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# Effectively reducing reagent concentrations for electrochemical reactions in aqueous solutions using plasmon-activated water

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ABSTRACT

Most of chemical reactions are performed in aqueous solutions, which are conventionally prepared using laboratory-ready and environmentally friendly deionized (DI) water. Water is generally considered as a passive reactant or as a spectator solvent. In this work, we demonstrate the added reagents for reactions in aqueous solutions can be effectively reduced by utilizing plasmon-activated water (PAW) with reduced hydrogen-bonded (HB) structure instead of conventional DI water with strong HB structure. For electrochemical reactions performing the similar currents the electrolytes used in PAW-based systems are ca. 90% concentrations compared to those used in DI water-based systems. Moreover, these concentrations used in PAW in situ-based systems can be further reduced to ca. 80% of magnitudes for maintaining the similar current levels. More interestingly, the recorded current of oxygen evolution reaction (OER) on a catalytic Pt electrode in the PAW-based system (0.09 M KOH) is significantly higher than that in the DI water-based system (0.1 M KOH). That means that the efficiency of the OER performed in a low-electrolyte-concentration alkaline solution can be markedly enhanced by utilizing PAW in spite of the electrolyte concentration is reduced by 10% of magnitude compared to the DI water-based system. These interesting findings promise the PAW for the effective and green reactants and solvents.

## 1. Introduction

In general chemistry, we are noticed that the rates of chemical reactions may be affected by concentrations of reactants, concentration of catalyst, temperatures and surface areas of solid reactants. For reactants in aqueous solutions water is generally considered as a passive reactant or as a spectator solvent. Actually, liquid water has emerged as a promising active reactant using its characteristic property of donor-bridge-acceptor for proton transfer and electron donating [1–5]. Moreover, liquid water is conventionally considered an independent reactant. However, as shown in the literature regarding the hydrogen evolution reaction (HER), the interaction energy of $H3O^{+}{-}OH^{-}$ is 46.9 kJ mol$^{-1}$, but it increases approximately 2.5-times when $H_3O^+$ associates with an additional four water molecules by hydrogen bonds (HBs) [6]. Due to our knowledge regarding the water structure on the molecular level is limited, therefore, this effect of the HB network of water structure on the corresponding chemical reactions is less studied in the literature. In our group, these facts inspired us to create active plasmon-activated water (PAW) with intrinsically reduced HBs, which was obtained from deionized (DI) water at room temperature using hot electron transfer (HET) on resonantly illuminated gold nanoparticles (AuNPs) [7]. The created free-standing and electron-doping PAW is energetic and pH neutral. This unique electronic feature makes it stable at least for one week, as shown in our previous report [8]. Also, in the previous work [7], Raman and IR vibrational spectroscopies were used to examine the difference of PAW from the conventional DI water. The PAW in situ was obtained by irradiating DI water-wetted AuNPs supported on ceramic particles with laser light at 532 nm in situ Raman spectrum measurement. Compared to DI water, the observed reduced HBs of PAW in situ was more significant. The created PAW can be innovatively employed as an environmentally friendly etching agent (vapor from hot electron-activated liquid water) [9]. Also, this PAW can promote water's fundamental activities of solubility, ionic conductivity and extraction at room temperature compared to DI water [10].

It is recognized that increasing the temperature and the concentration of reactant would increase the corresponding reaction rate.

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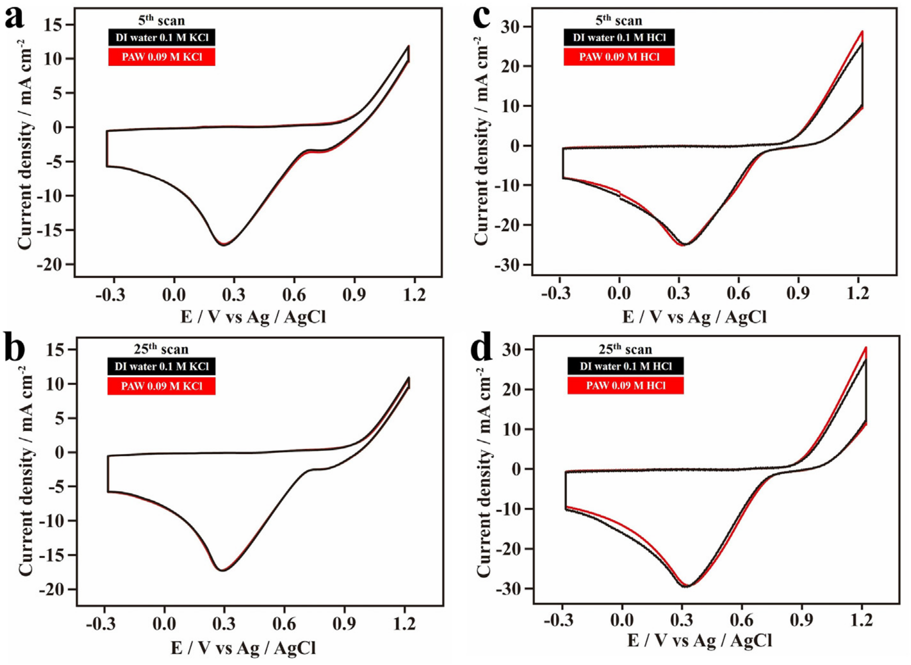

**Fig. 1.** Cyclic voltammogram (CV) on the same Au electrode showing the 5th (at the beginning) and the 25th (at the end) scans with oxidation-reduction cycle (ORC) treatments at 0.5 V s$^{-1}$ to roughen the Au electrodes in plasmon-activated water (PAW)-based and deionized (DI) water-based solutions with different electrolytes and concentrations of electrolytes (0.1 M for DI water; 0.09 M for PAW). Experimental conditions: in ambient experimental conditions with normal illuminations from indoor fluorescent lamps. (a) The 5th scans in KCl solutions. (b) The 25th in KCl solutions. (a) The 5th scans in HCl solutions. (b) The 25th in HCl solutions.

For increasing the rate of reaction a general strategy is to develop effective platinum-based and cheap catalysts with different chemical compositions and structures to reduce the necessary activation energy in the reaction [11–15]. In electrochemical reactions, electrolytes are necessary for initiating the reactions in conducting solutions. Compared to pure water at room temperature, both adding electrolyte in water [16] and increasing the temperature of water [17] can reduce the HB structure of water molecules themselves. However, the influences of HBs of water on the corresponding reaction rates were less investigated in the literature. Actually, the original tetrahedral HB network of bulk water can be destroyed when liquid water is confined in a nanosized environment or localized at interfaces [18–21]. These heterogeneous interactions result in corresponding changes in water's HB-dependent properties [22,23]. Because the substantial amount of these kinds of water is small and the dynamic HB network is on a picosecond time scale [24–26], which have limited the scaling-up of the corresponding using as bulk water in general chemical reactions. In this work, we demonstrate the added reagents for reactions in aqueous solutions can be effectively reduced by utilizing PAW with reduced HB structure instead of conventional DI water with strong HB structure.

## 2. Experimental section

### 2.1. Preparations of PAW ex situ and PAW in situ

PAW (ex situ) was prepared using a previously described method [7]. PAW in situ was prepared in a PAW-filled glass cell containing an electrochemically roughened Au substrate with AuNPs. In the experiments, the glass cell with PAW was resonantly illuminated with green light-emitting diodes (LEDs) to create PAW in situ at the AuNPs (See details in SI and Fig. S1).

### 2.2. Preparation of electrochemically roughened Au substrate

The Au electrode with a bare area of 0.238 cm$^2$ was cycled in a deoxygenated 0.1 M KCl aqueous solution (40 mL based on PAW or DI water) from −0.28 to +1.22 V vs. Ag/AgCl at 500 mV s$^{-1}$ under indoor fluorescent lamps for 25 scans. Respective durations at the cathodic and anodic vertices were 10 and 5 s. Finally, the potential was held at the cathodic vertex before the roughened Au electrode was removed from the solution and thoroughly rinsed with DI water This oxidation-reduction cycle (ORC) procedure for surface-enhanced Raman scattering (SERS) studies were generally employed in our [27] and other laboratories [28,29] (See details in SI).

### 2.3. Oxygen (or hydrogen) production measurements

Oxygen (or hydrogen) evolution reactions (OERs or HERs) were measured by linear sweep voltammetries (LSVs) in a three-electrode system consisting of a polished Pt electrode (or a roughened Au electrode) with a bare area of 0.238 cm$^2$, a Pt sheet, and Ag/AgCl as the working, counter, and reference electrodes, respectively. The corresponding electrochemical measurements were performed in a 40-mL solution with 0.05 M KOH for OERs (or 0.05 M $H_2SO_4$ for HERs) at a scan rate of 0.05 V s$^{-1}$. Other neutral electrolytes of KCl and different concentrations were also performed. Before measurements, the aqueous solutions had been carefully deoxygenated by bubbling highly purified nitrogen for 30 min.

## 3. Results and discussion

### 3.1. Electrochemical ORC reactions on Au substrates

As shown in the literature regarding SERS studies [30,31], controllable and reproducible surface roughness can be easily generated by controlling the electrochemical ORC procedure in chloride-containing aqueous solutions. Fig. S2 demonstrates typical triangular voltammetric curves in the 5th and the 25th scans for anodic dissolution and cathodic redeposition of Au respectively onto Au substrates in DI water solutions containing 0.1, 0.09 and 0.08 M KCl under normal illumination from indoor fluorescent lamps. In the ORC procedure, 0.1 M chloride-electrolyte was generally employed. As shown in Fig. S2a for the 5th scan, the cathodic redeposition current at ca. 0.25 V vs Ag/AgCl was −4.05 ± 0.12 mA in 0.1 M KCl. However, this current was reduced by 15% and 22% of magnitudes for experiments performed in 0.09 and 0.08 M KCl, respectively. Similarly, as shown in Fig. S2b for the 25th scan, the cathodic redeposition current at ca. 0.25 V vs Ag/AgCl was −4.11 ± 0.09 mA in 0.1 M KCl. However, this current was reduced by 14% and 21% of magnitudes for experiments performed in 0.09 and 0.08 M KCl, respectively. These results suggest that the ORC efficiency