Electronic Supplementary Material (ESI) for Analyst.

Supporting Information to

# Differential Pulse Voltammetry Detection of Dopamine and Ascorbic Acid by Permselective Silica Mesochannels Vertically Attached to the Electrode Surface

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## S1. Electrochemical characterization of SMCs

Three redox mediators, including $Fe(CN)_6^{3-}$, $Ru(NH_3)_6^{3+}$ and ferrocenemethanol (FcMeOH), were used for electrochemical examination of the SMC film deposition and the effective molecular transport through the SMCs. As shown in **Figure S1**, cyclic voltammetric responses of each mediator at a bare ITO electrode, an ITO electrode covered by a thin film of SMCs before and after surfactant removal were compared. Apparently, the presence of the surfactant template SMC film on an ITO electrode led to the complete suppression of electrochemical responses of $Fe(CN)_6^{3-}$ and $Ru(NH_3)_6^{3+}$, indicating a full coverage of the electrode surface by SMCs and organic surfactant templates. Since neutral FcMeOH can permeate in the organic surfactant phase, a significant current response with peak potential shifted positively by ca. 200 mV was observed. In contrast, after surfactant templates were removed, well-defined current responses were displayed for three mediators. Moreover, they are comparable to those obtained at a bare ITO electrode. These electrochemical data suggest the deposition of SMC film was successful and molecular transport from the solution to the underlying ITO electrode surface through the vertically aligned SMCs was effective.

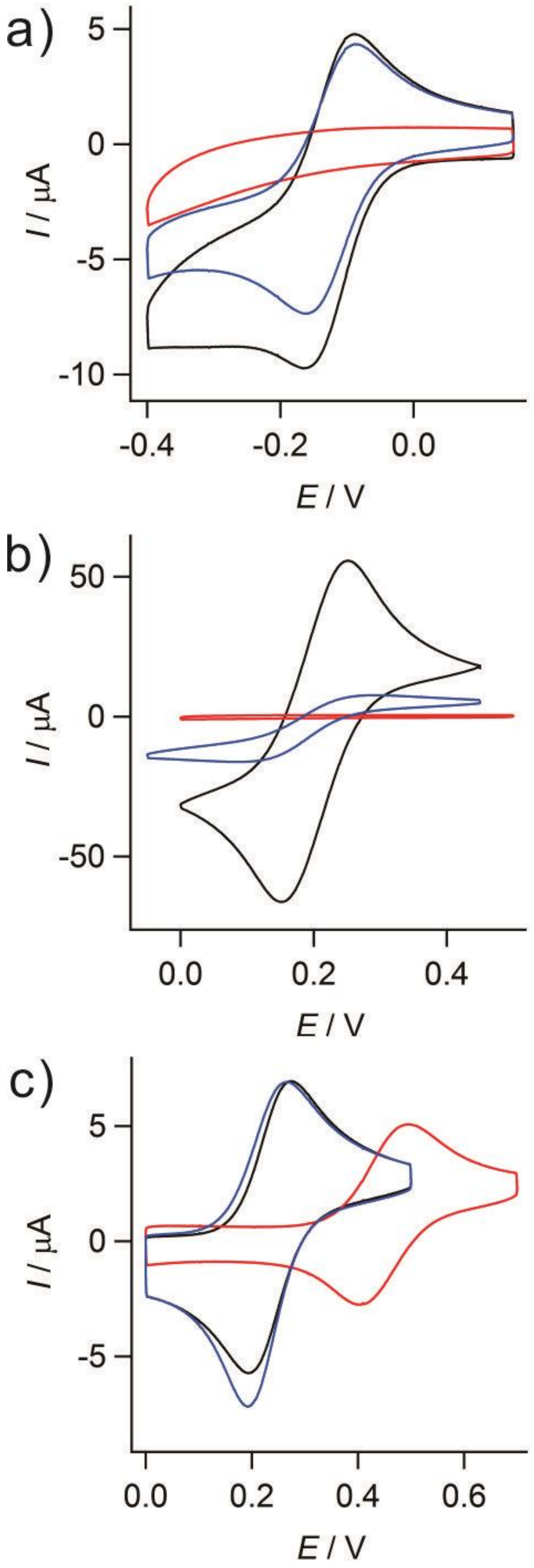

**Figure S1.** CVs obtained for a bare ITO electrode (black), SMC covered ITO electrode before (red) and after (blue) removal of surfactant templates in 0.1 M acetate buffer containing 50 μM $Ru(NH_3)_6^{3+}$ (a), 500 μM $Fe(CN)_6^{3-}$ (b) and 50 μM FcMeOH (c). The scan rate was 0.05 V $s^{-1}$.

## S2. SMC film thickness/mesochannel length control

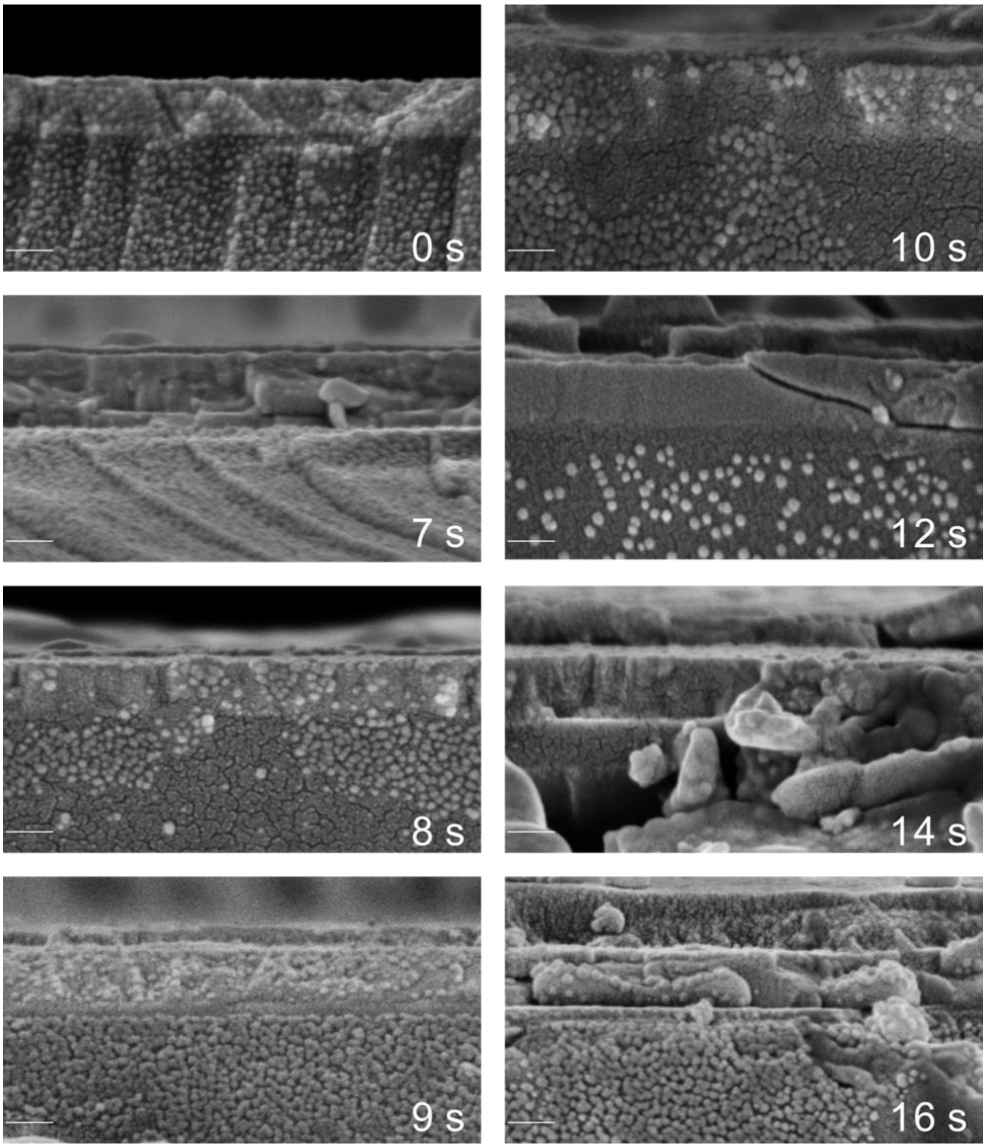

**Figure S2.** Cross-sectional FE-SEM characterization of SMC films electrogenerated on ITO plates when increasing the electro-depositon time from 0 s to 16 s. The scale bar corresponds to 100 nm.

SEM images displayed in **Figure S2** show the variation of SMC film thickness with the electro-deposition time. The top, middle and bottom layers correspond to the SMC film, ITO and glass, respectively. Apparently, the SMC film increases with increasing the electro-deposition period. No obvious growth was observed during the initial 7 s, but the growth after 7 s became rather fast, as shown in **Figure S2**. After 10 s, the thickness of the SMC film reached ca. 50 nm. On the other hand, a very long electro-deposition period led to the formation of much thick heterogenous coating made of silica spheres.

## S3. Characterization of channel surface modification with TMAC

Quantitative element analysis was done on the basis of x-ray photoelectron spectroscopy (XPS) measurement on the VG ESCALAB MARK Π spectrometer (CAE mode, 50 eV, anodes of Mg Kα with radiation at 1253.6 eV).

Grafting TMAC to channel wall was confirmed by the x-ray photoelectron spectroscopy (XPS) measurement, as shown in **Figure S3-b**, with a binding energy band at ca. 405 eV. The presence of nitrogen signal indicated the successful functionalization and the calculated ratio of Si/N was 10.94 while the unmodified mesoporous silica film containing surfactant has the Si/N ratio of 12.92. Additionally, as shown by the top-view TEM image in **Figure S3-a**, the nanopore structure remained ordered after TMAC modification. However, it should be noted that the present post-modification method can guarantee a monolayer grafting but not a uniform distribution of the grafted ammonium groups. More groups maybe grafted at the mesopore entrance and less inside the channels.

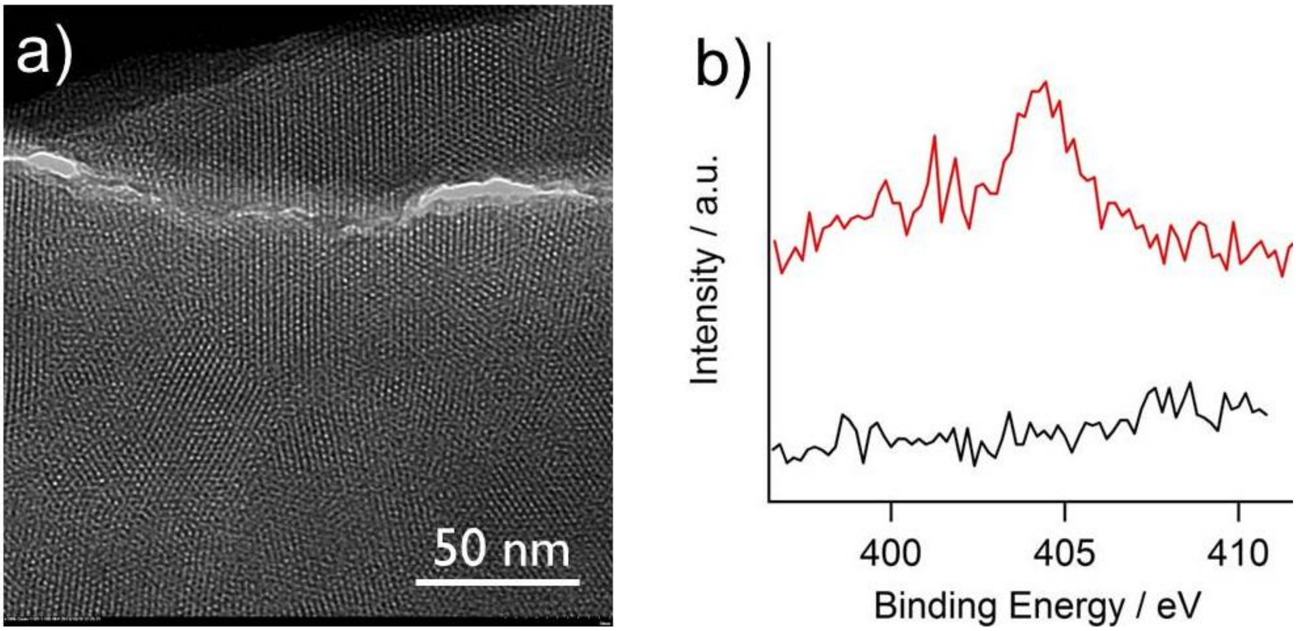

**Figure S3.** a) Top view TEM image of TMAC-modified SMCs. b) XPS results of Nitrogen signal for SMCs before (black) and after (red) TMAC modification.

## S4. Permselective behavior of unmodified SMCs

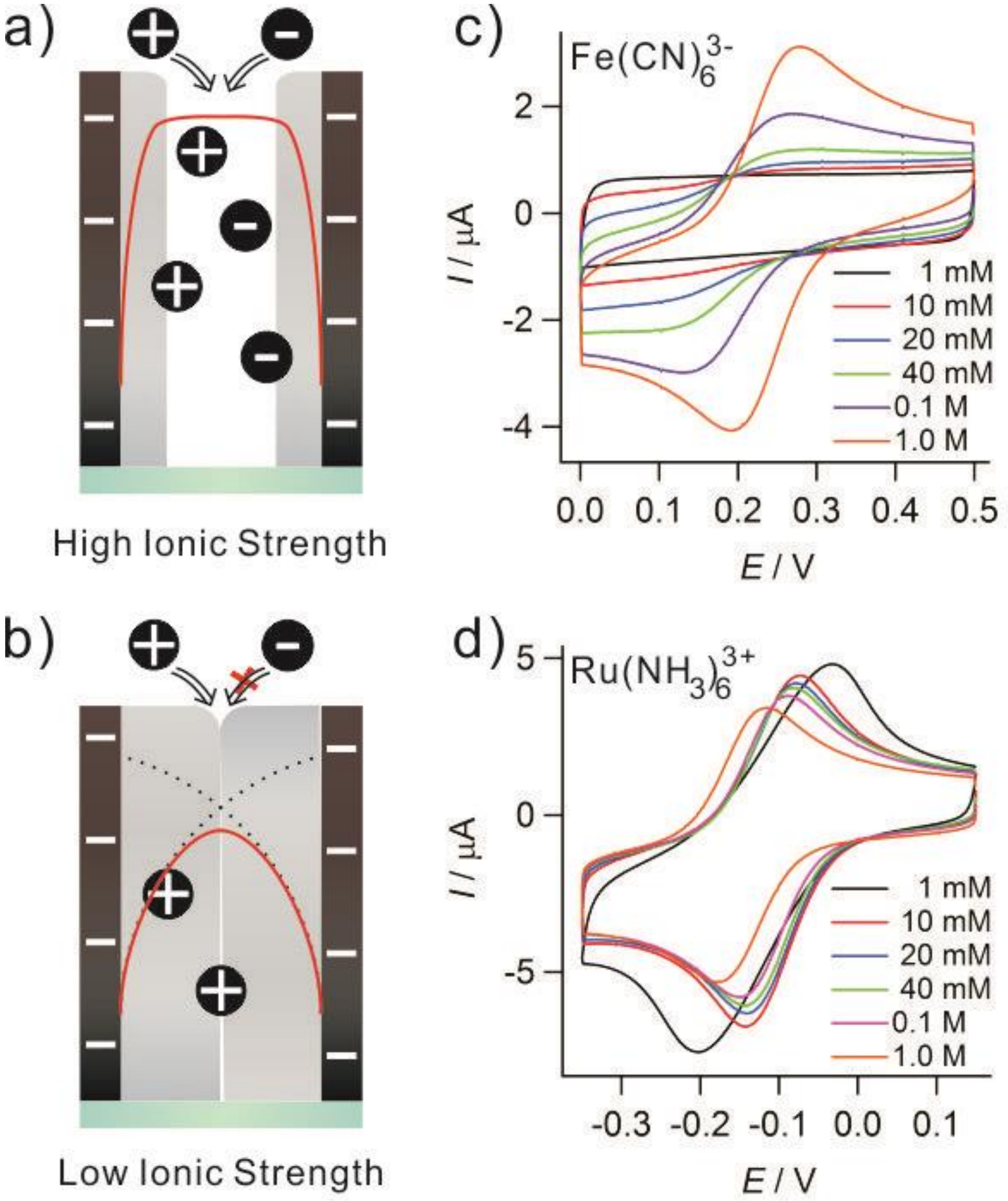

**Figure S4.** (a, b) Schematic illustration of the permselective transport of ions across a negatively charged SMC modulated by the ionic strength. The gray zone represents the electrical double layer (EDL) and the red curve denotes as the imaginary electrostatic potential profile. (c, d) Cyclic voltammetric responses in aqueous solutions containing 30 μM $Fe(CN)_6^{3-}$ (c) and 30 μM $Ru(NH_3)_6^{3+}$ (d) at various concentrations of acetate buffer. All CVs were obtained at a scan rate of 0.05 V $s^{-1}$.

## S4. AA and DA detection

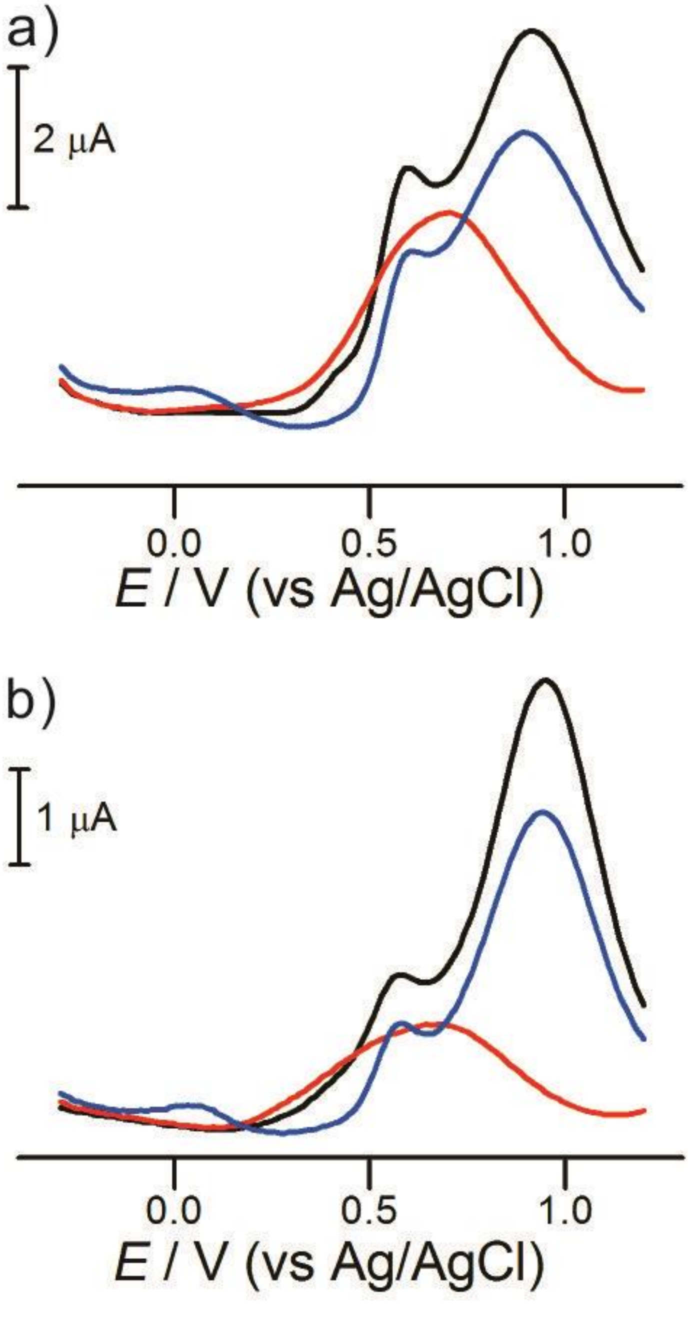

**Figure S5.** DPV responses of a bare ITO electrode (a) and a SMC film modified ITO electrode (b) in 0.1 M acetate buffer (pH 4.5) containing 0.1 mM AA (red), 0.1 mM DA (blue) and both (black), respectively.

**Figure S5** shows that the current responses of AA and DA at a bare ITO and at a SMC film modified ITO electrode are convoluted each other. Therefore, their quantitative detection cannot be achieved with these two electrodes.