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Supporting information

pH-responsive nanocontainer based on hydrazone- bearing hollow silica nanoparticles for targeting tumor therapy

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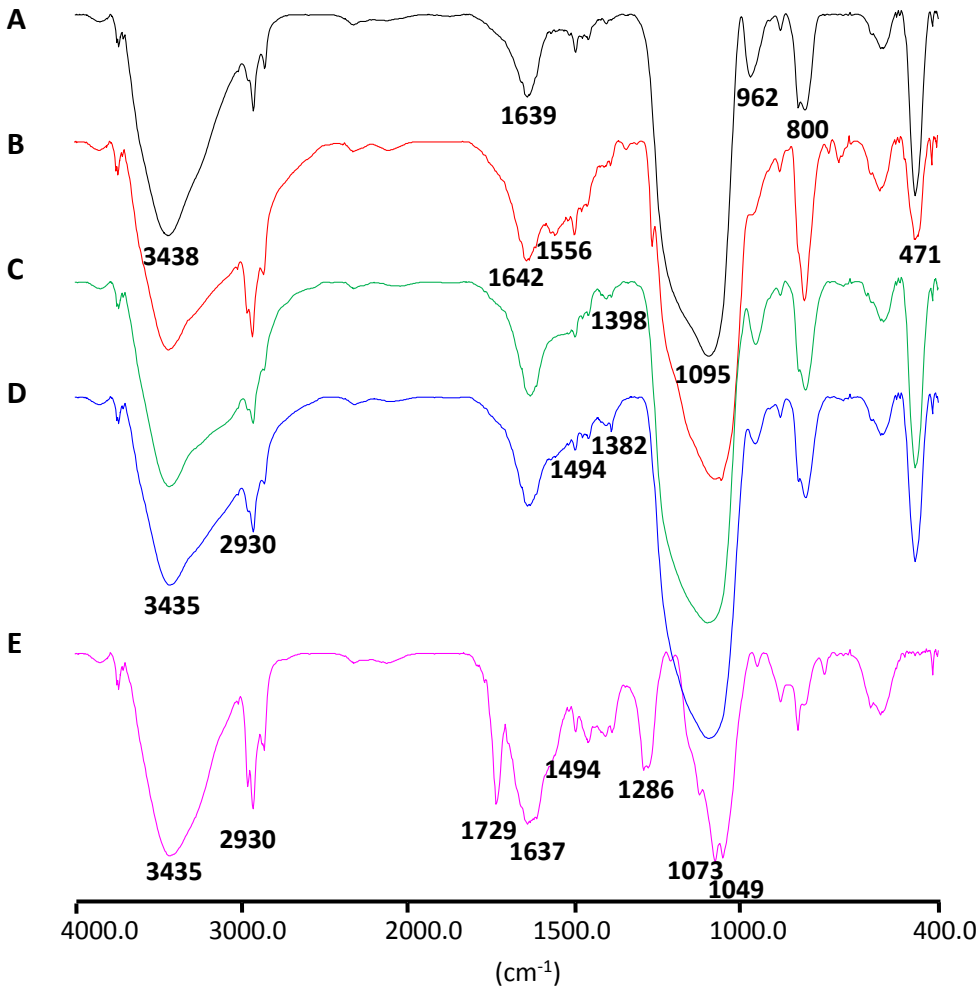

Figure S1. The FTIR spectra of HMSNs (a), HMSNs-NH_2 (b), HMSNs-PA (c), HMSNs-PA-HA (d), and HA-$NHNH_2$ (e), respectively.

As shown in Figure S1 a, the native HMSNs shows the intrinsic characteratic paeks, in which 471 cm^{-1} (Si-O bending), 800 cm^{-1} (Si-O-Si bending), 962 cm^{-1} (Si-OH bending) and 1090 cm^{-1} (Si-O stretching), respectively.[S1, S2] After modification with APTS, distinctive absorption peaks of $-NH_2$ (1642 cm^{-1} and 1556 cm^{-1}) were observed in the spectrum of HMSNs-NH_2 (Figure S1, b),[S2] suggesting the successful grafting of APTS to HMSNs. Following conjugation with PA molecules, the distinctive characteratic peak of $-CH_3$ at 1398 cm^{-1} appeared in the spectrum of HMSNs-PA (Figure S1, c). It was contributed to the succesful introduction of PA molecules. Meanwhile, functionlized HA molecular (HA-$NHNH_2$) shows a broad bond at 3435 cm^{-1} (O-H stretching), a shoulder peak at 2930 cm^{-1} (C-H stretching), and the distinctive absorption peak at 1729 cm^{-1} (C=O) in the spectra of HA-$NHNH_2$ (Figure S 1e). After HA-$NHNH_2$ was conjugated into HMSNs-PA, the producted HMSNs-PA-HA not only exhibit typical bonds at 3435 cm^{-1} (O-H) and 2930 cm^{-1} (C-H stretching) from HA, but also the similar absorption peaks with that of HMSNs-PA with slight shift, moreover, the carboxyl groups signals (1729 cm^{-1}) was disappeared (Figure S 1d), which was consistent with a previous study, [S3] suggesting that the HA was successful conjugated into HMSNs, in other words, HMSNs-PA-HA was successfully synthesized.

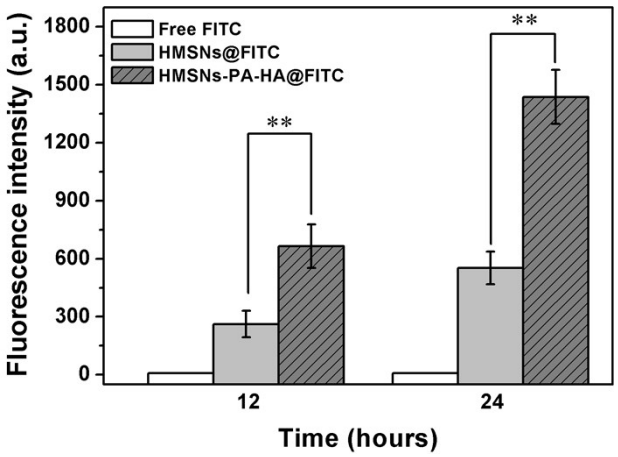

Figure S2. The quantification analysis of nanoparticles in HepG2 cells after treatments with FITC, HMSNs@FITC and HMSNs-PA-HA@FITC (0.12 mg/mL) for 12 and 24 h, respectively. Error bars represent means ± SD (n=4), **$p < 0.01$.

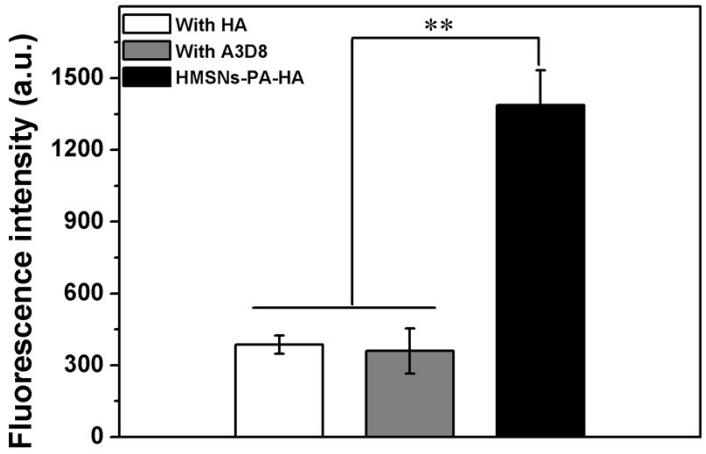

Figure S3. The quantification analysis of nanoparticles in HepG2 cells pretreated with HA, A3D8 or not for 2 h and then incubated with 0.12 mg/mL HMSNs-PA-HA@FITC at 37 °C for 4 h. Error bars represent means ± SD (n=4), **p < 0.01.

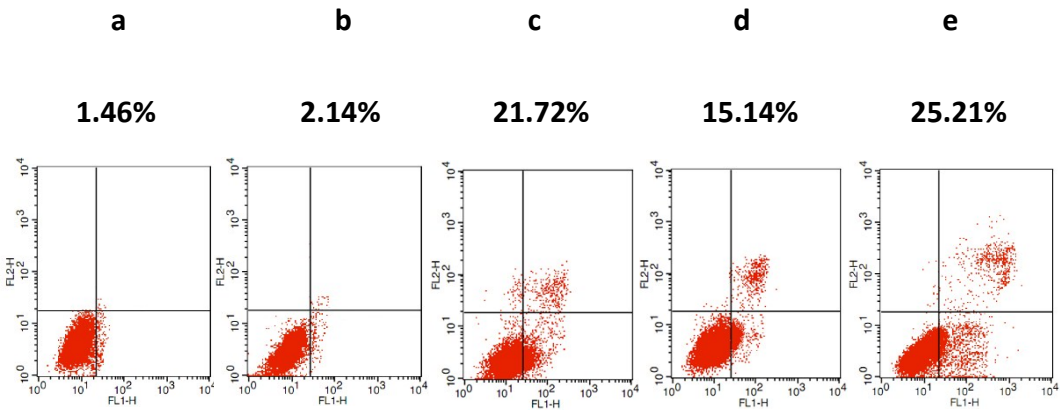

Figure S4. FCM quantitative analysis of HepG2 cells treated with TCPS (control, a), HMSNs-PA-HA (b), DOX (c), HMSNs@DOX (d), and HMSNs-PA-HA@DOX (e), respectively.

Table S1. BET and BJH parameters of HMSNs, HMSNs-PA and HMSNs-PA-HA nanoparticles.

Materials	S_{BET} (m^2/g)	V_P (cm^3/g)	BJH W_{BJH} (Å)
HMSNs	907.3481	0.895968	26.6768
HMSNs-PA	497.6089	0.435486	18.3639
HMSNs-PA-HA	190.5998	0.26985	13.4501

Table S2. Zeta potentials of different HMSNs nanoparticles.

Materials	Zeta potential (mV)
HMSNs	-13.6±3.37
HMSNs-NH_2	24.4±4.04
HMSNs-PA	8.6±4.17
HMSNs-PA-HA	-16.2±2.83

References

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S2. L. L. Dai, J. H.Li, B. L.Zhang, J. J.Liu, Z. Luo, K. Y. Cai, *Langmuir*, 2014, **30**, 7867-7877.

S3. M. H. Yu, S. Jambhrunkar, P. Thorn, J. Z. Chen, W. Y. Gu, C. Z. Yu, *Nanoscale*, 2013, **5**,178-183.