Sieving behaviour of nanoscopic pores by hydrated ions†

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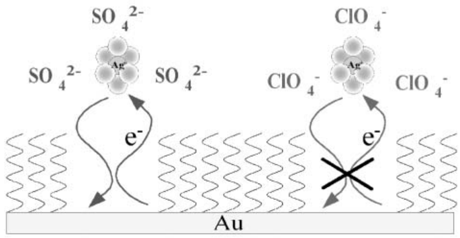
In this study, for the first time, the anion dependency of Ag-deposition on self-assembled monolayers (SAMs) with alkyl chains long enough to meet the densely packed and well-organized surface is reported. Irrespective of pH, types of terminal groups of the SAMs, and the convective mass transfer condition, SAM structures show the "sieving behaviour" to the Ag deposition by the composition of the electrolytes.

With their ease in forming nanoscale interfaces, self-assembled monolayers (SAMs) provide a convenient, flexible, and simple pathway and have proven to be popular for the creation of ideal environments to tailor the interfacial properties of metals, metal oxides, and semiconductors.[1] One technique used to modify the composition at the surface of thin films is underpotential deposition (UPD). UPD is an electrochemical method for generating monolayer or submonolayer coverages of one metal on another metal at more positive potential than the reversible or Nernst potential; that is, it occurs when the adatom–substrate interaction is stronger than the adatom–adatom interaction.[2] As self-assembled monolayers and underpotentially deposited layers share a common feature in that they can form highly organized adlayers on the surface of an underlying material, the combination of these subjects has become important for research that focuses on chemically and structurally well-defined electrochemical interfaces.[3] Such methods functionalize the surface with a highly organized single layer of material, where the composition of the layer is readily controlled. The difference between these methods is that the self-assembly method produces a thin organic layer on the metal surface while the UPD procedure coats the metal surface with monolayers or submonolayers of a dissimilar metal. The present report concerns the first anion dependency of silver electrodeposition upon decanethiol SAMs with the kinetic hindrance to the electron transfer reaction within a generic timescale (Scheme 1).

In order to determine the quality of decanethiol SAMs *i.e.* the order of the surface packing and the surface coverage, an electron transfer reaction in 10 mM $K_3Fe(CN)_6$ + 0.1 M KCl at 10 mV s^{-1} as well as a desorption experiment in 0.5 M KOH at 50 mV s^{-1} were performed before a silver deposition within the UPD regions. A typical diffusion-controlled redox reaction (solid line) appears on a bare Au/wafer while no Faradaic current and little charging current flows (dotted line) under the given timescale for decanethiol SAMs as shown in Fig. 1(A). This indicates that the van der Waals interaction between alkyl chains is strongly retained in the SAM structure. The stripping of thiol molecules on a Au surface begins to increase at −1.35 V, and the maximum peak appears at −1.46 V, as shown in Fig. 1(B). As all of the stripped molecules from the surface do not diffuse out to the solution, a readsorption peak is repeatedly observed at −1.28 V regardless of how many scans are conducted although the intensity gradually reduces. Assuming that the desorption process is related to one electron reaction, the surface coverage corresponds to



Scheme 1 Sieving behaviour of nanoscopic pores formed by decanethiol SAMs to the hydrated Ag^+ ion depending on the anion.

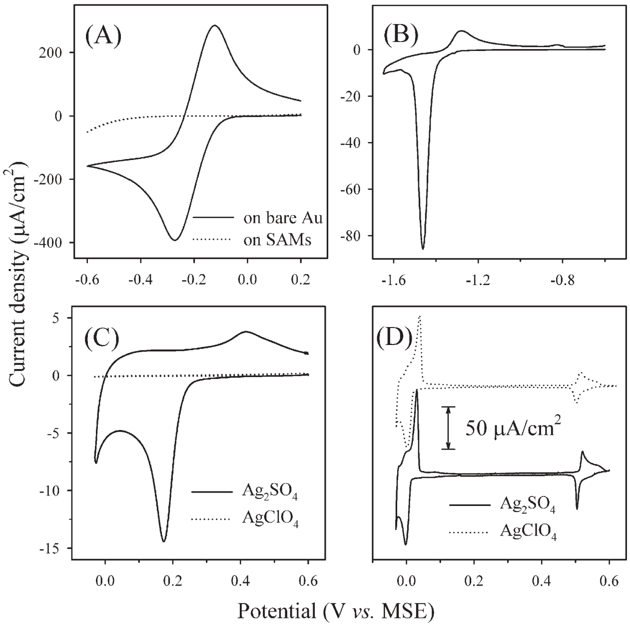


Fig. 1 CVs on bare Au (solid line) and on decanethiol SAMs (dotted line) in 10 mM $K_3Fe(CN)_6$ + 0.1 M KCl at 10 mV s^{-1} (A). Reductive desorption of decanethiol SAMs in 0.5 M KOH at 50 mV s^{-1} (B). CVs on decanethiol SAMs (C) and on bare Au (D) in 1 mM Ag_2SO_4 + 0.1 M H_2SO_4 (solid line) and 1 mM $AgClO_4$ + 0.1 M $HClO_4$ (dotted line) at 10 mV s^{-1}.

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† Electronic supplementary information (ESI) available: CVs on the hexanethiol SAMs; CVs for the Cu, Pb, Tl systems; CVs depending on the pH and the convective condition; XPS; Experimental section. See DOI: 10.1039/b601613h

1.0×10^{-9} mol cm^{-2}. Such results demonstrate that the decanethiol SAMs have well-ordered structures with strong binding properties to Au surfaces.

Fig. 1(C) shows cyclic voltammograms (CVs) on decanethiol SAMs obtained 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^{-1}. On the basis of the electrochemical appearances that Ag deposition is dependent upon the anions employed, the SAMs behave like a sieve passing an ion with a defined size or property. It is well-known that a metal deposition on a bare metal substrate exhibits different atomic structures depending on the kinds of electrolytes utilized; however, events in which metal penetrates into the bush of SAMs, except for the retardation of an electron transfer, have not been studied much. Compared to the Ag deposition on bare Au substrates, where there is little difference in the features in the sulfates (solid line) and in the perchlorates (dotted line) as shown in Fig. 1(D), the introduction of decanethiol SAMs onto Au surfaces causes the Ag deposition to change dramatically. The cathodic current at the sulfate system that shifts negatively as a result of the kinetic hindrance of the SAMs begins to increase at 0.24 V, corresponding to the first UPD event at approximately 0.5 V, as shown in Fig. 1(D), while no peak appears in the perchlorates within a given potential window.

This phenomenon stems from the size and hydrophobicity of anions. A sulfate ion with an ionic volume of 25 cm^3 mol^{-1} and a hydrophilic character (more hydrated) shows more affinity to the bush of decanethiol SAMs than to the perchlorate ion with an ionic volume of 49.6 cm^3 mol^{-1} and hydrophobicity (less hydrated).[4] It is interesting that the sieving behaviour of SAMs exhibit only an Ag system, rather than a Cu, Pb, or Tl system (See ESI 1†), meaning that the hydrated cation as well as the anion is tightly connected with it. Considering the formation enthalpy of metal salts, Ag, among the metal–sulfur systems has the lowest value of −34.0 kJ mol^{-1} while the formation enthalpies of Cu–S, Pb–S, and Tl_2–S are −79.5, −100.4, and −97.1 kJ mol^{-1},[5] respectively, revealing that the anion dependency appears only in a system in which the metal–sulfur binding is sufficiently weak. In addition to this, the sieving behaviour of the SAM structures to the Ag deposition depending on the anions occurs in a system with a sufficient packing density of thiol molecules. The hexanethiol SAMs show nearly the same electrochemical features irrespective of the anions although there is a negative shift of the cathodic peaks (See ESI 1a†). Therefore, the sieving behaviour of the decanethiol SAMs to the Ag deposition is a particular phenomenological result governed by the size and hydrophilicity of the anions, the binding property of the metal to sulfur, and the order of the SAM molecules on the Au surface.

Fig. 2(A) shows cyclic voltammetry in the anion mixtures consisting of perchlorates and sulfates, in which the total molar concentration becomes 0.1 M. As the ratio of sulfates increases, the peak intensity increases and the Ag deposition peaks are shifted in the positive direction. This behaviour indicates that the sulfate ions determine if the Ag metal ion penetrates into the SAMs.

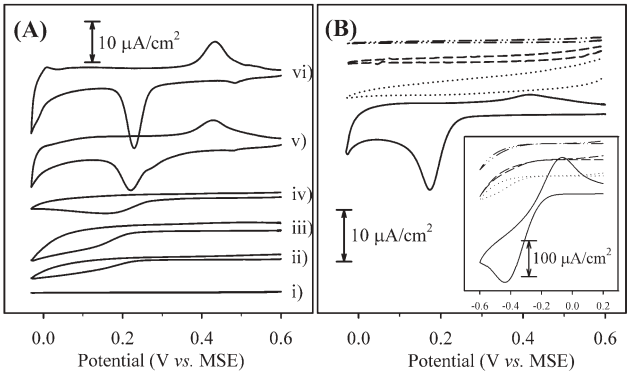

Fig. 2 The nature of an Ag deposition in terms of anion composition (A). CVs on decanethiol SAMs in 1 mM Ag^+ + 0.1 M H^+ + 0.1 M anions comprising with molar ratios of 1 : 0 (i), 9 : 1 (ii), 4 : 1 (iii), 1 : 1 (iv), 1 : 4 (v), and 1 : 9 (vi) of perchlorates : sulfates at 10 mV s^{-1}. The dependency of an Ag deposition in terms of anions (B). CVs on decanethiol SAMs in 1 mM Ag^+ + 0.1 M H_2SO_4 (solid), 0.1 M HNO_3 (dotted), 0.1 M $HClO_4$ (dashed), and 0.1 M KPF_6 (dash-dot-dot) at 10 mV s^{-1}. Inset: CVs in 10 mM $K_3Fe(CN)_6$ + 0.1 M KCl after Ag deposition and stripping in each electrolyte. Line shapes correspond to the systems used in Fig. 2(B).

The intrinsic properties of the anions, such as the ionic volume and the hydrophilicity or the order of hydration, that drive the interesting sieving behaviour of the decanethiol SAMs were considered in Fig. 2(B). The ionic volume of the sulfate (25 cm^3 mol^{-1}) is the smallest in the present systems; the ionic volume of the perchlorate is 49.6, and that of the nitrate is 34.5; that of hexafluorophosphate is unavailable. Consequently, one can conclude that the smaller size of the anions make the Ag easier to be deposited. In addition, the hydrophilicity of the anions plays a key role in the penetration of the Ag ions into the defects formed by the decanethiol SAMs. In the present systems, the hydration of the anions decreased in the order of $SO_4^{2-} \gg NO_3^- > ClO_4^- > PF_6^-$. In other words, the sulfate was the most hydrophilic anion among these. The inset shows the CVs in 10 mM $K_3Fe(CN)_6$ + 0.1 M KCl at 10 mV s^{-1} after three consecutive potential sweeps from 0.6 V to −0.03 V, according to individual solutions with different anions. Since a greater Ag deposition leads to a greater amount of breakage in the SAM structures, the case of the Ag deposition in sulfates exhibits the most noticeable electron transfer reaction. However, the electrochemical feature of the sulfate system shows a little kinetic retardation, revealing that decanethiol molecules are not completely desorbed and are reorganized. To completely strip decanethiol molecules from the Au surface under the present experimental condition (1 mM Ag_2SO_4 + 0.1 M H_2SO_4, 10 mV s^{-1}), at least 40 potential cycles must be conducted (data not shown here). In addition, it is interesting that the charging current values in the inset follow the hydration order (nitrates > perchlorates > hexafluorophosphates), indicating that the anion has an influence on the charge transfer reaction in the decanethiol SAMs.

Generically, the length of alkyl chains (the number of methylene units) as well as the kinds of terminal groups influence the molecular order and surface coverage of SAMs. Through electrochemical measurements of SAMs with alcohol or carboxyl terminal groups and hexyl or undecyl chains, the dependence of the sieving behaviour on the type of anion was investigated as shown in Fig. 3. From eight CVs, comprehensive knowledge concerning the Ag deposition on SAMs considering the kinds of anions can be obtained, as follows:

The Ag deposition prefers sulfates to perchlorates regardless of what terminal groups are employed in normal alkyl thiol molecules.

The longer the alkyl chain of the SAM molecules, the harder the Ag deposition and the more hindered the electron transfer, with a

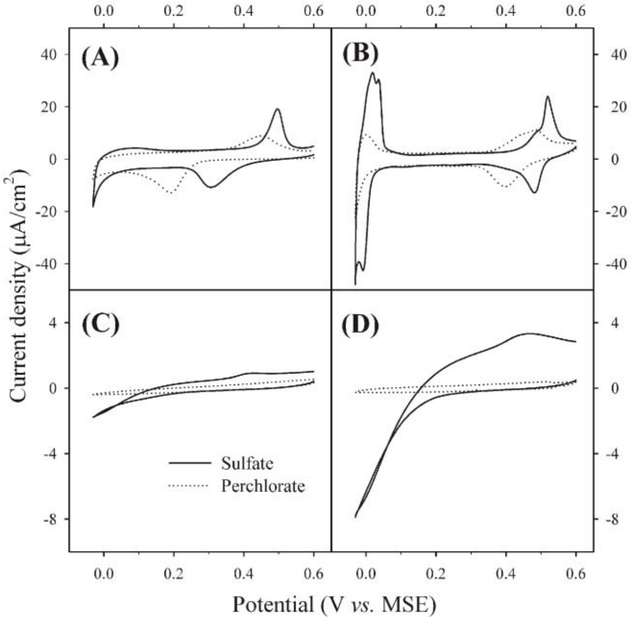

Fig. 3 The dependency of an Ag deposition in terms of terminal groups of SAMs. CVs on SAMs of 6-mercapto-1-hexanol (A), 3-mercaptopropionic acid (B), 11-mercapto-1-undecanol (C), and 11-mercaptoundecanoic acid (D) in 1 mM Ag_2SO_4 + 0.1 M H_2SO_4 (solid lines) and 1 mM $AgClO_4$ + 0.1 M $HClO_4$ (dotted lines) at 10 mV s^{-1}.

greater shifted peak potential [Comparing (A) with (C) and (B) with (D)].

The order of surface arrangements in SAMs with alcohol groups is superior to the order with carboxyl groups, resulting from the increase of currents and the positive shift of the peak potential [Comparing (A) with (B) and (C) with (D)].

In any case, the tendency of the Ag deposition preferring sulfates to perchlorates is maintained irrespective of terminal groups of the SAMs. Therefore, it is possible to confirm that the sieving behaviour of decanethiol SAMs for an Ag deposition stems from the anions themselves.

As the metal deposition has comparatively different properties concerning the concentration of hydrogen ions, the pH dependency of Ag in each anion is investigated by changing the cation part of the electrolyte salts (See ESI 2†). Replacing hydrogen ions with potassium ions gives a pH of 5. However, electrochemical features show the same tendencies as the case of the acidic condition shown in Fig. 1(c). Basic solutions were prepared by adding ammonia as an alternative into the neutral solutions because the hydroxide ions form insoluble silver hydroxide. Although potential windows shift to a negative direction and the portion of the charging current increases, the tendency for the Ag deposition on decanethiol SAMs preferring sulfates to perchlorates remains with the basic solution. This indicates that the hydrogen ion does not play a significant role in Ag deposition on the decanethiol SAMs. Therefore, one can conclude that sulfate anions give an easier pathway to the Ag penetration irrespective of the pH (acidic, neutral, basic), as mentioned earlier.

To eliminate the assumption in which the driving force for the sieving behaviour of SAMs comes from the kinetic hindrance of organic molecules on the Au substrate, a rotating disk electrode (RDE) experiment was performed (See ESI 3 †). Although the Au electrodes utilized in this experiment have a lower quality than those used in the stationary system, the tendency of the preference for sulfates for the Ag deposition is maintained even in the RDE. The inset exhibits a Levich's plot for the Ag deposition in perchlorates. In fact, the Levich's plot does not supply any meaningful insight in the UPD region because the UPD is a thermodynamic property and is governed by the binding character of an adatom and a substrate. It does, however, play a key role in determining the correct rotation speed as it influences the charging event.

In conclusion, the combined effects of the hydrated ions in an Ag deposition on decanethiol SAMs lead to the sieving behaviour of the SAMs even with a sufficient molecular ordering at a metal–organic interface. The driving forces of this phenomenological result stem from the ionic volume, the degree of hydration or the affinity to water of the anions, the binding property of the metal to sulfur, and the order of the SAM molecules on the Au surface. Irrespective of the pH, the kinds of terminal groups of SAM molecules, and the convective mass transfer, the Ag deposition prefers sulfates to perchlorates on decanethiol SAMs. Sulfates allow the pores of the SAM defects to take silver ions. Although further microscopic studies should be conducted with local probe methods, it is expected that the present results not only accelerate the rate of fundamental learning on the degree of hydration, the electron transfer, and the defect of SAMs at a chemically and structurally defined metal–organic interface but also add to the knowledge concerning the development of an anion sensor.

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