## **Supplementary Information**

## Robust polydopamine nano/microcapsules and the permeation and release behavior

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## Preparation of polydopamine capsules

The oxidation polymerization of dopamine has two possibilities in the presence of substrates: heterogeneous nucleation at template surfaces or self-nucleation in bulk solution. The concentration is the key to regulate the two aspects: for concentration above 0.3 mg/mL, a large amount of Pdop was precipitated after 24 h at the bottom of bottle, which will make it extremely difficult to separate from Pdop@SiO<sub>2</sub>; below the concentration, solution only turned to dark brown, while no visible precipitates were found. So the deposition concentration of dopamine was chosen below the critical concentration.

In this reported study, the concentration of 3-Hydroxytyramine hydrochloride was chose as 0.1, 0.2 and 0.3mg/mL. SiO<sub>2</sub> beads and 3-Hydroxytyramine hydrochloride were mixed in 10 mM Tris-HCl (pH 8.5). The solution was stirred for 24 h to obtain Pdop coated SiO<sub>2</sub>, which was centrifuged and rinsed with water. Then Pdop@SiO<sub>2</sub> was immersed in 0.5% HF solution for 48 h to dissolve SiO<sub>2</sub> template. Then the resultant capsules were rinsed with 0.5% HF solution, water and dried. Pdop@polystyrene (PS) was obtained using as the same method. Then Pdop@ PS was immersed in THF to dissolve PS for 48h. The obtained Pdop capsules we centrifuged, rinsed with THF, ethanol and dried.

## Measurement of loading and release behavior

Before the permeability and release behavior were characterized, the standard curves between the absorbance and the concentrations of Rh 6G in different solvents were measured. First, the absorbance of 10 mg/L Rh 6G in solvents including

different pH buffer solution and other solvent was measured by UV-Vis in the range of 400-600 nm. The absorption peak of Rh 6G appeared at about 525 nm. Then 1.0 mg dry capsules were immersed the above 5mL Rh 6G solution, respectively. After stirred regular time intervals, the solutions containing Pdop capsules were centrifuged and the absorbance was measured by UV-Vis. The permeation quantity was measured by standard curves and permeation ratio was calculated by  $[(C_0-C)/C_0](\%)$ , where  $C_0$ and C are the original dye concentration and concentration after uptake. After the 100% uptake in pH 7 buffer solution, the solution was centrifuged and rinsed with pH 7 buffer solution. Then the samples were immersed in solvent including the different pH buffer solution and other solvent to characterize the release behavior, respectively. After regular intervals the solutions containing Pdop capsules were centrifuged and then the absorbance was measured by UV-Vis. Last, the release quantity was measured by standard curves and release percentage and release amount were obtained.



Figure S1. Microscopy image (left) and corresponding fluorescence image (right)  $2\mu m$  pdop capsules for deposition three cycles after loading Rh6G.