characteristic	Advantages	Disadvantages
Soft-templating method	Micelle, vesicle or gas bubbles as the core template.[1]	The synthetic process is relatively simpler.	It is very difficult to control particle/pore size, morphology and dispersity of HMSNs at nanoscale.
Hard-templating method	Non-silicate particle (such as PS, PTBA and carbon spheres) as the core template.[2-4]	The core template and mesopore template can be removed at the same time by calcination[2-4] or even extraction.[2, 3]	It is time-consuming or expensive to obtain highly dispersed core template.
	SiO_2 nanoparticle as the core template, CTAB as the mesopore template.[5, 6]	The mesopore template CTAB can be removed by either calcination or extraction.[5, 6] The core template SiO_2 nanoparticle also works as the silica source for shell formation and don't need to be removed or the pore channels are aligned perpendicularly to the surface of HMSNs.[6]	The synthetic process is relatively complex and time-consuming.
	SiO_2 nanoparticle as the core template, C_{18}TMS as both the mesopore template and silica source (**our method**).	The synthetic process is simple. HMSNs with different dispersity, mesoporous structures and particle sizes can be obtained simply by changing C_{18}TMS percentage.	The core template and mesopore template can't be removed at the same time, and the mesopore template can only be removed by calcination.

Table S2 Experimental parameters and texture properties of HMSNs.

Sample	V_{C18TMS} (mL)	V_{Na2CO3} (mL)	$T_{etching}$ (h)	S_{BET} ($m^2 g^{-1}$)	V_{BJH} ($cm^3 g^{-1}$)	D_{BJH} (nm)
HMSNs-$C_{1.00}$	1.00	100	0.5	503	0.89	2.90
HMSNs-$C_{1.25}$	1.25	100	0.5	535	0.79	2.62, 3.66
HMSNs-$C_{1.50}$ (E_{100})	1.50	100	0.5	466	0.68	2.62, 3.60
HMSNs-$C_{1.75}$	1.75	100	0.5	238	0.46	4.07
HMSNs-$C_{2.00}$	2.00	100	0.5	144	0.37	5.34
HMSNs-$C_{2.25}$	2.25	100	0.5	104	0.11	3.78
HMSNs-$C_{2.50}$	2.50	100	0.5	79.7	0.10	3.84, 5.60
HMSNs-$C_{2.75}$	2.75	100	0.5	51.3	0.14	6.41
HMSNs-$C_{3.00}$	3.00	100	0.5	32.7	0.05	7.28
HMSNs-$C_{3.25}$	3.25	100	0.5	12.8	0.04	11.54
HMSNs-$C_{3.50}$	3.50	100	0.5	19.9	0.06	~
SiO_2@mSiO_2-$C_{1.50}$	1.50	0	0	403	0.40	2.34
HMSNs-E_{150} ($T_{0.5}$)	1.50	150	0.5	282	0.58	3.65
HMSNs-$T_{1.5}$	1.50	150	1.5	282	0.78	4.12
HMSNs-$T_{2.5}$	1.50	150	2.5	274	0.69	3.71
HMSNs-$T_{3.5}$	1.50	150	3.5	250	0.76	4.05
HMSNs-$T_{4.5}$	1.50	150	4.5	227	0.66	4.65

Table S3 Adsorption isotherm parameters by Langmuir and Freundlich models of RB on HMSNs-$T_{1.5}$.

Langmuir isotherm model				Freundlich isotherm model		
Q_m [mg g^{-1}]	K_L [L g^{-1}]	R_L (C_0 = 50 - 608 mg L^{-1})	R^2	K_F [mg g^{-1}]	1/n	R^2
108.6	0.01732	0.087 - 0.53	0.99669	12.66	0.34453	0.97233

Table S4 Adsorption isotherm parameters by Langmuir and Freundlich models of NR on HMSNs-$T_{1.5}$.

Langmuir isotherm model				Freundlich isotherm model		
Q_m [mg g^{-1}]	K_L [L g^{-1}]	R_L (C_0 = 25 - 100 mg L^{-1})	R^2	K_F [mg g^{-1}]	1/n	R^2
24.65	1.522	0.0065 - 0.026	0.999991	21.91	0.02612	0.98981

Table S5 Kinetic parameters of RB adsorption on HMSNs-$T_{1.5}$ by pseudo-first-order and pseudo-second-order models.

C_0 [mg L^{-1}]	Experimental Q_e [mg g^{-1}]	Pseudo-first-order			Pseudo-second-order		
		k_1 [min^{-1}]	Q_{1cal} [mg g^{-1}]	R^2	k_2 [g mg^{-1} min^{-1}]	Q_{2cal} [mg g^{-1}]	R^2
100	49.53	0.138	5.66	0.4341	0.164	49.60	0.99998

Table S6 Kinetic parameters of NR adsorption on HMSNs-$T_{1.5}$ by pseudo-first-order and pseudo-second-order models.

C_0 [mg L^{-1}]	Experimental Q_e [mg g^{-1}]	Pseudo-first-order			Pseudo-second-order		
		k_1 [min^{-1}]	Q_{1cal} [mg g^{-1}]	R^2	k_2 [g mg^{-1} min^{-1}]	Q_{2cal} [mg g^{-1}]	R^2
100	24.45	0.167	11.15	0.8907	0.0511	24.93	0.99978

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