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Oxygen Evolution Reaction Electrocatalyzed on Fenton-treated Gold Surface

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Hydroxyl radicals from the Fenton reagent remove meta-stable surface gold atoms (low coordinated high-energy surface atoms) on Au surface, thus precluding the formation of stable oxides. The resultant smooth surface, on hydroxyl-radical activation electrocatalyzes oxygen evolution reaction in 0.1 M NaOH at overpotentials lowered by 190 mV @ 10 mA.cm^{-2}

Gold, initially thought to be inert has interesting electrochemistry in addition to its importance in nanochemistry[1]. It plays a major role in two opposing electrochemical reactions, viz., oxygen-reduction (ORR) and –evolution (OER) in alkaline medium involving transfer of four electrons[2]. Gold is known to be the best catalyst-support for OER because of its promotional interaction (due to its high electronegative character) with first transition elements such as Ni and Co[3]. Interestingly, gold surface itself can participate in the process of OER in alkaline solutions, though at high overpotentials . Obviously, the potential-dependent surface conditions dictate the course of this reaction; lesser the stability of gold oxides higher the rate of oxygen evolution[4]. The *formation of stable bulk oxides on noble metals is the primary reason for the slow kinetics of OER*[5]. It is also now confirmed that the decomposition of Au-OOH intermediate in both acidic and alkaline solutions results in the formation of monolayer gold oxide followed by oxygen evolution[6]. It is worthwhile trying to see if the thesis of all these studies on polycrystalline gold surface can reveal the nature of active sites required for this important reaction. The polycrystalline gold displays certain faradaic processes especially in alkaline solutions, the reason being the formation of "incipient oxides" prior to the formation of monolayer oxide in the double layer region. The incipient oxides arise from the oxidation of low-coordinated gold atoms or clusters (in other words, *asperities*) which are very reactive. There is a gamut of anodic oxidation reactions such as oxidation of alcohol, carbohydrate, aldehyde, acids that are catalyzed by the incipient oxides[7]. It is intriguing to interrogate if these asperities play any role in water oxidation reaction yielding O_2. The studies presented in this report are an attempt to understand the relationship between asperities on bulk- and nanoparticle-gold[8] and OER activity. Surface asperities were found by Scholz et al[8] to be electrocatalytic to reactions involving inner-sphere electron transfer and free-radical intermediates (like reduction of oxygen and proton,

oxidation of hydroquinone), removal of which leads to the deactivation of Au surface towards these reactions. The premise here is to carry out water oxidation on gold in the presence and absence of asperities. For the first time, we show Fenton-treated (ft) (asperity-free) Au surface to be electrocatalytic unlike in the reports of Scholz.

In the course of investigations on the behaviour of gold in the anodic region, we observed electrocatalysis of OER after the asperities are removed by the hydroxyl radicals. The observations presented in Fig.1 may form the basis for understanding the nature of active sites involved in OER. Fig.1 shows the effect of Fenton treatment (ft) on OER; a regular shift of onset potential[9] with increasing duration of Fenton treatment (SI.Part(b)) is accompanied by significant increase in current density. The onset of oxygen evolution is seen at 1.8V *vs.* RHE on the mechanically polished gold (mp-Au) which is in agreement with the results of Bell et al[3]. After one hour of Fenton treatment, the onset potential (measured at a current density of 10 mAcm^{-2} at which severe oxygen gas evolution does not occur, Fig.S1) decreases by 190 mV compared to that on the mp-Au surface. The corresponding current increases enormously with very high i/E slope 264 mAcm^{-2}/V. In order to check if the behaviour of Au surface follows the trends observed by Scholz et al., we carried out the physical/electrochemical surface characterization before and after Fenton treatment (time duration = 1 hour): (1) atomic force microscopy (AFM) reveals surface smoothening (Fig.S2(a-d), SI. Part (c).); (2) in acid medium (a) the charge under the gold reduction peak decreases drastically (Fig.3); (b) the redox of the outer-sphere ET reactions (e.g., Ru(NH$_3$)$_6^{2+/3+}$ redox (Fig.S3)) remain unchanged; and (c) whereas the ft-Au surface is deactivated towards the surface-sensitive reactions (e.g., hydroquinone redox and oxygen reduction reactions (Fig.S3). After ensuring the attainment of Scholz's surface conditions in acidic medium, we tested the electrochemical behaviour of the ft-Au surface (on prolonged exposure to hydroxyl radicals) vis-à-vis mp-Au in 0.1M NaOH instead of an acid solution. Fig.3 shows the voltammogram of gold surface in 0.1M NaOH in the pre-monolayer formation region, viz., 1.38 to 1.58V vs. RHE before and after Fenton treatment. The contrast can be easily noticed in the gold response in H$_2$SO$_4$ vs NaOH solutions. Gold reduction charge, when examined in 0.5M H$_2$SO$_4$[8] decreases from 485 to 128 µC.cm^{-2} after Fenton treatment, but remains unchanged in the case of 0.1M

NaOH (Fig.S5). This suggests that both low-coordinated atoms (asperities or in other words, metastable metal surfaces, MMS[9]) and fully coordinated atoms (in other words, equilibrated metal surfaces EMS)[9] are equally reactive towards anodic oxidation in alkali. Both mp- and smoothened ft-Au surfaces were then subjected to potential excursion into the anodic region in 0.1 M NaOH solutions (Fig.1). Figure 1 shows the reduction peak, X arising from Au reduction and Y, from the oxygen reduction reaction (ORR), in addition to the features of OER in the anodic direction. The voltammetry of ORR does not differ before and after Fenton-treatment of the gold surface, obviously due to the outer-sphere nature of ORR in the alkaline medium (Fig.S4) in contrast to the inner-sphere nature of OER. According to Bard et al[10], oxygen reduction in alkaline medium follows outer-sphere electron transfer mechanism and hence no changes are expected in its kinetics on the ft-Au surface (in contrast, OER is slower in the acidic medium due to limited surface oxidation, Fig.S4). There is a concomitant increase in the ORR peak current at 0.82V *vs*.RHE with increasing oxygen evolution current at 1.80 V *vs* RHE which in turn varies with the duration of exposure to hydroxyl radicals. Hence, the oxygen reduction current at 0.82V *vs*. RHE (Fig.1) can serve as a measure of the extent of oxygen evolution (as the latter is carried out in oxygen-free argon atmosphere).

In this context, we have studied OER kinetics on mp-Au (in presence of asperities) and ft-Au (in the absence of asperities) surfaces. Incidentally, the position of the potential at 1.58V *vs*. RHE at pH = 13 points to the equilibrium, $H_2AuO_3^-/HAuO_3^{2-}$ (gold hydrous oxide) in the potential-pH Pourbaix diagram for gold. These changes in OER onset potential and current density might be due to the increased instability of the gold oxides on the ft-Au surface. Though adsorption of OH- occurs at several hundred millivolts before oxide formation, OER does not take place at low overpotentials. As OER is a consequence of oxide decomposition it depends on the gold-oxygen bond strength.
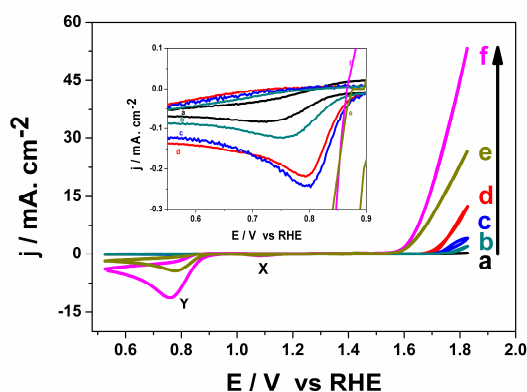

Figure 1: Cyclic voltammetric response of gold surface in 0.1M NaOH: mp-Au (a), ft-Au: Treatment time: 10 (b), 30 (c), 60 minutes (d). Electrodeposited nickel on mp-Au (e); on smoothened ft-Au (f); (scan rate =10 mV/s) Inset shows ORR response at 0.88V *vs*. RHE.

Kinetic analysis of the current-potential curves using the Tafel relationship, η = a + b ln i reveals the mechanistic details of OER on mp- and ft-Au surfaces. For each experiment, the Au electrode surface was exposed to hydroxyl-radicals for a pre-set time duration and the electrode was then transferred to the test solution containing 0.1M NaOH. Steady-state polarisation curves were then recorded for both mp- and ft-Au surfaces for various time duration of exposure.
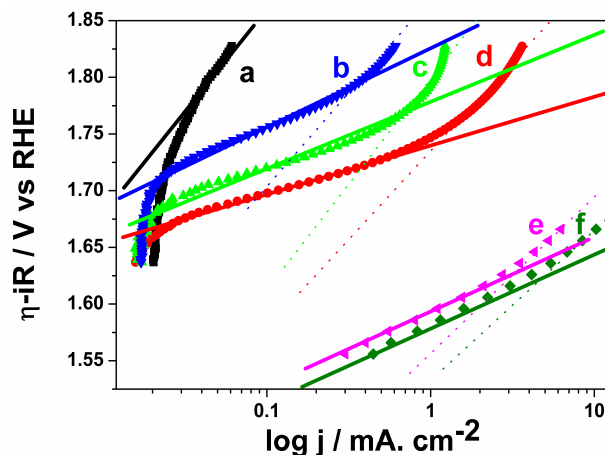

Fig. 2 Tafel Plots for OER on (a) mp-Au, (b) ft-Au, Fenton-treatment for (b) 10, (c) 30, (d) 60 minutes. Nickel-electrodeposited on (e) mp-Au; and (f) smoothened ft-Au in 0.1M NaOH.(thick line indicates slopes at lower over potential, dotted lines indicate slopes at higher overpotential)

Typical iR-corrected Tafel plots for the hydroxyl-activated surfaces in 0.1M NaOH solutions are shown in (Fig. 2). An important kinetic feature evident in Fig.2 is the variation in the Tafel characteristic with increasing time duration of Fenton-treatment. At low overpotentials, the Tafel slope (b) depends on the extent of exposure of mp-Au surface to hydroxyl radicals. When the exposure is for 60 minutes b is ca. 35 mV/decade whereas for other time durations of 30, 10 and 0 minutes, the b values are ca. 67, 89 and 134 mV/decade respectively[11]. The Tafel slopes observed for all the electrode surface conditions at higher overpotentials are around *ca*.135 ± 10 mV/decade. The electrochemical impedance analysis performed in the lower overpotential region of OER (1.62V vs RHE, Fig.S6) also clearly shows decreasing R_{ct} on ft-Au surface (Table 1). The R_{ct} value for the ft-Au gold surface, 2.65 kΩ is 6.7 times lower than that of the mp-Au surface. The time constant (RC) for the ft-Au surface at OER onset potential is 7.8 ms, which is much lower than that of the mp-Au surface (100 ms). Reduction in the time constant value reflects faster rate of electron release compared to the mp-Au surface. These two parameters again suggest that the ft-Au surface is highly active for OER.

In the alkaline medium, the OH^{-} adsorption and $Au/H_2AuO_3^-$ formation are very facile at 1.62V *vs* RHE. Hence, their contribution to the overpotential is negligible. The Au-O bond formation appears to be highly irreversible on the mp-Au surface (MMS) with the bond strength varying with the nanoscale surface morphology of gold. In the case of smoothened ft-Au surface, the surface is left with equilibrated gold atoms (completely filled d–orbitals). Here, the stability of gold oxides formed on the smoothened surface may be relatively lower than those formed on the mp-Au surface. The gold oxide present on the smoothened ft-Au surface is likely to be unstable in the alkaline medium. This is due to the fact that decomposition of the gold oxide $(HAuO_3^{-2})^{12}$ on the smoothened ft-Au is more favored than on the mp-Au surface in alkaline medium. Hence, the OER overpotential on the smoothened surface is lesser than the roughened surface. To explain this phenomenon it is instructive to consider the effect of exposure of mp-Au surface to hydroxyl radicals which removes asperities, leaving behind a smooth Au surface with a layer of nascent oxides (undefined) formed as a result of hydroxyl-radical activation. The EMS is also affected by hydroxyl radicals, leading to gold oxide formation. These gold oxides are reduced electrochemically during the potential scan into

the gold reduction potential region. These reduced gold surfaces may act as newly generated nascent MMS. It may also be that the hydroxyl radicals merely activate the EMS but not fully oxidize the surface to form partial Au oxides. In other words, nascent MMS (Au nuclei) are repeatedly created.
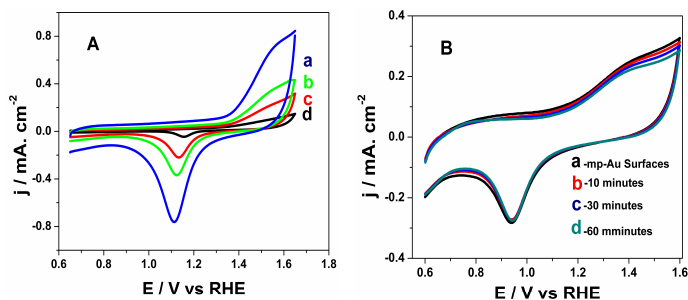

Figure 3: Cyclic voltammetric response of gold surface; (Panel A) in 0.5M H_2SO_4, mp-Au (a); ft-Au, Treatment time (in minutes): 10 (b), 30 (c), 60 (d). (Panel B) in 0.1M NaOH, mp-Au (a); Treatment time (in minutes): 10 (b), 30 (c), 60 (d). Scan Rate: 50 mVs^{-1}.

Under the voltammetric conditions, oxygen gas evolution occurs quite vigorously initially at an α-oxide coated gold surface, and β-oxide formation apparently occurs as a side reaction, i.e., gas evolution involves repetitive formation and decomposition of an unstable higher oxide (probably AuO_2), and the resulting disturbance of the α-oxide film leads to a gradual accumulation of an outer, porous, gold β-oxide deposit[13]. In the course of potential cycling, each cycle results in the formation and reduction of the place-exchanged α-oxide in the negative potential sweep leading to the formation of some MMS atoms that in turn are converted to β-oxide species in the next positive sweep. Fresh MMS surface is generated for a few hundred cycles and this factor puts a limit on the longevity of the electrode for OER. In order to ascertain if the negative potential shift of the OER onset potential is caused by the presence of Fe ions arising from the Fenton-reagent, a control experiment involving the treatment of Au surface in a solution of ferrous ammonium sulphate was carried out. However, no electrocatalytic effect on OER is seen, but only in the presence of hydrogen peroxide it showed activity towards OER. This control experiment confirms that the negative potential shift and increased exchange current density are the result of enhanced kinetics of OER on the hydroxyl-radical-activated ft-Au surface, with the current increasing as a function of treatment time. In addition, the x-ray photoelectron spectrum (XPS) (above 700 eV) does not show features other than those for the polycrystalline Au surface (Fig.S7). This analysis rules out the possibility of the presence of Fe ions on the Au surface upon Fenton-treatment, as was observed in other cases[14]. Considering Au's superiority as a catalyst-support material, we have studied OER on nickel-deposited gold surfaces, before and after hydroxyl-radical-activation (SI.Part (d)). Ni deposited on ft-Au surface shows better activity than that of Ni deposited on mp-Au surface (Fig.1). Though oxygen evolution starts at nearly the same potential, ca. 1.55V *vs*.RHE for both Ni-deposited surfaces (SI. Part (d)), Ni on ft-Au surface (52.4 mA.cm^{-2}) shows higher current density than the mp-Au surface (22.3 mA.cm^{-2}). The promotional effect of EMS gold (ft-Au) on Ni for OER can be explained based on the possible increase in the electro-negativity of EMS due to the removal of highly electropositive clusters or asperities [9,15]. The present results establish that the electrocatalysis of OER at the Fenton-treated Au electrode is solely due to the attack of the surface by hydroxyl radicals, causing removal of metastable surface gold atoms and activating the equilibrated gold surface through formation of unstable gold oxides at the smoothened electrode. Nonetheless, it is reasonable to assign a mechanism based on (i) the observation of electrocatalysis in the present studies; (ii) different Au-O bond strengths arising from the extent of hydroxyl-radical activation on the EMS, showing a transition from stable to unstable oxide formation. Possible inter-conversions among the unstable oxides may also occur to sustain oxygen evolution till a thick oxide layer is formed. At very high potentials after the onset of OER, a thick layer of Au-oxide (irreversible oxide formed by place exchange mechanism) may form/break or decomposition of such thick (compact) layer leads to increased O_2 evolution that accelerates the loss of gold to the electrolyte[16]. However, the negative potential shift in the OER onset will help minimizing the loss of Au. Incidentally, Strasser et al[15] recently reported lowered passivation (oxide-derived) potentials in the case of Ru and Ir and Pt bulk surface being more electrocatalytic to OER than the nanoparticle-counterparts. Our results indicate that Au oxide reduction on EMS results in metastable Au surfaces that accelerate OER catalysis. Mechanistically, a gap in the understanding of the nature of hydroxyl-activation of the equilibrated gold surface (after removal metastable atoms) needs to be bridged by spectroelectrochemical studies.

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