Communication

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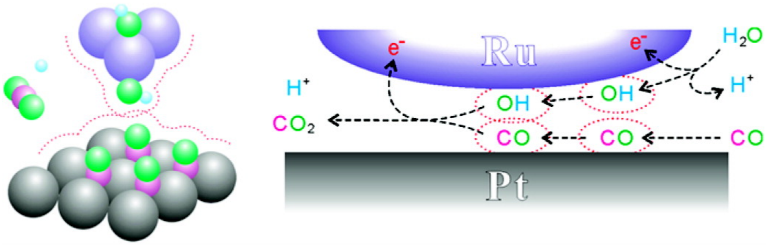

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Direct Observation of Electrocatalytic Synergy

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Here we describe an approach that directly and unambiguously establishes the synergistic effect between surfaces when brought into close proximity (Å's regime) through the use of an STM (scanning tunneling microscope). As a model system, we have employed the electrocatalytic oxidation of CO chemisorbed onto a Pt(111) single-crystal electrode upon engaging a Ru tip. Synergistic effects are believed to play key roles in heterogeneous catalytic processes involving multicomponent systems. A well-known example in electrocatalysis is the oxidation of CO on the bimetallic Pt−Ru surface.[1,2] Briefly, Ru is more active than Pt in the water-discharge reaction (R1) that produces OH_{ads}, a required reactant in the reaction with $Pt{-}CO_{ads}$ to yield CO_2 (R2).

$$\mathrm{Ru} + \mathrm{H_2O} \rightarrow \mathrm{Ru{-}OH_{ads}} + \mathrm{H^+} + \mathrm{e^-} \qquad \text{(R1)}$$

$$\mathrm{Pt{-}CO_{ads}} + \mathrm{Ru{-}OH_{ads}} \rightarrow \mathrm{Pt} + \mathrm{Ru} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{e^-} \qquad \text{(R2)}$$

In general, synergistic effects should be universal in catalytic processes involving two different molecules as reaction partners. Since the two reacting molecules are generally different in chemical nature, the optimal surfaces to adsorb and activate them should also be different. Combining surfaces with optimal reactivity toward the individual reactants should give rise to enhanced catalytic activity when compared to a single surface. Detailed studies of such synergistic effects could provide most valuable mechanistic insights into numerous catalytic processes. An especially relevant question is whether synergistic effects can be directly observed for reactions taking place at the boundary between two surfaces.

One of the basic requirements for a surface reaction to occur between a molecule **a** adsorbed on surface **A** and a molecule **b** adsorbed on surface **B** is that they have sufficient overlap/interaction at the boundary (Figure 1a). However, this does not necessarily imply that surfaces **A** and **B** must be in actual physical contact; rather, they need to be sufficiently close so that the reaction is rendered feasible (Figure 1b).

Such a concept can be implemented through the use of an STM since it operates on the relevant dimensional regime of Å's. It should thus be possible to employ an STM to bring two surfaces (**A** and **B**; tip and substrate), onto which reactants **a** and **b** are adsorbed, sufficiently close so that reaction between **a** and **b** is enabled (Figure 1c). In addition, the STM tip would detect and monitor the signal (Faradaic current in the present case) arising from such a reaction.

An ideal test model system is the oxidation of CO at the interface between Pt and Ru surfaces, akin to a Pt−Ru bimetallic catalyst. One could employ a Ru tip to approach a Pt substrate in a CO-saturated solution. By controlling the potential, the Pt surface can be covered by CO_{ads}, while OH_{ads} could be generated on the Ru surface via the water-discharge reaction (R1). Upon engaging the Ru and Pt surfaces, the CO electrooxidation reaction (R2) could be induced, and the Faradaic current associated with the reaction detected at the Ru tip.

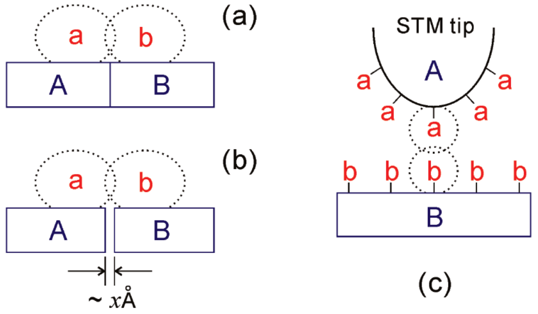

Figure 1. Schematic depiction of the synergistic effect between two surfaces. (a) Conventional dual component catalyst in which molecules **a** and **b** interact/react at the boundary of components **A** and **B**. (b) The concept of separating surfaces **A** and **B** with a sufficiently small distance gap (e.g., a few Å's), so that molecules **a** and **b** can still interact and react. (c) The implementation of part b by using an STM to bring two surfaces in very close proximity and then by monitoring the signal arising from the induced reaction.

To achieve this, the STM must be operated under constant-height mode so that the distance between the Ru tip and the Pt substrate is maintained constant during electrochemical STM measurements. The current at the tip would consist of the tunneling current and the Faradaic current with the latter being the quantity of interest, and the former an interference which could be essentially eliminated by shutting down the feedback loop and nulling the bias voltage between the tip and the substrate (see the Supporting Information for experimental details). The residual tunneling current can thus be made sufficiently small to be negligible and independent of the potential applied. Hence, the recorded tip current would be largely dominated by the Faradaic contribution.

A number of additional stringent requirements must be met with one of the main challenges arising from the drifting behavior of the piezos,[3] which makes it very difficult to maintain (at room temperature) a fixed tip position (in the nanometer regime) relative to the substrate surface. To mitigate the impact of such drift, we employed a Pt(111) single-crystal electrode and placed the tip over a large flat terrace to minimize the probability of "crashing" the tip onto the surface. We repeated the measurements on multiple occasions and with different tips to ensure reproducible results.

A Pt(111) single-crystal electrode, prepared by the well-established flame-annealing method,[4] was employed as the STM substrate. Figure 2a shows an STM image of the Pt(111) electrode obtained with a Ru-coated Au tip (vide infra) under electrochemical

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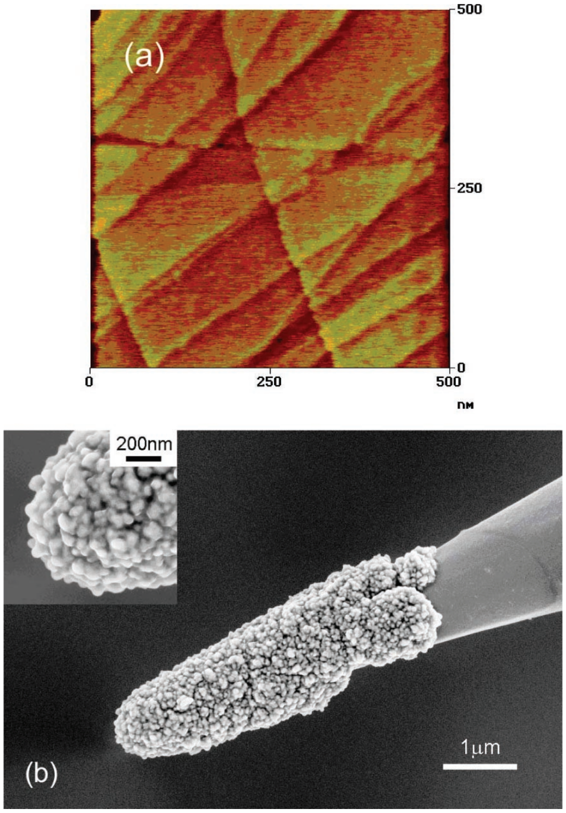

Figure 2. (a) STM image of the Pt(111) electrode recorded with a Ru-decorated Au tip under in-situ EC-STM conditions (0.1 M $HClO_4$ as the supporting electrolyte, the potential of the Pt(111) substrate was 0.15 V vs RHE, the bias voltage was 10 mV). (b) Representative SEM image of a Ru-decorated, Apiezon wax-masked, Au tip. Inset shows a higher resolution image of the apex of the tip area.

conditions with 0.1 M $HClO_4$ as supporting electrolyte. The image reveals large and well-defined terraces with typical dimensions in excess of 100 nm. For observing the catalytic synergy, the Ru tip was centered over one such terrace and scanned slowly over a small area, typically 5×5 nm^2.

Ru tips were prepared by electrochemical deposition of Ru onto a Au tip (Figure S1, see the Supporting Information for experimental details). Figure 2b presents an SEM image of a thus-prepared Ru/Au tip. The image reveals that the tip consists of globular clusters with a typical radius of ca. 30−50 nm (inset in Figure 2b). The tip exhibited a pseudocapacitance response typical of Ru, with a “charging” current on the order of 10 pA (Figure 3a). After electrochemical characterization, the Ru tips were screened by STM imaging over an HOPG substrate. Only those tips producing well-defined and atomically resolved STM images for HOPG were chosen for subsequent experiments.

Direct observation of the electrocatalytic synergy was finally achieved by engaging a Ru tip to a Pt(111) substrate in a CO-saturated $HClO_4$ solution and subsequently measuring the current response of the Ru tip with respect to the applied potential (see the Supporting Information for experimental details). The potential region investigated was limited to the range of +0.1 to +0.6 V (vs RHE), since over this range the adsorbed CO completely passivates the Pt(111) surface. At potentials beyond +0.6 V, CO oxidation begins on Pt(111) surfaces.

Figure 3b presents a cyclic voltammetric profile at 50 mV/s for a Pt(111) electrode in contact with a CO-saturated 0.1 M $HClO_4$ solution. It is evident that for potentials of up to +0.6 V, the surface is completely passivated. As the potential sweep is extended to more positive values, the typical response for the oxidation of CO is observed. Notice that there is a current in the reverse sweep because there is CO present in solution.

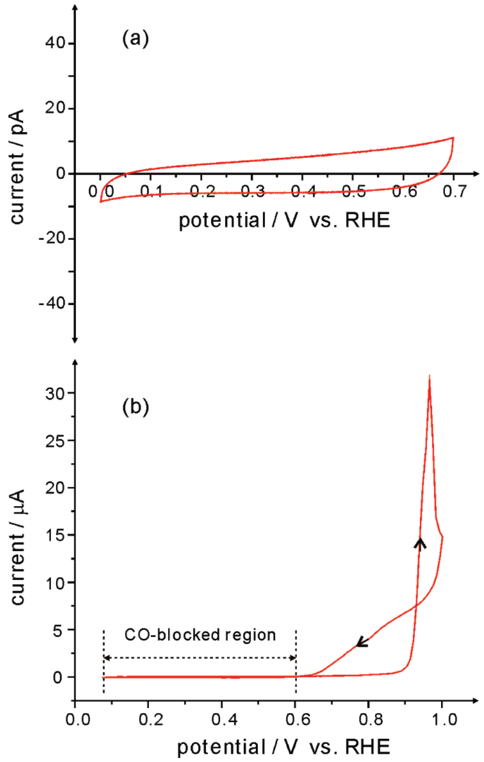

Figure 3. (a) Representative cyclic voltammogram at 50 mV/s for a Ru-decorated Au tip electrode in a deaerated 0.1 M $HClO_4$ solution. (b) Cyclic voltammogram at 50 mV/s of a Pt(111) surface in a CO-saturated 0.1 M $HClO_4$ solution. The CO blocking potential region (up to +0.60 V) was used as the working potential region in our study.

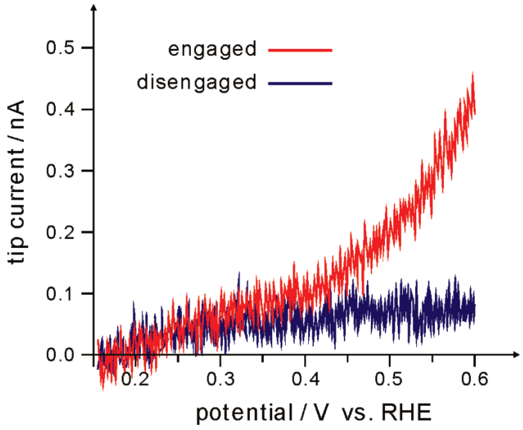

Figure 4. *I*−*V* curves of the Ru tip recorded upon engaging with and disengaging from the Pt(111) surface in a CO-saturated 0.1 M $HClO_4$ solution. Typical operating parameters for STM engaging were 10 mV in bias voltage and 2 nA in set-point current. *I*−*V* curves were recorded by simultaneously scanning the potentials of the Ru tip and the Pt(111) substrate with zero potential difference between them. The potential scanning rate was 50 mV/s.

Figure 4 presents voltammetric scans (at 50 mV/s) for a Ru tip under conditions where the tip is far from (disengaged) as well as in close proximity to (engaged) the Pt(111) surface with adsorbed CO. In the disengaged position, only charging currents were observed. The voltammetric response is dramatically different when the Ru tip is engaged with the CO-covered Pt(111) surface. As seen in Figure 4, under these conditions, there is a great enhancement in the anodic current with an onset potential around +0.35 V, a value that falls well within the range reported for CO oxidation at Ru-decorated Pt(111) model catalysts.[2]

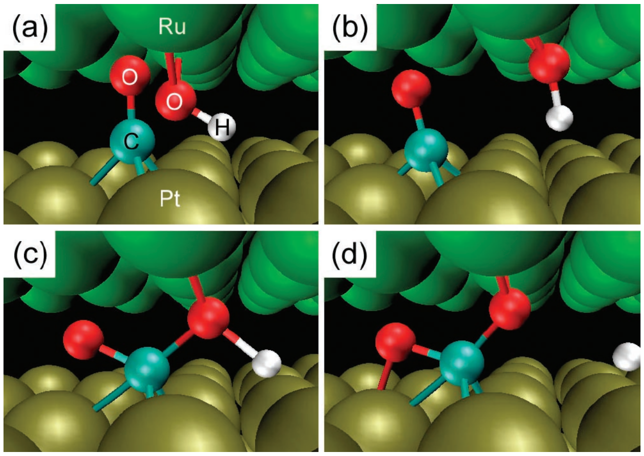

Figure 5. DFT simulations, as a function of separation, for bringing Ru and Pt surfaces, with OH and CO adsorbed respectively, into close proximity. (a) A representative initial state of the molecular dynamic process with adsorbates siting at nearest energy-favorable positions. (b) When the distance between surfaces is 4.5 Å, the calculation converges to a state in which OH_{ads} and CO_{ads} are further separated. (c) When the distance between surfaces is reduced to 4.0 Å, OH_{ads} and CO_{ads} start to interact and form a transition state. (d) Subsequent convergence of panel c, resulting in the dissociation of the O−H bond.

Ⓦ A movie demonstrating the whole molecular dynamic process of the O−H bond breaking is provided.

This experiment has been reproducibly repeated with different tips and with consistent results observed in all cases. Such a current enhancement was never observed in a CO-free solution or with a bare Au tip. In addition, the model reaction studied is elementary so there is no side reaction or intermediates involved. Thus, concerns about positive feedback of reaction intermediates can be safely ruled out. This unambiguously demonstrates that the current enhancement can only be ascribed to the electrooxidation of CO induced by the synergistic effect that occurs upon engaging the Ru tip with the CO-covered Pt(111) surface. Moreover, the tip $I-V$ curve recorded after disengaging the tip from the substrate recovered completely to what it was before engaging, indicating that the change in the tip $I-V$ curve is reversible and that no Pt atoms were incorporated into the Ru tip during the experiment.

To evaluate the validity of the magnitude of the observed anodic current upon engaging the Ru tip with the CO-covered Pt(111) surface, we estimated the surface diffusion limiting current of CO oxidation based on a simplified model presented in detail in the Supporting Information. The value obtained from such an analysis shows that, taking the surface diffusion coefficient of CO on Pt (111) as 10^{-6} cm^2/s,[5] the surface diffusion limiting current would be beyond 1 nA, which is more than sufficient to sustain the electrocatalytic currents observed.

A fundamental and key consideration relates to the tip-substrate distance. Whereas a knowledge and control of the absolute value of the tip to substrate distance would be of great value, such information is rarely available in STM experiments due to the strong environmental fluctuation under electrochemical conditions.[3,6] Nevertheless, we employed density functional theory (DFT) calculations to simulate the engaging situation between a Ru surface and a Pt surface, with OH and CO adsorbed, respectively (Figure 5a), and to observe the critical distance to induce reaction R2. It appears that when the distance between the Ru and Pt surfaces is greater than 4.0 Å, OH_{ads} and CO_{ads} prefer to stay away from each other (Figure 5b). Only if the Ru and Pt surfaces are brought closer to reach a critical distance of 4.0 Å, do the $Pt-CO_{ads}$ and $Ru-OH_{ads}$ species interact to form a transition state (Pt−OC···OH−Ru), as shown in Figure 5c. This transition state is similar to that calculated for a Pt−Ru alloy surface[7] and subsequently leads to the spontaneous dissociation of the O−H bond (Figure 5d), upon which reaction R2 is accomplished with the H atom oxidized to H^+.

The experimental result presented in Figure 4 provides clear and compelling evidence for the electrocatalytic synergy between the Ru tip and the Pt surface in the oxidation of adsorbed CO. Furthermore it provides mechanistic details that are simply inaccessible when employing conventional experimental conditions. For example, whereas reaction R2 clearly involves charge transfer, one cannot, with conventional methods, establish the direction of electron flow. Under our experimental conditions, however, we can experimentally observe that the current flow is to the Ru tip. There is also the question of whether the enhanced activity is due to alloying or simply having Pt and Ru sites in close proximity.[8] Again, whereas conventional measurements cannot distinguish between these two possibilities, we can unambiguously establish the significance of physical proximity of sites, though this does not rule out the possible contribution of the alloying effect in a practical catalyst. These seemingly simple observations, however, provide a great deal of valuable mechanistic insight in the deliberate design of more active catalysts.

This experimental approach could also provide insights on activity-morphology relationships of a catalytic surface. This is a topic of great fundamental and technological relevance, but one that has lacked an effective method for study. Our experimental arrangement should not be confused with scanning electrochemical microscopy (SECM)[9] which can be used to monitor electrochemical reactions taking place within the diffusion layer (on micrometer scale), which is fundamentally different from the situation discussed in the present work.

Whereas, in this Communication we describe the application of this approach to the electrocatalytic oxidation of CO, there are numerous other processes that could, in principle, be investigated. Moreover this technique could be employed as a new approach for catalyst exploration and characterization.

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Supporting Information Available: Experimental and computational details, and supplemental figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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