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Supporting Information for:

Macromolecules on Nano-Outlets Responding to Electric Field and pH for Dual-Mode Drug Delivery

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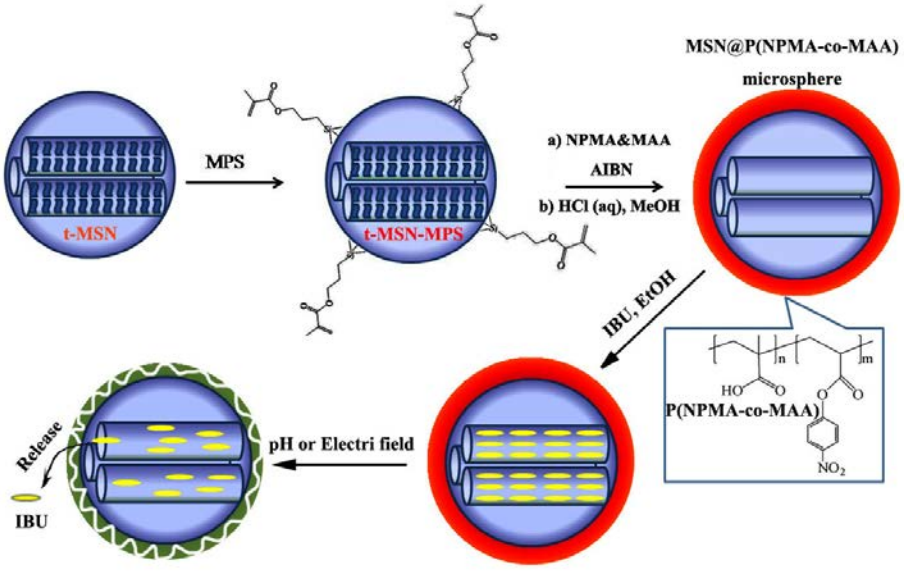
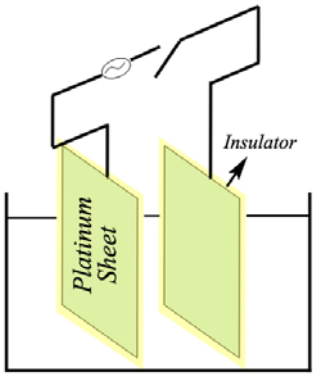
The synthesized procedure of the polymer film on the surface of the mesoporous silica nanoparticles is discussed in the EXPERIMENTAL SECTION as displayed in the following Scheme S1. The functional electrical and pH responsive moieties are coalesced together by using surface modified free radical polymerization method. Then, macromolecules are fabricated on the outlets of MSNs to form a thin polymer film.



Scheme S1. The synthesized procedure of the polymer film on the surface of the mesoporous silica nanoparticles.

The electrical stimulus was performed through a home-made electrode with two platinum sheets, which is coated by insulator to prevent the electrochemical reactions. In this case, the interfacial impedance is minimized to achieve better performance.

The two platinum sheets, between which samples were placed, were placed away for ca. 8mm, and ±8V alternating voltage was provided to form electric fields with varied directions.



Scheme S2. The illustration photo of the home-made electrode.

FTIR spectroscopy is used to investigate surface modification of the MSN particles with MPS and PNMMS. The absorption peaks at 1090 cm^{-1} are assigned to the Si-O-Si vibration, whereas the peaks around 1630 and 3430 cm^{-1} are attributed to the absorbed water and hydroxyl groups. The presence of peaks at 1700 and 2920 cm^{-1} (Figure S1a, the red curve) which are owing to the ester C=O and C-H bonds of the silane agent MPS give the evidence of modification of MSN with MPS. The weakened peaks at 1530.6 and 1347.1 cm^{-1} are owing to the N-O asymmetrical stretching vibration of nitryl indicating the successful coating of PNMMS on the MSN microspheres (Figure S1a, the blue curve). The peak at 797cm^{-1} corresponds to the vibration of Si-C bonds. The specific surface areas of various samples are calculated with the BET (Brunauer–Emmet–Teller) methods. Pore size and pore size distribution (PSD) plots were obtained by BJH method using the cylindrical pore

model. The reduction of the adsorption capacity after MPS coating reveals that the functional molecules have been modified on the mesoporous silica nanospheres. The depression of surface area S_{BET} and V_{BJH} from 1044 m^2/g and 1.271 cm^3/g (MSN) to 901.54 m^2/g and 0.816 cm^3/g (DMDR system) also indicates the successful PNMMS coating. After IBU loading, adsorption capacity for the DMDR system is sharply reduced indicated by the reduction of S_{BET} and V_{BJH} to 414.83 m^2/g and 0.412 cm^3/g. The results reveal that the drugs are successfully stored in the mesoporous channels. The regression of the surface area and surface volume after drug release are observed, which indicates the intactness of delivery channels in system while drug release. From the pore size distribution diagram of the samples, we observe the intactness of the channel structures after coating. The average pore diameter is 2.88 nm after IBU loading, and returns to 4.11 nm after the fully release of IBU molecules, which is much closed to the value 3.96 nm before drug storage.

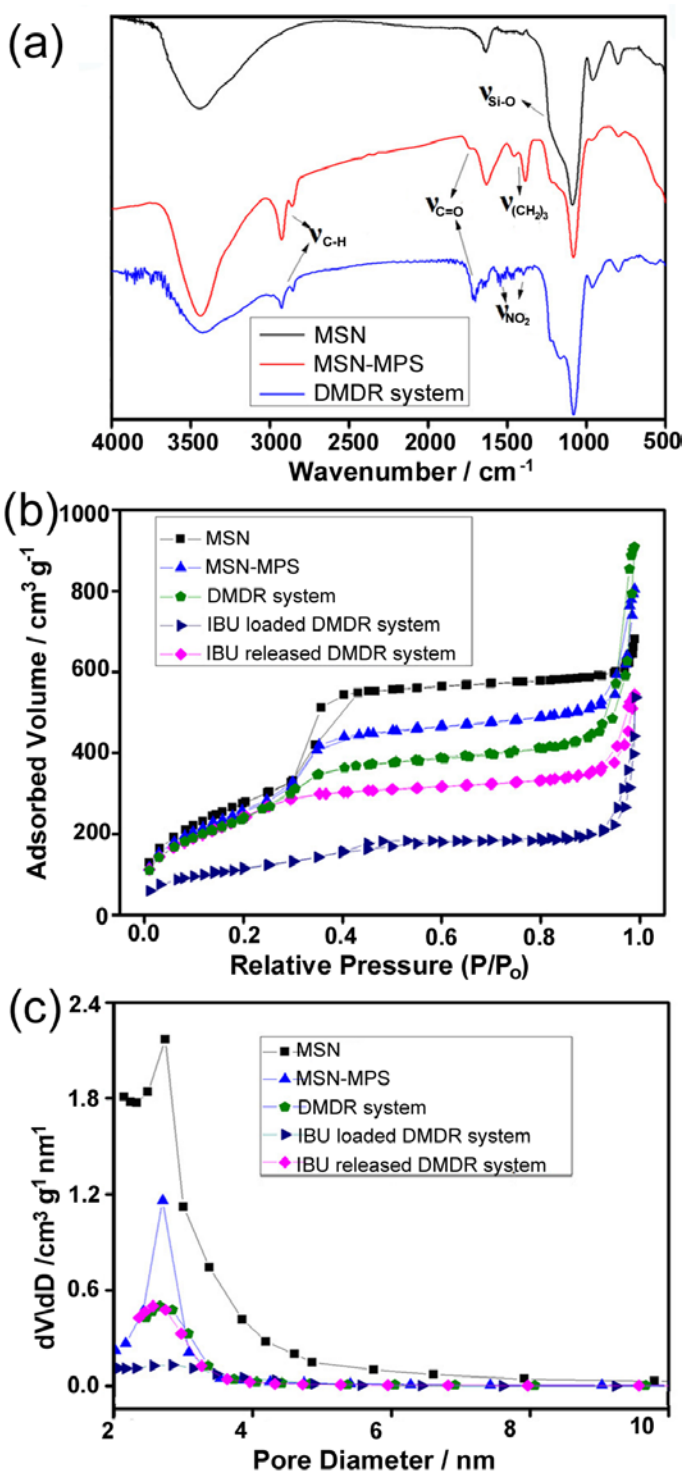


Figure S1. (a) FTIR spectra of MSN without or with MPS (MSN-MPS) and PNMMS coating (DMDR system); (b) N_2 adsorption-desorption isotherms of MSN, MSN-MPS, DMDR system, drug loaded DMDR system and DMDR system after drug release and (c) the corresponding pore diameter distributions.

Table 1. Structural properties of various obtained samples

Samples	BET area (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)
MSN	1044.57	4.31	1.271
MSN-MPS	951.89	4.02	0.956
DMDRs	901.54	3.96	0.816
IBU loaded DMDRs	414.83	2.88	0.412
IBU released DMDRs	888.47	4.11	0.872

For MSN particles, the weight loss all cross the temperature range results mainly from the absorbed or bound water and impurities (Figure S2). For MPS coated MSN, the weight loss below 180℃ is ascribed to desorption of the absorbed water and the impurities. The weight loss between 180 and 400℃ is because of the thermal decomposition of the functional molecules MPS. However, the weight loss between 180 and 400℃ comes from the decomposition of the coating copolymer for DMDR system which has a higher decomposition temperature at 378.9℃. For IBU loaded DMDR system, the decomposition of the coating copolymer and the drugs contributes the weight loss between 180 and 400℃. Weight loss of all samples above 400℃ owes to desorption of bound water and combustion of coating macromolecules, which display an exothermic peak at 489.9℃. Therefore, we can calculate that the content of macromolecules on the surface of MSNs is about 20.5%, and the drug storage capacity is about 17.36% (197.17mg of ibuprofen per gram of DMDR system).

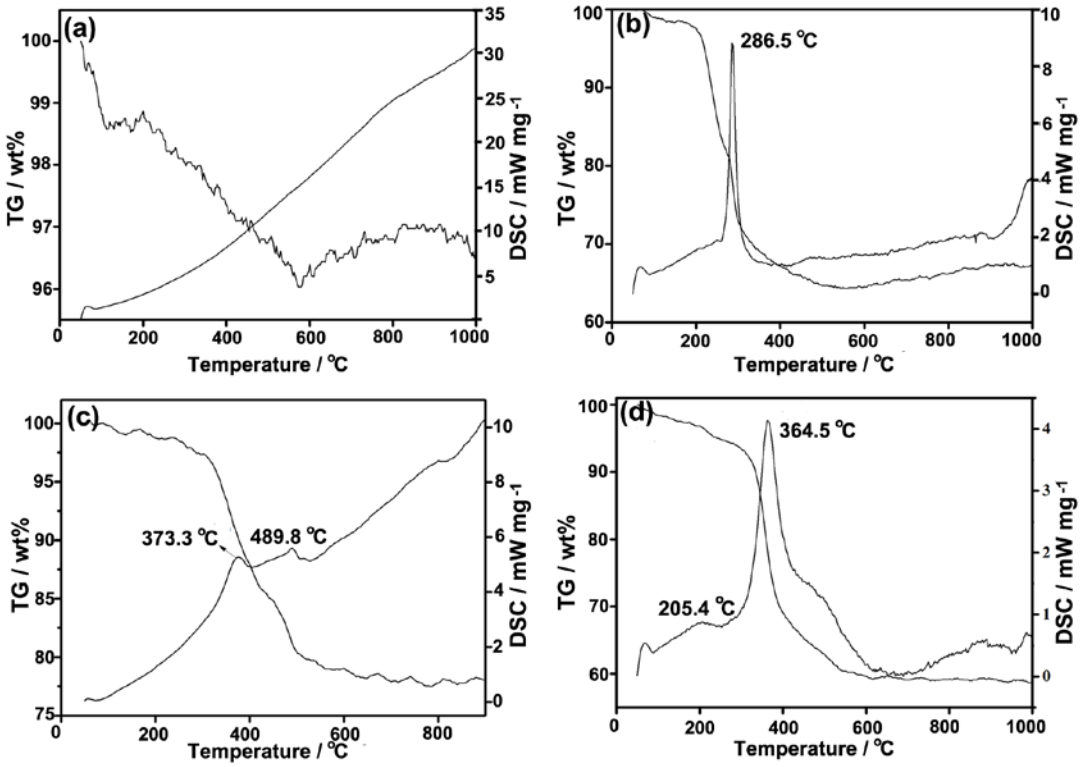


Figure 3. TG-DSC profiles of various samples obtained at a heating rate of 10℃ /min in the air: MSN (a), MSN-MPS (b), DMDR system (c), drug loaded DMDR system (d).

Table 2. The TG-DSC analysis results of various obtained samples

Samples	W_t loss (%)			Drug storage (mg_{IBU}/g_{DMDRs})
	0~180℃	180~400℃	>400℃	
MSN	1.44	2.55	/	/
MSN-MPS	3.37	29.17	/	/
DMDRs	1.33	13.33	7.17	/
IBU loaded DMDRs	3.1	28.1	9.76	197.17