Supporting Information

Potential for Plasmon-Activated Water as A Comprehensive Active Green Energy Resource

Hsiao-Chien Chen,a,1 Chih-Ping Yang,a,1 Chien-Tai Hong,b,c,1 Chun-Tsung Hsu,d Chi-Chang Hu,d Yu-Chuan Liu,a,*

aDepartment of Biochemistry and Molecular Cell Biology, School of Medicine, College of Medicine, Taipei Medical University, No. 250, Wuxing St., Taipei 11031, Taiwan

bDepartment of Neurology, School of Medicine, College of Medicine, Taipei Medical University, No. 250, Wuxing St., Taipei 11031, Taiwan

cDepartment of Neurology and Dementia Center, Shuang Ho Hospital, Taipei Medical University, No. 291, Zhongzheng Rd., New Taipei City 23561, Taiwan

dDepartment of Chemical Engineering, National Tsing Hua University, No. 101, Sec. 2, Kuang-Fu Rd., Hsinchu 30013, Taiwan

* Author to whom correspondence should be addressed. Yu-Chuan Liu, Phone: +886-2-2736-1661, ext. 3155; E-mail: liuvy@tmu.edu.tw.

1 H.-C. C., C.-P. Y. and C.-T. H. contributed equally to this work.
MATERIALS AND METHODS

Chemicals and Materials. NaCl, H₂SO₄ and KOH were purchased from Sigma-Aldrich Organics. KCl was purchased from Acros Organics. Urea was purchased from J.T. Baker. All of the reagents were used as received without further purification. Deionized (DI) water (18.2 MΩ cm) was provided by a Milli-Q system. All experiments were performed in an air-conditioned room at ca. 24 °C. The water temperature was ca. 23.6 °C.

Hydrogen Evolution Reaction and Oxygen Evolution Reactions. The HER or OER was performed by linear sweep voltammetry (LSV) in a three-electrode system consisting of an electrochemically roughened Au electrode (0.238 cm²), a Pt sheet, and a KCl-saturated Ag/AgCl electrode as the working, counter, and reference electrodes, respectively. Typically, the corresponding electrochemical measurement was performed in a deoxygenated 35-mL PAW (or DI water) solution with different electrolytes at a scan rate of 0.05 V s⁻¹ under illumination with green LEDs or dark atmosphere.

Preparation of Photocatalyst and Reaction of Hydrogen Peroxide. First, 30 g of urea was placed in an alumina crucible in a Muffle furnace and was heat to 550°C for 3 h. The powders were washed by ethanol and DI water to remove residual species. Finally, the prepared photocatalyst of graphite carbon nitride (g-C₃N₄) was collected by filtration before drying at 50°C for 12 h. Then 5 g of AuNPs coated-ceramics (40 mesh), 100 mL of DI water and 0.5 g of g-C₃N₄ were placed in 200 mL serum bottle (name as DI water in situ system). In experiment, the reaction bottle was illuminated by white light LEDs. The H₂O₂ production reaction was begun while the oxygen was introduced into the bottle until the reaction was complete. Also, the similar reaction without adding 5 g of AuNPs coated-ceramics was performed and named as DI water system for reference. The reactions bottles were placed on a platform of an orbital shaker, operating at 500 rpm.

Measurement of Oxygen Reduction Reaction. The ORR activity of commercial Pt/C (20%, E-TEK, USA) in both the DI water and PAW systems was investigated using rotating ring-disk electrode (RRDE) voltammetry. Suspension of the Pt/C sample was prepared by adding 5 wt% Nafion® (E.I. du Pont de Nemours, USA) and 99.5% ethanol (Kanto Chemical, Japan) in a 1:15 volume ratio. The homogeneous suspension was coated onto a glassy-carbon (GC) electrode for RRDE voltammetry with a loading mass of 0.2 mg cm⁻². The potential of the Pt-ring electrode was set at 1.2 V vs RHE to oxidize
intermediates generated from the disk electrode. In the ORR study, both 0.1 M KOH and neutral electrolytes (saline solutions with 0.9 wt% NaCl) were tested. An Ag/AgCl (Argenthal, 207 mV vs SHE at 25°C) was used as the reference electrode, and a platinum wire with an exposed area equal to 4 cm² was employed as the counter electrode.

**Measurement of Dielectric Constant.** Two identical semi-transparent Pt-coated F-doped SnO₂ (FTO) electrodes (with 75% transparency) were prepared by sputtering (Eversolar® P-200, Everlight Chemical Co., Taiwan). These two Pt-coated FTO electrodes were assembled into a cell with a spacer (a Surlyn film, SX1170-60, Solaronix SA, Switzerland). The cell gap was fixed at about 25 μm. The as-prepared PAW, reverse osmosis (RO) water, or DI water without any supporting electrolyte was injected into the cell to form a simple package of a cell for measuring the capacitive responses. An impedance spectrum analyzer, IM6 (ZAHNER, Germany), with Thales software was employed to measure and analyze the EIS spectra. The ac potential amplitude was equal to 10 mV with its frequency from 0.1 Hz to 100 kHz. Impedance spectra were measured when the cell voltage was set at 0.5 V for 60 sec.

**ADDITIONAL DISCUSSIONS**

The mean electron transfer number \((n)\) of the ORR can be estimated on the basis of the RRDE voltammograms according to the following equation:

\[
\frac{4I_D}{I_D + \left(\frac{I_R}{N}\right)}
\]

where \(I_D, I_R,\) and \(N\) represent the disk current, ring current, and the current collection efficiency of the electrode (0.37 ± 0.02), respectively.

Figure. S1a shows the LSVs performed on DI water and PAW neutral solutions (0.1 M Na₂SO₄) under resonant illumination with green LEDs or dark atmosphere. Similarly, the magnitudes of the recorded currents of the cathodic HERs performed in the PAW-based systems are increased, as compared to that performed in the DI water in dark, especially for HER performed in PAW in situ. Figure S1b shows the corresponding increased efficiencies of HERs performed in different PAW-based systems compared to HER performed in DI water-based system. The current is –0.169±0.005 mA at –0.7 V vs RHE for HER performed in system of DI water in dark. The currents are –0.216±0.028 mA (increased by 28%), –0.204±0.012 mA (increased by 21%) and –
0.222±0.013 mA (increased by 31%) at –0.7 V vs RHE for HERs performed in systems of DI water in situ, PAW in dark and PAW in situ, respectively. Comparing with the increased efficiencies in the PAW in dark and in the PAW in situ, it indicates that the increased efficiency can be more significantly enhanced by ca. 50% of magnitude for HER performed in PAW in situ. Also, the current is –1.96±0.04 mA at –1.1 V vs RHE for HER performed in system of DI water in dark. The currents are –2.20±0.21 mA (increased by 12%), –2.44±0.10 mA (increased by 24%) and –2.64±0.16 mA (increased by 35%) at –1.1 V vs RHE for HERs performed in systems of DI water in situ, PAW in dark and PAW in situ, respectively. Similarly, this increased efficiency can be more significantly enhanced by ca. 50% of magnitude for HER performed in PAW in situ compared to in PAW in dark.

Figure S2a shows the LSVs performed on DI water and PAW neutral solutions (0.1 M Na₂SO₄) under resonant illumination with green LEDs or dark atmosphere. Similarly, the magnitudes of the recorded currents of the anodic OERs performed in the PAW-based systems are increased, as compared to that performed in the DI water in dark, especially for OER performed in PAW in situ. Figure S2b shows the corresponding increased efficiencies of OERs performed in different PAW-based systems compared to OER performed in DI water-based system. The current is 0.684±0.128 mA at 2.4 V vs RHE for OER performed in system of DI water in dark. The currents are 0.901±0.024 mA (increased by 32%), 1.090±0.176 mA (increased by 59%) and –1.278±0.125 mA (increased by 87%) at 2.4 V vs RHE for OERs performed in systems of DI water in situ, PAW in dark and PAW in situ, respectively. Comparing with the increased efficiencies in the PAW in dark and in the PAW in situ, it indicates that the increased efficiency can be more significantly enhanced by ca. 50% of magnitude for OER at 2.4 V vs RHE performed in PAW in situ. Also, the current is 2.745±0.416 mA at 2.8 V vs RHE for OER performed in system of DI water in dark. The currents are 3.662±0.404 mA (increased by 33%), 4.818±0.656 mA (increased by 76%) and 5.766±0.579 mA (increased by 110%) at 2.8 V vs RHE for OERs performed in systems of DI water in situ, PAW in dark and PAW in situ, respectively. Similarly, this increased efficiency can be more significantly enhanced by ca. 50% of magnitude for OER performed in PAW in situ compared to in PAW in dark.

REFERENCES AND NOTES

1 Liu, Y. C.; Hsu, T. C.; Tsai, J. F. Thermal Stability of Electrochemically Prepared Surface-Enhanced Raman Scattering-Active Metals Substrates. J. Phys. Chem. C, 2007, 111, 10570–10574.
Figure S1. Linear sweep voltammograms (LSVs) of hydrogen evolution reactions (HERs) in DI water and PAW containing 0.1 M Na$_2$SO$_4$ at the same electrochemically roughened Au electrode under illumination with green LEDs or dark atmosphere. (a) LSVs of HERs at a scan rate of 0.05 V s$^{-1}$. (b) The increased efficiency of HER with the applied potential based on created PAW in reference of DI water in dark atmosphere.
Figure S2. Linear sweep voltammograms (LSVs) of oxygen evolution reactions (OERs) in DI water and PAW containing 0.1 M Na$_2$SO$_4$ at the same electrochemically roughened Au electrode under illumination with green LEDs or dark atmosphere. (a) LSVs of HERs at a scan rate of 0.05 V s$^{-1}$. (b) The increased efficiency of OER with the applied potential based on created PAW in reference of DI water in dark atmosphere.
Figure S3. SEM images of electrochemically roughened Au electrodes. (a) as-prepared Au electrode. (b) used Au electrode after experiment of HERs or OERs. The bar represents 1 µm.