Supporting Information

Versatile surface engineering of porous nanomaterials with bioinspired polyphenol coatings for targeted and controlled drug delivery

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Experimental

1. Materials and characterizations

Cetyltrimethylammonium bromide (CTAB), Tetraethylorthosilicate (TEOS) and Epigallocatechin-3-gallate (EGCG) were used as acquired without any further purification (Sigma-Aldrich). Phosphate buffered saline (PBS) and sodium hydroxide (NaOH) were purchased from Fisher Scientific.

TEM images were taken by a Tecnai G2 F20 S-TWIN transmission electron microscope at 120 kV. The nitrogen adsorption-desorption isotherms were measured at -196 °C with a Quantachrome Nova 4200E porosimeter. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method according to the adsorption branch of the isotherm. The X-ray photoelectron spectra (XPS) were recorded on a Thermo-VG Escalab 250. Fluorescence measurements were carried out on a FluoroMax-4 spectrofluorometer (Jobin Yvon).

2. Cell Culture

CCRF-CEM (human acute lymphoblastic leukemia), Ramos (human Burkitt's lymphoma), and K562 (chronic myelogenous leukemia) cell lines were purchased from ATCC (Manassas, VA). All cells were cultured in RPMI 1640 medium (ATCC, Manassas, VA) supplemented with 10% FBS and 100 IU/mL penicillin-streptomycin (Cellgro, Manassas, VA).

3. DNA synthesis

Amine-terminated aptamer (FITC-sgc8-NH_2: 5'-3': FITC-T_6-ATC TAA CTG CTG CGC CGC CGG GAA AAT ACT GTA CGG TTA GA-NH_2) and library DNA (FITC-N-NH_2: FITC-T_6-N_{41}-NH_2) with FITC modifications were synthesized on an ABI 3400 DNA/RNA synthesizer (Applied Biosystems, Foster City, CA, USA). The synthesis and deprotection processes were carried out according to the instructions provided by the reagents' manufacturers. Subsequently, the deprotected DNA was precipitated by adding 1/10 volume of 3 M NaCl and 2.5x volume of cold ethanol. After placing in a freezer at -20 °C for 30 min, the DNA products were collected by centrifugation at 4,000 rpm for 30 min. The DNAs were then dissolved in 400 μL of 0.2 M triethylamine/acetate (Glen Research Corp) and purified by HPLC (ProStar, Varian, Walnut Creek, CA, USA) with a C18 column (5 μm, 250 mm×4.6 mm, Alltech) using acetonitrile and 0.1 M triethylammonium acetate (TEAA) aqueous solution as the mobile phase. The collected DNA products were dried and detritylated by dissolving and incubating DNA products in 200 μL 80% acetic acid for 20 minutes. The detritylated DNA product was precipitated with NaCl (3 M, 25 μL) and ethanol (600 μL). UV-Vis measurements were performed with a Cary Bio-100 UV/Vis spectrometer (Varian) for probe quantification.

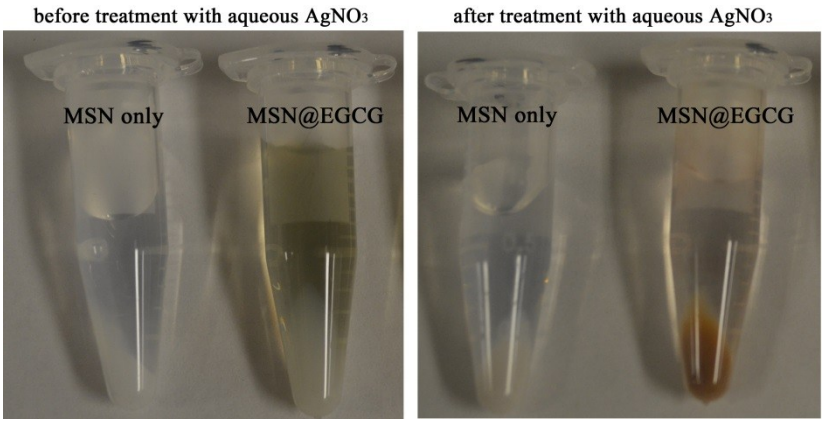

Fig.S1. Photographs of MSNs and MSN@EGCG before (left) and after (right) treatment with aqueous $AgNO_3$.

The MSNs were suspended in 0.2 mg/mL solution of EGCg in buffered saline (100 mM bicine, 0.6 M NaCl, pH 7.8) for 1 h at room temperature. After centrifugation, no residue or any observable color changes resulted. However, the presence of a thin EGCg coating was revealed by treatment with an $AgNO_3$ solution, resulting in the deposition of a dark metallic silver film on the surface, presumably through a redox reaction between Ag^+ ions and the polyphenolic coating.

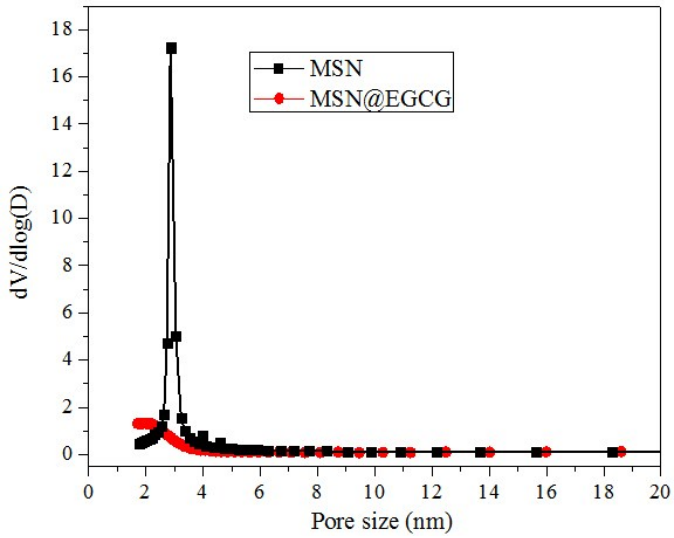

Fig. S2. The pore size distributions of MSNs and MSN@EGCg.

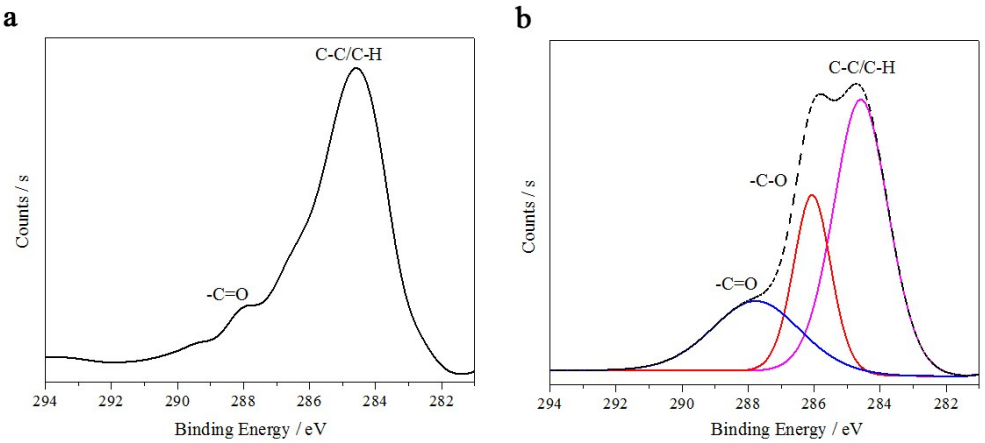

Fig. S3. XPS analysis of (a) MSNs only and (b) EGCG-coated MSNs.

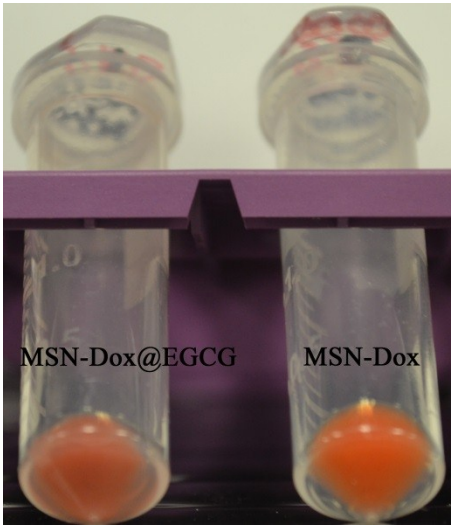

Fig. S4. Photographs of MSN-Dox and MSN-Dox@EGCg.

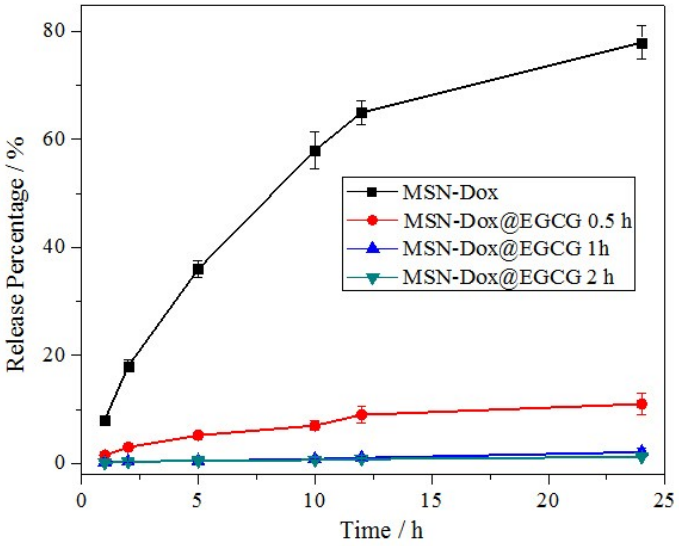

Fig. S5. Dox released from MSN-Dox and MSN-Dox@EGCg in a physiological environment (1×PBS, pH 7.4) at different coating times.

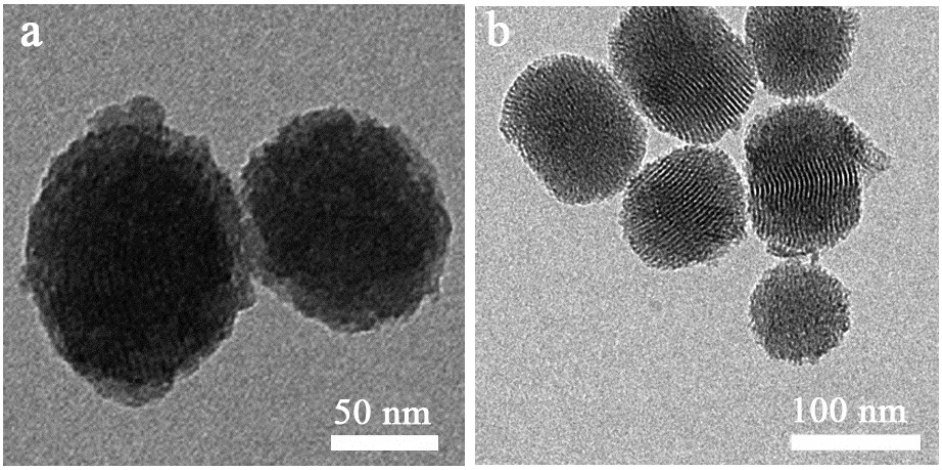

Fig. S6. TEM images of MSN@EGCg (a) before and (b) after treatment with GSH solution (10 mM).

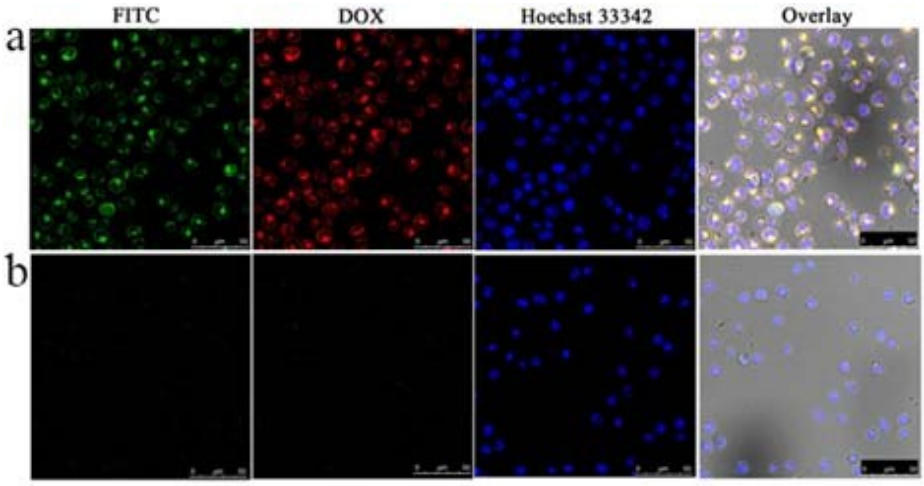

Fig. S7. Confocal fluorescence images of (a) CEM cells and (b) Ramos cells treated with MSN-Dox@EGCg-Apt. The nucleus was stained with Hoechst 33342 (blue). Scale bar: 50 μm.

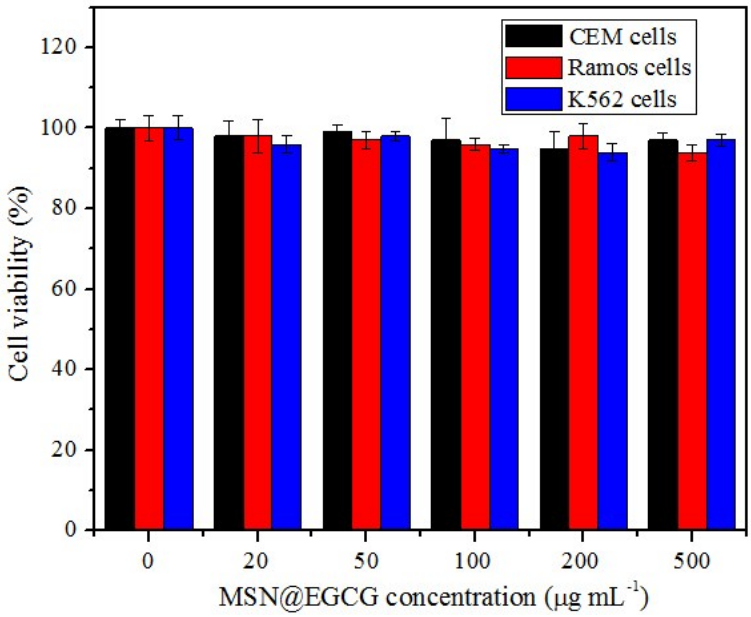

Fig. S8. Cell viabilities of CEM, Ramos and K562 cells incubated with MSN@EGCg at different concentrations.

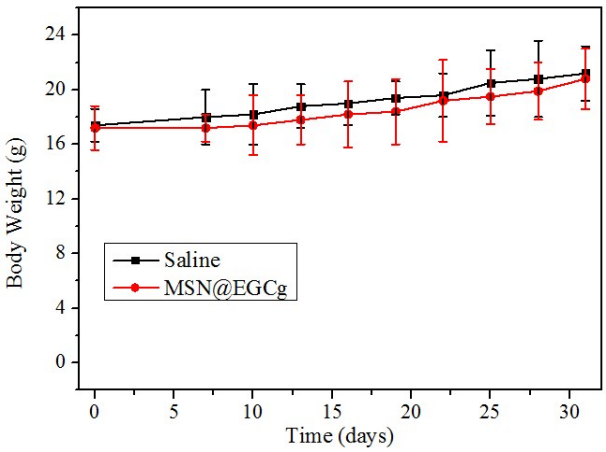

Fig. S9. Body weight of mice treated with saline and MSN@EGCg.

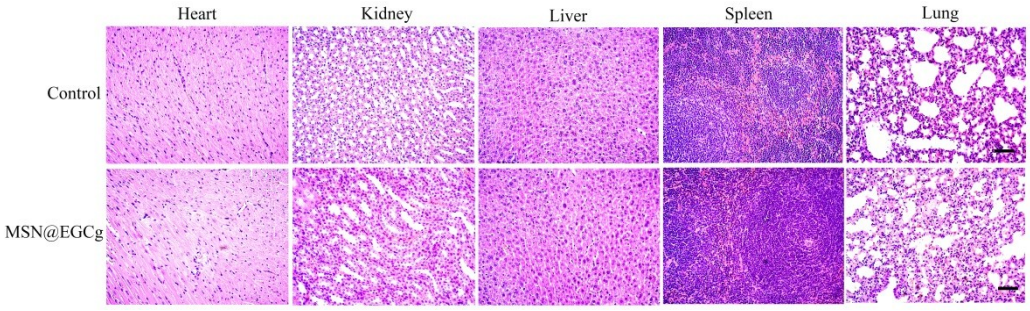

Fig. S10. H&E stained images of major organs collected from mice treated with saline (control) and MSN@EGCg for 31 days. No noticeable abnormality was observed in major organs including, heart, kidney, liver, spleen and lung. (Scale bar = 50 μm).