



Comprehensive facilitating of water oxidation reaction by ultrasonic attenuation of hydrogen-bonded structure of water

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ABSTRACT

The balance between water-metal interactions and water-water hydrogen bonding (HBs) controls the process of water adsorption on metallic surfaces. In other hand, the yield of oxygen evolution reaction (OER) is dependent on the binding energy of H₂O at electrode surface. Therefore, on a specific metal substrate, attenuation of HBs may be a promising route for improving OER. In this study, the computational and experimental evidences indicate that the performance of ultrasonically irradiated deionized water (USI-DW), participated in water oxidation reaction (WOR), is different from its in the intact bulk water. To date, establishing of new electrocatalysts with lower overpotentials (η) and higher current densities (J) in OER have been mostly considered based on metals and oxide materials. Here, we ultrasonically agitated the water clusters formed by strong HBs, and as a sustainable improvement route explored its particular effects on the efficiency of OER. The molecular modeling (MM) of the (H₂O)_n clusters ($n = 1-100$ molecules), the corresponding IR spectra, the molecular orbitals energy levels and the adsorption of free and cluster confined H₂O molecules on the Pt surface were studied by the appropriate quantum mechanical (QM) methods. The result of deconvolution of FTIR spectra recorded for USI-DW in the -OH stretching region ($\sim 2600-3900\text{ cm}^{-1}$) properly confirmed the expected increase of the single water molecules. The reduction in overpotentials was $82 \pm 8\text{ mV}$ and $158 \pm 12\text{ mV}$, to reach the J of 1 mA cm^{-1} at the typical pHs 12.2 and 13.1, respectively.

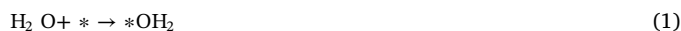
1. Introduction

Water molecules in liquid phase possess a disordered labile intermolecular network of hydrogen bonds (HBs). Several studies provided some strong evidences that hydrogen bonding forms a widespread, though short-lived, three-dimensional network in liquid water [1–4]. Water's HB plays a critical role in many chemical and physical events occurring in aqueous solutions [5,6]. The efficiency and strength of HBs in water molecules when acting on each other determine the size of water clusters. In fact, deviation from tetrahedral symmetry observed in bulk water results in some defects which can affect the scale of water clusters. Such cluster structural changes may influence the water involved reactions, especially in cases requiring the participation of individual water molecules in the interface of two different phases, e.g., heterogeneous catalyzed oxygen evolution reaction (OER).

The facile generation of clean energy is one of the vital scientific challenges of the 21st century. Because water is virtually an interminable raw material, water splitting has been used as a well-known route for the production of chemical energy. The electrocatalytic water oxidation reaction (WOR) inherently possesses a low efficiency, because its

slow kinetics caused by passing from a complex and multistep proton coupled electron transfer (PCET) process. To overcome this defect, almost all research works have been focused on establishing various heterogeneous and homogeneous water oxidation electrocatalysts to produce efficiently oxygen, with higher current density at lower overpotential [7]. Theoretically, an ideal catalyst should be able to mediate OER with zero overpotential, just above the equilibrium potential, however, practically this cannot be achieved because the associated binding energies of the intermediates [7,8]. In practice, the further reduction in overpotential has become the main goal of almost researches conducted in WOR.

In heterogeneous catalyzed water splitting, the first step is the chemisorption of water molecule and related species at electrode surface that triggered a complex electron coupled-proton coupled reaction, which finally results in spontaneous removal of four electron/four proton to liberate one molecule of O₂ [8–10]:



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Here, the mark “*” denote to the vacant site of the electrode surface, and the species correlated with it signify the surface with the corresponding chemisorbed components residing in the free site. Here, H_2O first adsorbs onto the surface O vacancy sites, after two subsequent oxidation processes, the primary adsorbed water molecules ($*\text{OH}_2$) form $*\text{O}$. Further oxidation lead to reaction of the $*\text{O}$ with another water molecule to produce the $*\text{OOH}$ intermediate. Finally, in the last oxidation step, O_2 is generated from the $*\text{OOH}$. The liberated protons, during each oxidation step (2–5), will ultimately participates in an electron transfer reaction at the cathode [10].

In electrochemistry, the microscopic events occurring in atomic/molecular scale at the interface of electrode/electrolyte solution mostly dictate the overall system behavior [7,11]. Accordingly, the facilitation of such interfacial processes, as an “*assisting route*”, can play an effective role in catalysis of water oxidation reaction [9]. Recently, Chen et al., have reported using the resonantly illuminated gold nanoparticles as an additive in water to create plasmon-induced activated water through destroying hydrogen bonds used for OER [12]. The comparison of voltammograms obtained for sAuNT-water and intact water revealed diminished overpotential (η) and increased current density (J) for the sAuNT-water system, signifying that it is favorable for promoting efficient oxygen production. The interaction energy of 47 kJ mol^{-1} between HB donor/acceptor in $\text{H}_3\text{O} \rightarrow \text{OH}$ can be increased by a factor approximately 2.5-times when water associates with several water molecules [13]. In brief, the adsorption process in Eq. (1) can be limited by the steric hindrance due to the bulky water clusters and involving oxygen's lone pairs participated in cluster network. This subject further persuade us to examine a new route to disturb the water H-bonded clustered structure for facilitated triggering of water oxidation reaction, without any change in chemical composition of water and merely through an external physical stimulus.

The effect of US on the viscosity of several water-soluble polymers in aqueous solutions have already been reported and have shown that it is able to affect the network of HBs [14]. Furthermore, the application of US waves in improvement of penetration of water encapsulate drugs has also been reported in the literature [15,16]. However, to the best of our knowledge, there is no previous report on the application of US in OER. Thus, starting from the above mentioned information, the ultrasound waves were employed to consider the behavior of shortly treated deionized water (DW) in OER.

As discussed above, the kinetics of OER is straightly affected by capability of chemisorption of water molecules on vacant sites of metal substrate [8,12]. This fact motivated us to establish a simple strategy for comprehensive facilitating water oxidation reaction, where during an innovative methodology, the efficiency of catalytic reaction has been increased by ultrasound irradiation. Here, we are not going to introduce the proposed method as an alternative to the previously extended water oxidation electrocatalysts in literature, but we suggest it as an easy method in improvement of OER, that can even accompany any developed heterogeneous catalyzed water oxidation reaction. According to our recent studies [17–19], the computational methods were employed to further explore the observed experimental data, where, the appropriate quantum mechanics (QM) methods were employed to calculate the structure and profile of IR spectra for single water molecule and small, medium and large water clusters [20,21]. The processes of binding of free and cluster-confined water molecules and those stabilities have been also considered. The obtained voltammograms in USI-DW clearly display significant diminishing in overpotential to reach a particular current density compared to DW.

2. Experimental

2.1. Chemical and instruments

Electrochemical measurements were carried out with a PalmSense3 computer-controlled potentiostat/galvanostat and run with the PSTrace software. All measurements were performed using deionized water (DW, $18.2 \text{ M}\Omega \text{ cm}$) provided from a Milli-Q system. Sodium hydroxide Tablet was purchased from Merck. The stock solution (3 M) of NaOH were freshly prepared using DW and diluted to deliver the desired pHs. All experiments were performed in an air-conditioned room at $23 \pm 2^\circ \text{C}$. Fourier transformation infrared spectroscopy (FTIR) was performed between 4000 and 500 cm^{-1} at a spectral resolution of 1 cm^{-1} on a Perkin-Elmer 1710 spectrophotometer. The FTIR spectra in OH stretching region ($\sim 2600\text{--}3900 \text{ cm}^{-1}$) have been successfully deconvoluted to the main components using Origin software. The pH was controlled with a Metrohm pH meter (model 780) with a combined glass electrode.

2.2. Calculations

All calculations were performed by Spatran '10-Quantum Mechanics Program (PC/x86) 1.1.0v4. 2011). The different structures, IR data and the electronic changes of molecular orbitals of the Pt- H_2O complexes were optimized by the hybrid QM-UHF/PM6 method. In this modelling, the H_2O clusters are implicated in the amorphous stabilization of certain supramolecular structures.

2.3. OER process

The water oxidation reaction was performed by a cyclic or linear sweep voltammetry in a three-electrode system including of a Pt electrode (0.07 cm^2) as a working electrode, a Pt wire (2 mm in diameter) as counter electrode and an Ag/AgCl (KCl, 3 M) as the reference electrode, respectively. The electrochemical measurement was conducted in 20 mL solution adjusted to the desired pH values at a scan rate of 0.05 V s^{-1} .

3. Results and discussion

3.1. OER studies

Considering the fact that the splitting of water into molecular oxygen takes place through several successive proton coupled electron transfer reactions (PCET, for more information about it see Refs. [22,23]), therefore, the higher current densities would be obtained in alkaline media [9,24,25]. Particularly, the voltammetric measurements was done in the arbitrary $\text{pH} = 12.2$. We performed some different electrochemical experiments to specify the effect of ultrasound irradiation (USI) (in an air tight filing-lip bottle, to avoid any degassing of dissolved O_2) on the efficiency of OER. Fig. 1A shows the obtained linear sweep voltammograms (LSVs) at $\text{pH} 12.2$, in the absence (a) and presence (b) of primarily irradiation for 90 s in a 20 kHz ultrasonic bath. The voltammograms exhibit a distinct difference in performance of OER. At the anodic potential of 1.2 V vs. NHE , the J value in DW and USI-DW were found to be 429 and $1268 \mu\text{A cm}^{-2}$, respectively. Meanwhile, the overpotentials to deliver J of 1 mA cm^{-2} , for DW and USI-DW systems were calculated to be 0.757 and 0.675 V , respectively.

Furthermore, the kinetics of OER was evaluated by examining the Tafel polarization plot for DW (Fig. 1B) and USI-DW (Fig. 1C), which expresses effect of potential on steady-state current density [26]. The Tafel slope describes irreversible electrode reactions that take place without any mass transport limitations [27]. At lower η values, the Tafel slopes found to be $159.1 \text{ mV decade}^{-1}$ for USI-DW, and $171.5 \text{ mV decade}^{-1}$ for DW, indicating an improved OER performance for USI-DW system over DW. The polarization curve of the USI-DW

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