

Direct observation of a cooperative mechanism in the adsorption of heavy metal ions to thiolated surface by *in-situ* surface plasmon resonance measurements†

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S-type adsorption kinetics, obtained by surface plasmon resonance spectroscopy measurements, suggest that the rate of Pt²⁺ adsorption on 1,6-hexanedithiol (HDT) on gold increases until the surface coverage reaches *ca.* 17%, after which, the adsorption profile of Pt²⁺ follows Langmuirian behavior for the surface coverage.

Interesting observations on the molecular level of heavy metal ion adsorption kinetics to a thiolated (–SH) surface have emerged. That is to say that the kinetics of the adsorption of heavy metal ions, such as Pt²⁺ and Hg²⁺ to thiolated surface have been reported to increase as a function of coverage (cooperative adsorption).¹ In order to explain such a non-Langmuirian cooperative adsorption behavior, it has been tentatively proposed that the environment of the thiolated surface is initially hydrophobic, resulting in the initial slow kinetics but, once complexation occurs, the thiolated surface becomes more hydrophilic (*e.g.*, possibly as a result of the formation of charged –SM⁺ moieties) permitting the facile approach of solvated heavy metal ions to the surface and eventually, leading to faster kinetics (Scheme 1). However, this hypothesis has been developed, based on the *ex-situ* analyses of the supernatant in a mixed solution consisting of adsorbents and heavy metal ions. Moreover, for porous materials, the adsorption kinetics are difficult to interpret qualitatively, due to the complex components, such as pore geometry. In order to observe this cooperative adsorption phenomenon *in-situ*, we focused on the analogy between a self-assembled monolayer (SAM) on SiO₂ (representative system for the adsorption of heavy metal ions) and that on a gold substrate. Assuming that 1,6-hexanedithiol on a gold thin film offers a nearly identical complexation environment as thiolated silica for heavy metal ions, in that the functional group density is comparable to that of a thiolated material such as

silica,^{2,3} it would be expected that surface plasmon resonance (SPR) measurements, an evanescent wave technique possessing maximum sensitivity on the surface and characterized by an exponential decay of sensitivity with the distance from the surface,^{4–6} could be used to detect the cooperative adsorption *in-situ*.

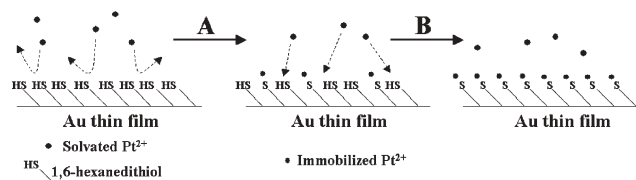
We utilized a six-phase, denoted as (012345), SPR system in the Kretschmann configuration using attenuated total reflection (ATR). The different phases were labeled as follows: 0, a glass slide (SF10), optically coupled to a 90° ATR prism; 1, a thin binder layer of Cr (5 nm); 2, a layer of Au thin film (50 nm); 3, a thiol-terminated self-assembled monolayer (SAM) of HDT; 4, a layer of adsorbed Pt²⁺; 5, an ambient dielectric medium of air (for the determination of parameters such as thickness and dielectric constant) or water (*in-situ* analysis). The time resolved SPR angle shift was measured using the fixed angle method which enabled the reflectance change, ΔR , to be correlated the SPR angle shift, $\Delta\theta_{SPR}$ linearly.⁷ The fixed incident angle for measuring the reflectance was adjusted before Pt²⁺ adsorption. The data for reflectance at a fixed incident angle was acquired by a computer in real time. During the monitoring of the reflectance, the prepared Pt ion solutions were allowed to flow into a teflon cell. The concentrations of metal ion were controlled as 0.1 and 1 mM in an aqueous solution.

We previously reported on the stepwise self-assembled 1,6-hexanedithiol multilayers by SPR in detail.⁸ The thickness and the dielectric constant of the HDT layer in the present study were estimated to be 5.9 Å and 2.0, respectively. According to Chempen 3D software (Hilton), the molecular length of the HDT was estimated to be 10.9 Å. Therefore, the HDT layer was estimated to be tilted by an angle of 57° to the surface normal. In the dielectric medium of air, when the HDT layer was fully saturated with Pt²⁺, $\Delta\theta_{SPR}$ was found to be 0.17°. In order to obtain this $\Delta\theta_{SPR}$, through the Fresnel equation, assuming that the thickness of the adsorbed Pt²⁺ layer is 0.6 Å from the ionic radius of Pt²⁺, the dielectric constant of fully-saturated Pt²⁺ layer is estimated to be 13 (see ESI†).

In order to convert $\Delta\theta_{SPR}$ to a surface coverage by metal ions for the *in-situ* analysis of Pt²⁺ adsorption on a thiolated gold substrate, the theory of Maxwell Garnett was employed here on the basis of neglecting the possible anisotropy of the adsorbed Pt²⁺ layer.⁹

$$\frac{(\epsilon_{\text{eff}} - \epsilon_4)}{(\epsilon_{\text{eff}} + 2\epsilon_4)} = \beta f \quad \text{where } \beta = \frac{(\epsilon_3 - \epsilon_4)}{(\epsilon_3 + 2\epsilon_4)} \quad (1)$$

Here f is the volume fraction (generally, this quantity is proportional to the surface coverage) occupied by Pt²⁺ and ϵ_3 and



Scheme 1 Proposed mechanism for Pt²⁺ adsorption to a thiolated surface assuming a series of two consecutive surface events.

† Electronic supplementary information (ESI) available: experimental and calculation details, schematic SPR configuration (Fig. S1), *in-situ* SPR curve of 1,6-hexanedithiol (HDT) on a gold substrate (Fig. S2). See <http://www.rsc.org/suppdata/cc/b5/b500652j>
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ϵ_4 are the dielectric constants of the fully adsorbed Pt^{2+} and the ambient material (water), respectively. From the fact that the optical response is proportional to the average film thickness (when adlayer thickness is very small),¹⁰ in this sense, it might be convenient to be assumed that a partially adsorbed Pt^{2+} layer is optically equivalent to a fully saturated Pt^{2+} layer with a dielectric constant of 13. On the other hand, a fixed film thickness of the Pt^{2+} layer and a variable dielectric constant could be considered to represent the adsorption event of Pt^{2+} in more reasonable way. To test these two assumptions, changes in $\Delta\theta_{\text{SPR}}$ as a function of surface coverage for a fixed thickness and for a fixed refractive index were calculated.¹¹ For the latter assumption, the effective dielectric constant of the adsorbed Pt^{2+} layer was obtained using eqn. (1) by varying the surface coverage. These two assumptions (one is the fixed thickness and the other is the fixed dielectric constant) are compared on the basis of $\Delta\theta_{\text{SPR}}$. As can be seen in Fig. 1 (upper figure), the difference in optical responses of these two cases for the same surface coverage are insignificant. It should be noted that the optical response is nearly identical for both cases until a surface coverage of 30% is reached. Therefore, this result shows that it is also reasonable to use the thickness of the Pt^{2+}

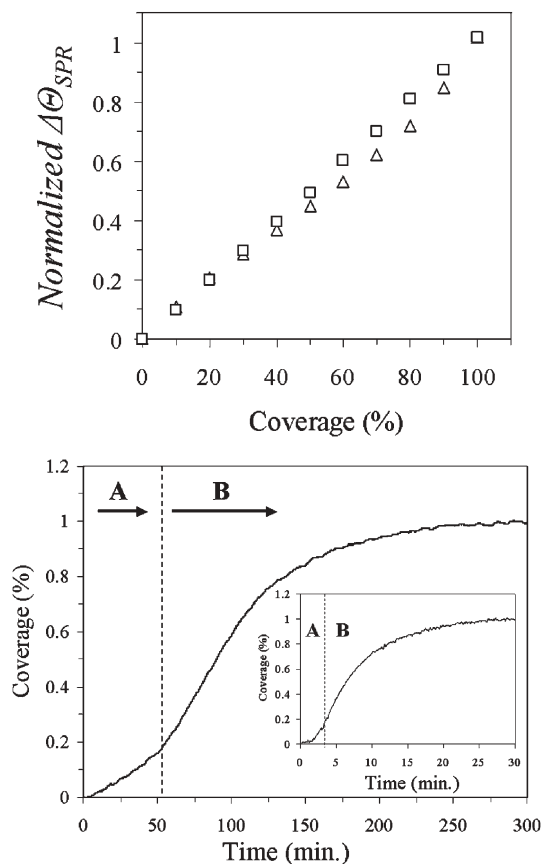


Fig. 1 (Upper figure) Calculated change of the relative SPR angle (normalized $\Delta\theta_{\text{SPR}}$) at a fixed wavelength of incident light as a function of increasing surface coverage. (\square) Layer of fixed thickness (0.6 Å) and variable effective dielectric constant (1.7769 ~ 13). (Δ) Layer of fixed dielectric constant (13) and variable thickness (0 ~ 0.6 Å). (Lower figure) *In-situ* SPR measurements of the adsorption kinetic of Pt^{2+} on HDT-Au in an aqueous solution at 0.1 mM of Pt^{2+} solution. Inset figure obtained from 1.0 mM of Pt^{2+} solution.

layer as a variable with a constant dielectric constant of 13, in order to probe the *in-situ* kinetics of Pt^{2+} adsorption.

Fig. 1 (lower figure) shows that the adsorption of Pt^{2+} to the thiolated surface follows S-type adsorption behavior. The thiolated surface is found to be saturated by Pt^{2+} within 240 min. Obviously, S-type adsorption kinetics indicate a cooperative mechanism, namely, an affinity that increases with coverage. It should be noted that this cooperativity continues for 50 min from the beginning of Pt^{2+} adsorption. Although the initial concentration of Pt^{2+} increases up to 1 mM (see inset), S-type adsorption behavior is still maintained. The observed cooperativity in the adsorption of 1 mM Pt^{2+} reduces after 3 min and Pt^{2+} adsorption is found to be completed in about 24 min. Considering that the instantaneous reaction rate defined approximately as the slope of the tangent drawn to the curve shows a variation of rate with time/coverage, the adsorption can be divided into A and B. In region A, the adsorption rate increases with coverage. In region B, the adsorption behavior is likely to be similar to the Langmuir type. The fact that the inflection point for the two cases appears at a coverage of around 17% suggests that, after the surface coverage reaches a certain value, the adsorption of Pt^{2+} follows Langmuirian behavior. In other words, the acceleration in

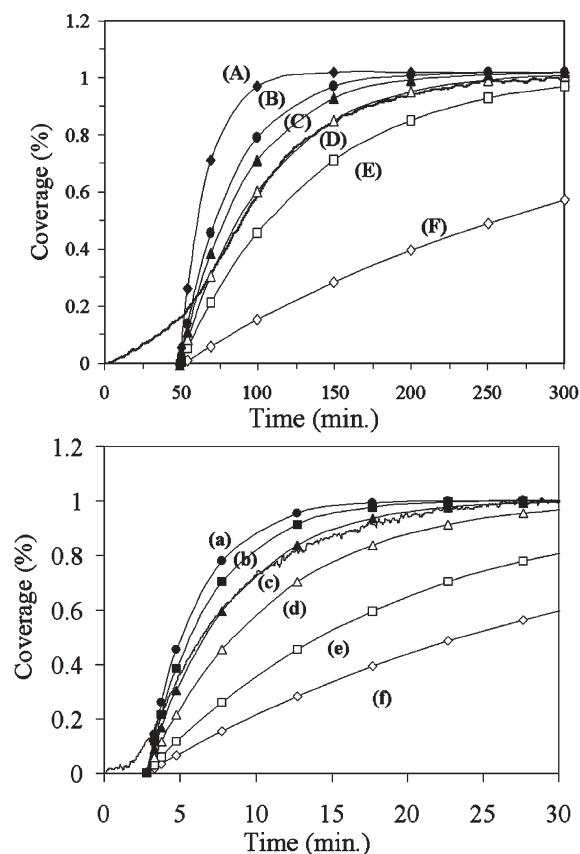


Fig. 2 (Upper figure) Comparison of *in-situ* Pt^{2+} adsorption data obtained at 0.1 mM solution with first-order Langmuir kinetics varying the rate constant, k_a of (A) 1.0×10^{-2} , (B) 5.0×10^{-3} , (C) 4.0×10^{-3} , (D) 3.0×10^{-3} , (E) 2×10^{-3} , and (F) 5.5×10^{-4} . (Lower figure) Comparison of Pt^{2+} adsorption data obtained at 1.0 mM solution in the same manner. In this case, the rate constant, k_a , in each prediction is (a) 1.0×10^{-2} , (b) 5.0×10^{-3} , (c) 3.0×10^{-3} , (d) 2.0×10^{-3} , (e) 1×10^{-3} , and (f) 5.5×10^{-4} , respectively.

adsorption rate decreases dramatically, as the coverage increases over 17%. A coverage-dependent acceleration in adsorption rate of Pt²⁺ is also evident from the fact that similar trends are also observed for the adsorption of 1 mM Pt²⁺. Consistent with this explanation, we also find that coverage with time in Fig. 2 (region B) follow a first-order Langmuir adsorption kinetics.¹²

$$\frac{d\Gamma}{dt} = k_a C_o \left(1 - \frac{\Gamma(t)}{\Gamma_{\max}} \right) \quad (2)$$

Here, $\Gamma(t)$ is the time-dependent surface coverage for the adsorbed Pt²⁺ molecules, Γ_{\max} is the maximum possible coverage.

The line in Fig. 2 shows the fit of the eqn. (2) to the experimental data and k_a is determined to be $3.0 \times 10^{-3} \text{ min}^{-1}$ from this fit. Furthermore, the parameter describing the two different cases are self-consistent. The same rate constant for Pt²⁺ adsorption is obtained in a kinetic analysis using a different initial concentration.

In summary, we show herein that surface plasmon resonance measurements allows the direct observation of a cooperative mechanism for the adsorption of Pt²⁺ to a thiolated surface. The acceleration in adsorption rate depends strongly on the extent of coverage. Cooperativity diminishes significantly as the coverage reaches ca. 17%. Since a kinetics analysis by SPR measurements is very flexible in terms of easily-tuned surface functionality, we further anticipate numerous applications of such a straightforward approach for examining the adsorption characteristics of heavy metal ions to a functionalized surface.

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