

Electronic supplementary information

Oxidation-induced surface deposition of tannic acid: towards molecular gates on porous nanocarriers for acid-responsive drug delivery

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Particle characterizations.

Transmission electron microscope (TEM) images were obtained by a JEM 2010 (JEOL, Japan) instrument with 200 KV acceleration voltages. Samples were dried on holey carbon-coated Cu grids.

Scanning electron microscopy (SEM) measurements were performed with a Zeiss DSM 962 microscope operated at an accelerating voltage of 10.0 kV.

Nitrogen sorption isotherms were measured with a ASAP2010 analyzer (Micromeritics, USA). The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method in a linear

relative pressure range between 0.05 and 0.25. The pore size distributions were derived from the desorption branches of the isotherms by the NLDFT method.

The FT-IR spectra were collected over the range of 4000–400 cm^{-1} on a Spectrum 100 infrared spectrophotometer (Perkin Elmer, USA) using KBr technique.

Thermogravimetric analysis (TGA) was conducted with a Q500 instrument (TA Instruments, USA). The materials were tested under an air atmosphere from 30 °C to 900 °C at a heating rate of 10 °C min^{-1} .

The concentrations of the drugs (DOX) in the solutions were analyzed with a UV-Vis Spectrophotometer (NanoDrop 2000c, Thermo) at the wavelength of 480 nm.

Fluorescence spectra were measured by a LS 50B Fluorescence Spectrometer (PerkinElmer, USA).

The structural change of TA was checked by reverse phase analytical HPLC monitoring, which was performed on a Thermo Spectra system equipped with a Hy persil ODS column (4.0 × 125 mm, 5 μm), eluting with $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (volume ratio 20/80) at a flow rate of 0.5 mL/min. Column effluent was monitored by UV detection at 280 nm.

X-ray diffraction (XRD) measurements were performed using a Kratky compact small-angle system (Hecus Braun, Austria). The system is equipped with a position-sensitive detector consisting of 1024 channels of 55.5 μm width each. A Seifert ID-300 X-ray generator, operating at a maximum intensity of 50 kV and 40 mA provided the Cu KR radiation at $\lambda=1.542 \text{ \AA}$.

The hydrodynamic size distributions and zeta potentials of the samples were measured using dynamic light scattering (DLS) techniques by a Zetasizer Nano instrument (Malvern, UK).

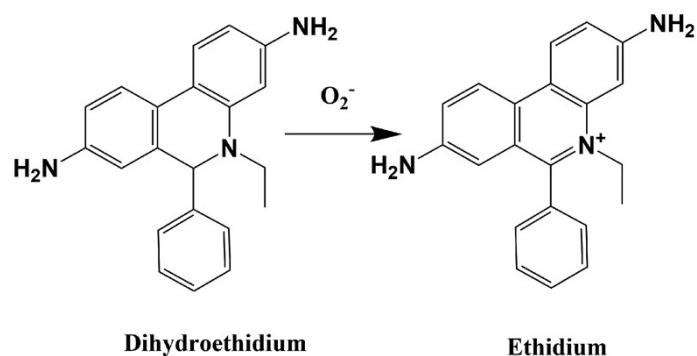


Fig. S1 Chemical structure of dihydroethidium (DHE) before and after oxidation by superoxide anion (O_2^-). It was reported that O_2^- is reduced to H_2O_2 by the electron transfer in the oxidation-reduction reaction.¹ In situ production of superoxide anion (O_2^-) by MSN was monitored by the change in the fluorescence spectra of DHE solution ($25 \mu M$)² after the introduction of the supernatant from 1 mL suspension of MSN in water (2 mg mL^{-1} , incubated at room temperature for 10-120 min). An excitation wavelength of 465 nm was used in all measurements of fluorescence determination. No further changes in the intensity and the peak wavelengths were observed for the samples incubated in water for a time longer than 120 min. The significant peak shifting to red-emission region and the enhancement in the fluorescence intensity was shown and discussed in the main text.

Table. S1 Comparison of textural parameters for MSN and MSN@TA.

Sample	Surface area(m²/g)	Pore volume^a (cm³/g)	Peak pore size (nm)
MSN	963	0.86	3.9
MSN@TA	742	0.47	-
DOX loaded MSN	865	0.72	3.8

a: The pore volume was calculated at a relative pressure value of 0.8 in order to exclude the contribution of textural porosities (as indicated by the second capillary condensation step from 0.9 to 1.0 in the relative pressures) resulting from the close packing of the nano-sized mesoporous silica materials.³

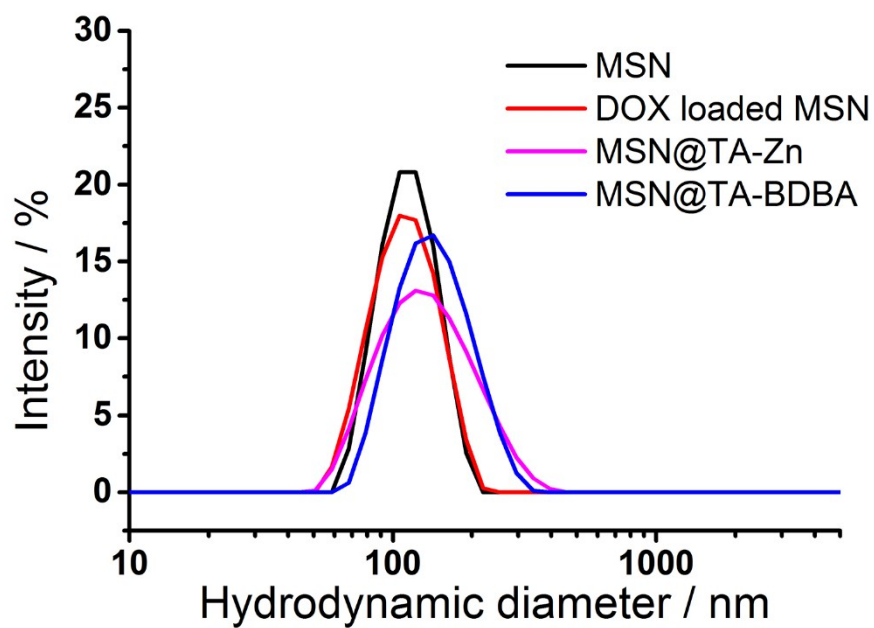


Fig. S2 Hydrodynamic diameter distributions of MSN, DOX loaded MSN, MSN@TA-Zn, and MSN@TA-BDBA measured by dynamic light scattering.

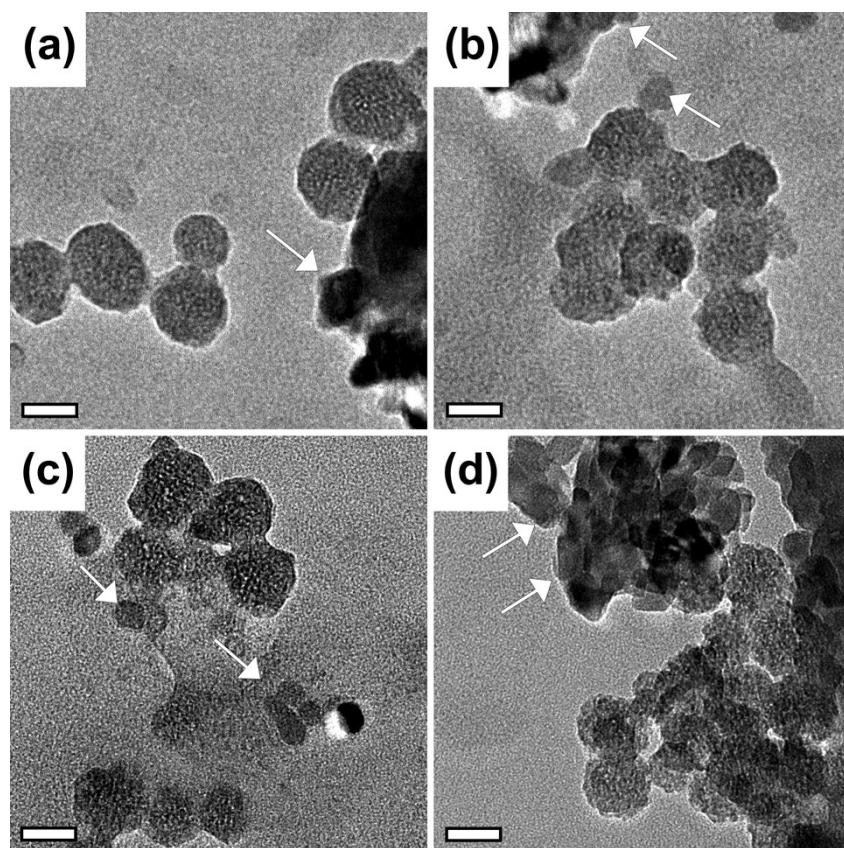


Fig. S3 TEM images of MSN@TA-Zn (a, b) and MSN@TA-BDBA (c, d) prepared at higher TA weight ratios (20 wt%, 40 wt%) with respect to MSN. The scale bars in a, b, c, and d represents 50 nm. The white arrows show the presence of MSN-free organic particles which is most likely related to self-crosslinked TA-Zn or TA-BDBA particles.

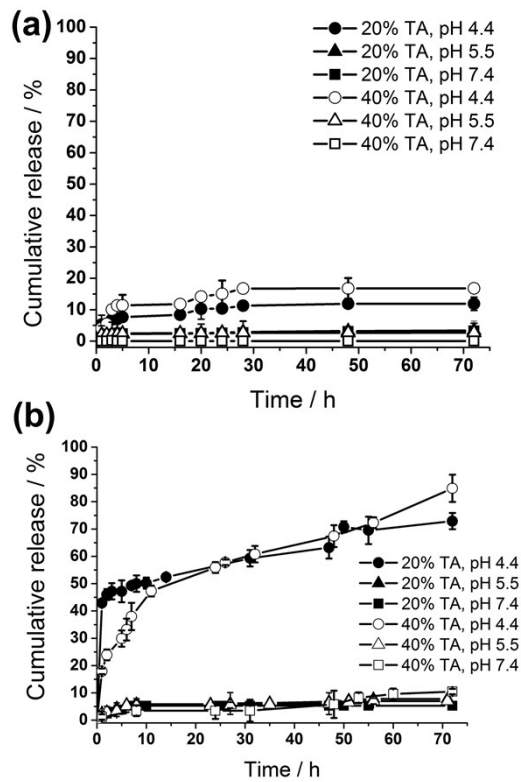


Fig. S4 Comparison of cumulative release profiles of DOX from (a) MSN@TA-BDBA and (b) MSN@TA-Zn particles prepared with 20-40% TA. The percentage numbers (20%-40%) refer to the weight ratios of tannic acid with respect to the weight of MSN particles (2 mg) used in the preparation of the drug loaded MSN@TA-Zn and MSN@TA-BDBA particles.

References.

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2. M. Misawa and J. Takahashi, *Nanomed. Nanotechnol. Biol. Med.*, 2011, **7**, 604-614.
3. J. Zhang, X. Li, J. M. Rosenholm and H.-c. Gu, *J. Colloid Interface Sci.*, 2011, **361**, 16-24.