

Supplementary Material (ESI) for Chemical Communications

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Sieving Behaviour of Nanoscopic Pores by Hydrated Ions

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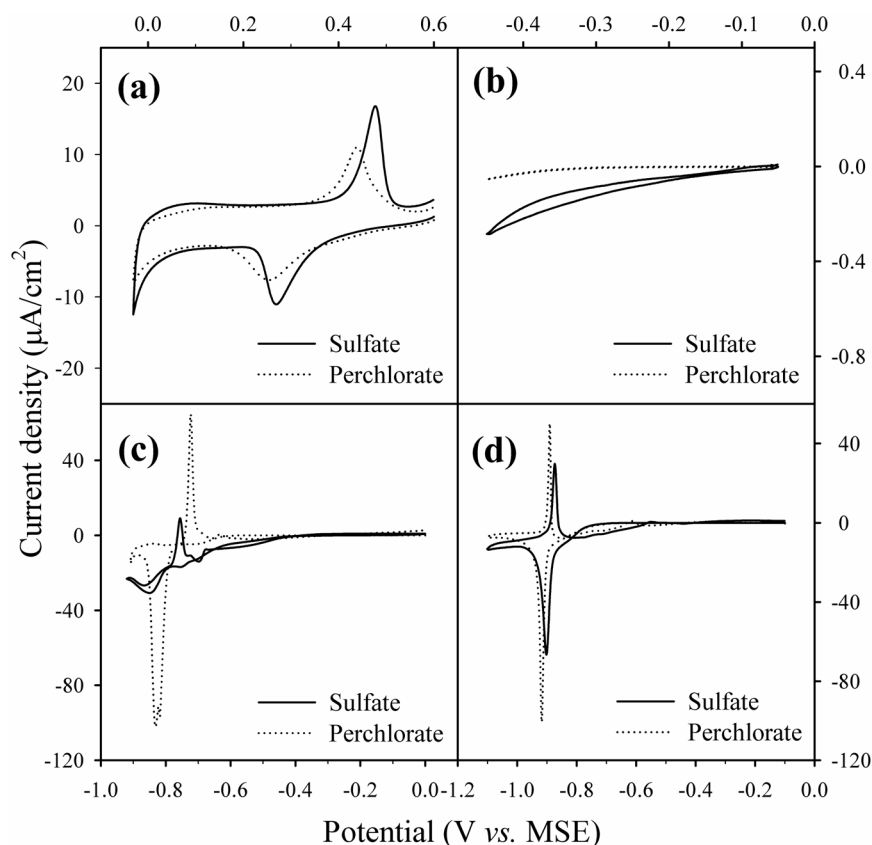
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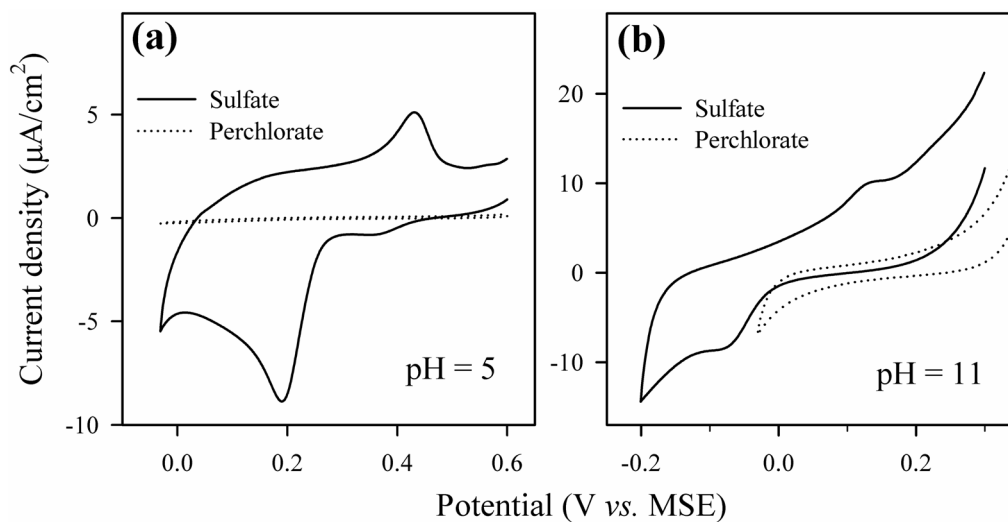
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1. The Ag deposition on hexanethiol SAMs and the Cu, Pb, Tl systems on decanethiol SAMs



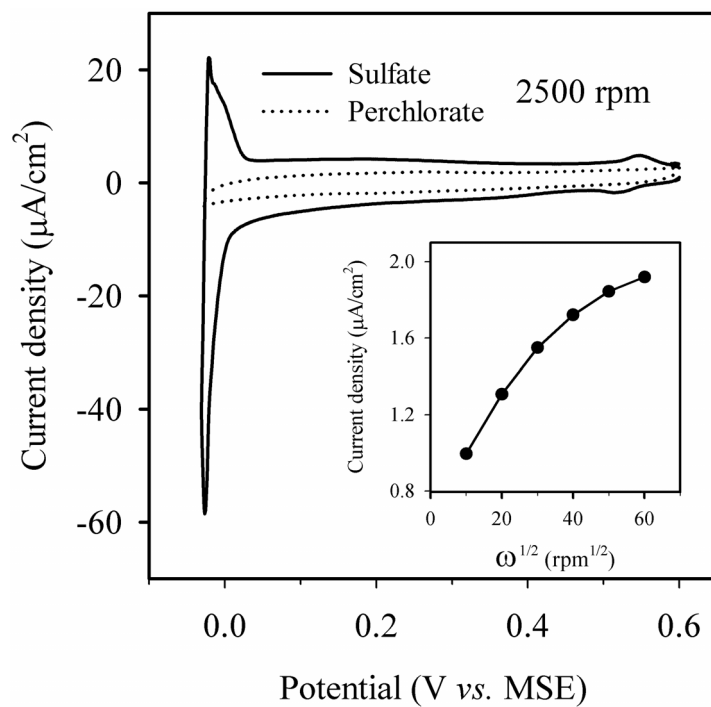
ESI 1. CVs on hexanethiol SAMs in 1 mM Ag_2SO_4 + 0.1 M H_2SO_4 (solid line) and 1 mM AgClO_4 + 0.1 M HClO_4 (dotted line) at 10 mV/s (a). CVs on decanethiol SAMs in 1 mM CuSO_4 + 0.1 M H_2SO_4 (solid line) and in 1 mM $\text{Cu}(\text{ClO}_4)_2$ + 0.1 M HClO_4 (dotted line) (b), in 1 mM PbSO_4 + 0.1 M H_2SO_4 (solid line) and in 1 mM $\text{Pb}(\text{ClO}_4)_2$ + 0.1 M HClO_4 (dotted line) (c), and in 1 mM Tl_2SO_4 + 0.1 M H_2SO_4 (solid line) and 1 mM TlClO_4 + 0.1 M HClO_4 (dotted line) at 10 mV/s (d). PbSO_4 is less soluble in H_2SO_4 .

2. CVs as pH.



ESI 2. The dependency of an Ag deposition in terms of pH. CVs on decanethiol SAMs in 1 mM $\text{Ag}_2\text{SO}_4 + 0.1 \text{ M K}_2\text{SO}_4$ (solid line) and in 1 mM $\text{AgClO}_4 + 0.1 \text{ M KClO}_4$ (dotted line) at 10 mV/s (a). CVs on decanethiol SAMs in 1 mM $\text{Ag}_2\text{SO}_4 + 0.1 \text{ M K}_2\text{SO}_4 + \text{NH}_3$ (solid line) and in 1 mM $\text{AgClO}_4 + 0.1 \text{ M KClO}_4 + \text{NH}_3$ (dotted line) at 10 mV/s (b).

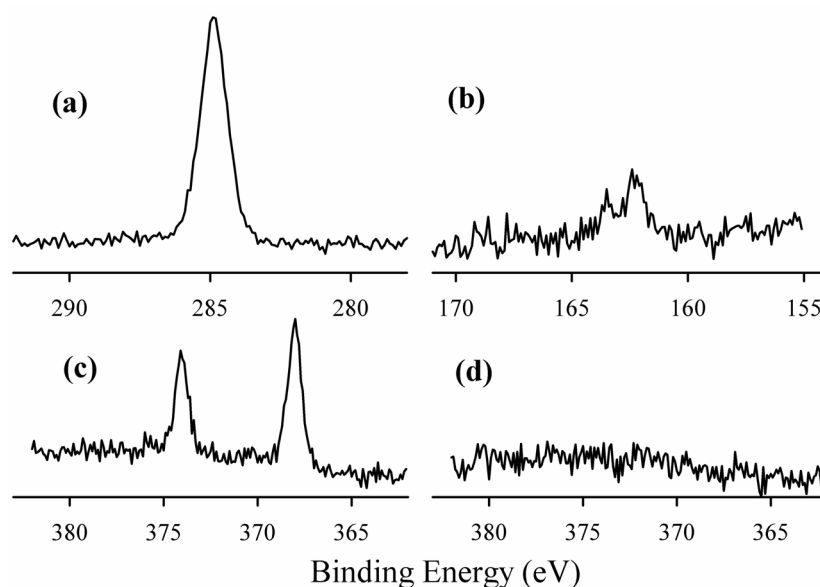
3. CVs on decanethiol-modified RDEs.



ESI 3. Convective mass transfer of Ag^+ ions to SAMs. CVs on decanethiol SAM-modified RDE in 1 mM Ag_2SO_4 + 0.1 M H_2SO_4 (solid line) and in 1 mM AgClO_4 + 0.1 M HClO_4 (dotted line) at 10 mV/s. Rotation speed = 2500 rpm. Inset: Levich's plot for the Ag deposition in perchlorates. Maximum currents taken at 0.2 V.

4. X-ray photoelectron spectroscopy.

X-ray photoelectron spectroscopy that gave information regarding the elemental composition of the materials was performed in order to determine what events occurred at the SAM structures following the Ag deposition. Repeated Ag deposition and stripping causes the quality of organized decanethiol SAMs to decrease, but the complete desorption of thiol molecules from the Au surfaces requires another experimental step, such as a reductive desorption in basic solutions or UV irradiation. It was unexpected that Ag4d was detected after the Ag deposition and stripping in sulfates, but this fact could be predicted from the CV exhibiting irreversible features between the deposition and the stripping, as shown in Fig. 1(c). The possibility that the silver metal penetrates under the thiol molecules and makes more resistant structures between the sulfur and the gold is considered, but further studies should be conducted to obtain verification for this. No occurrence of Ag deposition on decanethiol SAMs in perchlorates justifies only background signals in the Ag4d region, as shown in (d); therefore, the XPS results support the present statement above.



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ESI 4. X-ray photoelectron spectra of the C1s (a), the S2p (b), and the Ag4d after three consecutive potential sweeps in sulfates (c), and in perchlorates (d) for the decanethiol SAMs.

5. Experimental Section

Materials. The working electrodes for the electrochemical measurements were Au (thickness: 150 nm) substrates evaporated onto Si(100) wafer with Ti-adhesion layers (thickness: ca. 40 nm). Au (thickness: 250 ± 50 nm) substrates evaporated onto glass with Cr-adhesion layers (thickness: ca. 3 nm) were obtained from arrandeeTM, Germany for the STM imaging, in which all Au electrodes were annealed for 3 min in a hydrogen flame prior to use and slowly cooled in air. The oxide formation and stripping voltammetry of the surface in the pure electrolyte were found to closely match those in published literature for an Au(111) surface. Electrochemical solutions were prepared from ultrapure water (Modulab, US Filter, MA, > 18 M Ω). The following chemicals purchased from Aldrich were used without further purification: 1-decanethiol (96 percent), 6-mercapto-1-hexanol (97 percent), 3-mercaptopropionic acid (99 percent), 11-mercapto-1-undecanol (97 percent), 11-mercaptoundecanoic acid (95 percent), Ag₂SO₄ (99.999 percent), AgClO₄·H₂O (99.999 percent), CuSO₄·5H₂O (99.999 percent), TiNO₃ (99.999 percent), Ti₂SO₄ (99.995 percent), Pb(ClO₄)₂·xH₂O (99.995 percent), HClO₄ (double-distilled), H₂SO₄ (99.999 percent), HNO₃, KPF₆, KClO₄ (99.99 percent), K₂SO₄ (99.99 percent), and NH₃, K₃Fe(CN)₆, KOH.

Preparation of the decanethiol SAMs. Prior to the construction of the decanethiol SAMs prepared by immersing Au/Si(100) substrates into 1 mM decanethiol dissolved in an ethanol solution for 10 h, Au substrates were pretreated with a piranha solution (3:1 concentrated H₂SO₄:30 percent H₂O₂) followed by an abundant rinsing with deionized water.

Electrochemical Measurements. Cyclic voltammetry was acquired using a Pt (99.99 percent, 0.5 cm dia., Aldrich) wire as a counter electrode and a saturated mercury-mercurous sulfate electrode

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(MSE) as a reference electrode connected to the electrochemical compartment via a capillary salt bridge to lessen contamination from the reference electrode. All potentials in this paper are quoted relative to the MSE (0.64 V vs. NHE). The solutions were purged with Ar prior to use, and the atmospheres of the electrochemical cell were blanketed with Ar during all electrochemical measurements. The potential control and the sweeps were conducted with an Autolab potentiostat (PGSTAT 10, Eco Chemie, Netherlands). The RDE measurements were obtained using a BAS model RDE-1 rotator (Bioanalytical Systems, IN).

Instrumentation. Scanning tunneling microscopic images were collected in a constant current mode with a Topometrix TMX 2000. A silver wire (99.99 percent, 0.5 cm dia., Aldrich) was employed for the reference electrode, while a Pt wire was used as a counter electrode. The scanner was calibrated against the lattice spacing of a highly ordered pyrolytic graphite (HOPG) surface in air for the in-plane dimensions, and against monoatomic Au(111) steps for dimensions normal to the surface. The scanner was always stabilized for half a day to minimize thermal or acoustic vibrations before STM imaging and the x, y, z-calibrations. An electrochemically etched Pt/Ir wire (Molecular Imaging, AR) coated with Apiezon wax or polyethylene was used as a STM tip. All images are presented as unfiltered forms. X-ray photoelectron spectroscopy (XPS) was obtained with an X-ray photoelectron spectrometer (PHI Model 5800, Phys. Elec. Inc.).