

Electronic Supplementary Information

Heterojunction of Silver-Iron oxide on Graphene for Laser-coupled Oxygen Reduction Reaction

Wei-Quan Chen,^a Min-Chuan Chung,^a Joey Andrew A. Valinton,^a David P. Penaloza Jr.,^b Shiow-Huey Chuang,^c and Chun-Hu Chen^{a*}

^aDepartment of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan 80424

^bDepartment of Chemistry, College of Science, De La Salle University, Manila 1004, Philippines

^cDepartment of Applied Chemistry, National University of Kaohsiung, Kaohsiung, Taiwan

E-mail: chunhu.chen@mail.nsysu.edu.tw

Material synthesis

Synthesis of graphene oxide (GO)

Graphene oxide was synthesized using preformed acidic oxidizing medium (PAOM), a modified version of the Hummers' method¹. First, 3 g of potassium permanganate was dissolved in 13 mL of concentrated sulfuric acid, followed by adding NaNO₃ (0.5 g) and flaky graphite (1 g). The mixture was stirred overnight to complete the reaction. The mixture was then heated at 35°C for 15 minutes followed by a slow addition of DI water (23 mL) under an ice bath. Afterwards, an oil bath treatment was applied to rise the temperature to 80°C for 30 minutes, then cooled to room temperature in an ice bath, followed by a slow addition of 10 mL of H₂O₂ to turn the solution color into bright yellow. The products were washed using a hydrochloric acid solution and the residue underwent dialysis to obtain GO suspension. The concentration of the synthesized GO was measured to be around 10 mg/mL.

Synthesis of Ag/FNG

In a typical synthesis, the GO solution (1.58 mL) was added to 45 mL of DMF solution in a round bottomed flask. Subsequently, aqueous iron(II) acetate solution (0.2 M) was added into the mixture by a volume of 2.4 mL for a room temperature stir of 6 hours, followed by the addition of aqueous ammonia (1 mL). The mixture was then refluxed for 10 hours at 90°C. Addition of 0.5 mL of silver nitrate (0.1 M) was conducted, followed by the hydrothermal treatment for 3 hours at 150°C. The products were cleaned by water and ethanol centrifuge to yield Ag/FNG.

Synthesis of control samples (FNG, Ag/N-rGO, Ag/N-rGO-CTAB, etc.)

Various control samples, namely, the iron oxide-free samples which were prepared without addition of iron precursor (denoted as Ag/N-rGO), and the silver-free ones which were prepared without addition of silver precursor (denoted as FNG), were synthesized following the procedure of Ag/FNG.

The preparation of Ag/N-rGO-CTAB was generally the same as Ag/N-rGO, except that 12.43 mL aliquot of refluxed GO was mixed with 0.13 mL aqueous cetyltrimethylammonium bromide (CTAB) solution (0.1 M) and 0.13 mL aqueous AgNO₃ solution (0.1 M) before hydrothermal synthesis. The synthesis of Fe₂O₃ samples was done in the same manner as Ag/FNG but GO and the Ag precursor were not added. For the synthesis of heterojunction-free Ag/FNG sample, a similar procedure as Ag/FNG was conducted but the silver precursor was added after the hydrothermal step and stirred at room temperature for 15 minutes.

The etching of Ag from Ag/FNG was done by placing 4 mg of the catalyst in 1 mL of concentrated HNO₃ to which it was sonicated for 5 minutes. The mixture was then decanted, washed with distilled water, and was centrifuged multiple times. The remaining solid was dried at 80°C.

Characterization

Transmission electron microscope (TEM) images were obtained by Philips CM200 at 200 kV. Samples for SEM (scanning electron microscope) measurement were prepared by drop-casting onto silicon substrates, and the images were acquired by a Zeiss Supra 55 Gemini FE-SEM. The X-ray diffraction (XRD) patterns were acquired using Bruker D2 Phaser X-ray Diffractometer. The data of X-ray photoelectron spectroscopy (XPS) were obtained by a Kratos Axis Ultra DLD with a Mg/Al achromatic source. Samples for UV-Vis measurements were prepared by diluting 300 µL catalyst ink mixture (1 mg catalyst per 1 mL of deionized water/isopropyl alcohol) to 1 mL which was placed on a Jasco V-630 Spectrophotometer. The materials were digested with a mixture of HCl and H₂O₂ (1:10) for elemental analysis conducted with inductively coupled plasma-mass spectroscopy (ICP-MS) analysis on a PE-SCIEX ELAN 6100 DRC.

Electrochemical Measurements

Preparation of Electrodes

For the electrode preparation, 1 mg of the nanocomposites were dispersed in 1 mL of deionized water/isopropanol solution under sonication for 15 min to obtain a homogeneous suspension. Then 12 μL of the suspension was loaded onto a 3-mm glassy carbon electrode (GCE) surface with a 3-mm diameter, followed by adding a 10 μL drop of 0.1% Nafion in ethanol. A 20 μL of the suspension was also loaded onto disk electrodes of rotating disk electrode (RDE) (surface area: 0.196 cm^2) and rotating ring-disk electrode (RRDE) for the measurements.

Cyclic Voltammetry

All the fabricated electrodes were used to perform cyclic voltammetry (CHI 704E, CH Instrument) with a platinum wire counter electrode and a Ag/AgCl reference electrode. The electrolyte solution (0.1 M KOH) was saturated with oxygen by bubbling O_2 for 30 min before each run of the experiment. The results were collected after two test runs under a potential range between 0.2 to 1.0 V (vs. RHE) at a scan rate of 5 mVs^{-1} to confirm a steady collection of data. The O_2 -free control experiments of CV were conducted with N_2 bubbling until saturation.

Polarization curves acquired by Rotating Disk Electrode (RDE) and Rotating Ring-Disk Electrode (RRDE)

The RDE measurements were done under a basic solution (0.1 M KOH) saturated with O_2 against a Pt wire counter electrode and Ag/AgCl reference electrode at a scan rate of 5 mV/s . The rotations used for measuring ranged from 400 rpm to 2025 rpm. The conditions for RRDE were the same as the RDE but the rotation speed was kept at 1600 rpm and the ring current potential was kept at 1.4 V (vs RHE). The laser-coupled ORR (LORR) was conducted with the setup shown in Scheme S-1. The percentage of peroxide (HO_2^-) generated can be calculated by relationship between the disk current and the ring current using Equation 1:

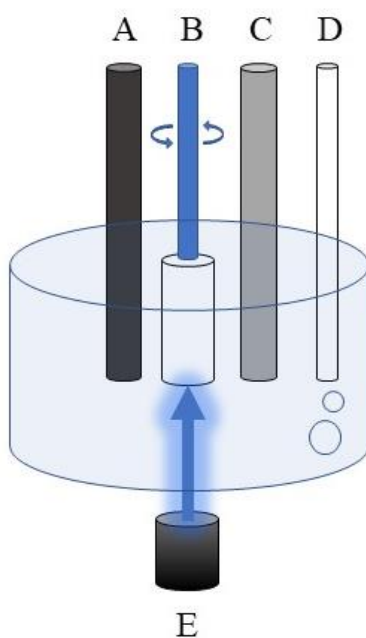
$$\%(\text{HO}_2^-) = \frac{200 \times \frac{I_{\text{Ring}}}{N}}{I_{\text{Disk}} + \frac{I_{\text{Ring}}}{N}} \quad (1)$$

where I_{ring} is the ring current, I_{disk} is the disk current, and N is the collection efficiency. The electron transfer number can be calculated using Equation 2:

$$n = \frac{4I_{\text{disk}}}{I_{\text{disk}} + \frac{I_{\text{ring}}}{N}} \quad (2)$$

Laser-coupled ORR (LORR) experiment

The LORR measurements were conducted combining with RRDE technique in 0.1 M KOH. Part A: Ag/AgCl reference electrode; part B: rotating ring-disk electrode; part C: Pt wire counter electrode; part D: O₂ bubbler; part E: 400 mW laser with wavelength of 405 nm. The laser beam sizes are slightly smaller than surface area of the electrode.



Scheme S1. The schematic illustration of LORR setup.

To determine the extent of oxygen reduction reaction of the synthesized catalysts under the influence of light, a rotating ring-disk electrode (RRDE) was used as a working electrode. The photochemical-coupled ORR measurements were carried out under direct illumination of the disk electrode using a 405 nm 400 mW laser beam focusing on the electrode surface. The irradiation intervals (light on and off) was controlled to be 20 seconds. Chronoamperometric curves were generated from samples with the same conditions as above, but the potential of the disk was kept at 0.25 V (vs RHE) and the ring disk was fixed at 1.4 V (vs RHE).

The photo-assisted peroxide yield change was defined as Equation 3:

$$\text{peroxide change} = \frac{\%(\text{HO}_2^-)_{\text{light}} - \%(\text{HO}_2^-)_{\text{dark}}}{\%(\text{HO}_2^-)_{\text{dark}}} \quad (3)$$

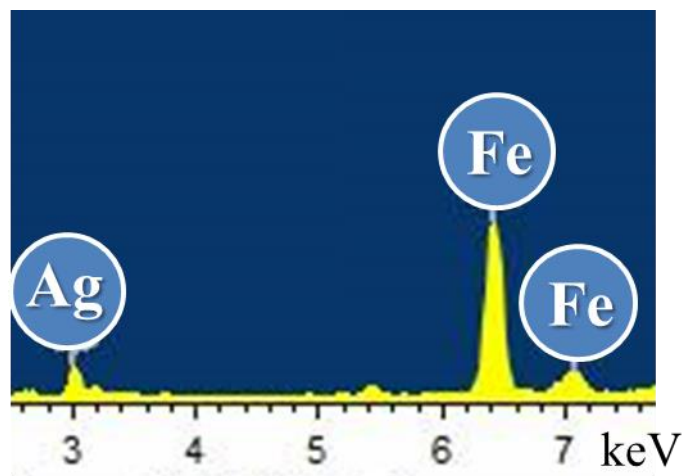


Fig. S1. Energy Dispersive X-ray profile for Ag/FNG.

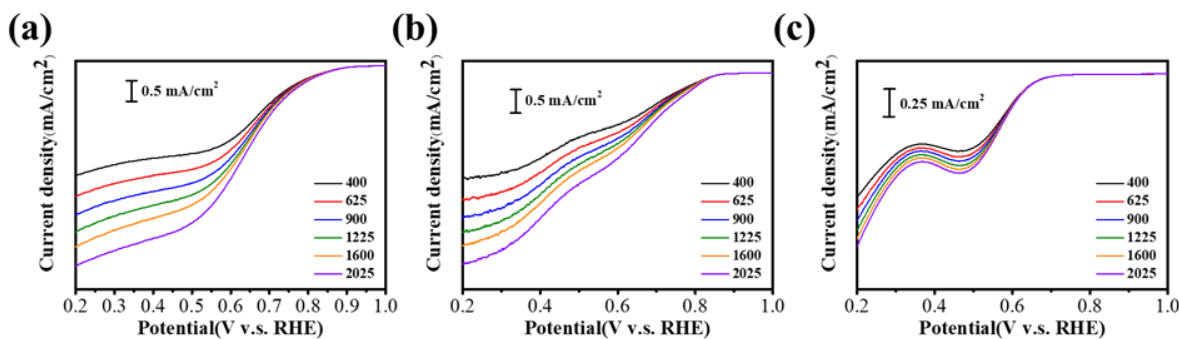


Fig. S2. The ORR polarization LSV curves for (a) Ag-rGO, (b) FNG, and (c) Fe₂O₃. The curves were measured at various rotation speeds using the rotating disk electrode. Measurements were done under O₂-saturated KOH solution (0.1 M).

Electrochemical Impedance Spectroscopy

The charge transfer properties of an electrocatalyst can be determined by Electrochemical Impedance Spectroscopy (EIS) where each sample was measured of its charge resistances under an applied current with different frequencies. The measurement of impedances on the material resulting to a Nyquist plot in which the plot is fitted to an equivalent circuit illustrating resistances within the material. The equivalent circuit that occurs within Ag/FNG, as well as FNG and Ag/rGO, is illustrated in Scheme S-2, where R_{soln} is the electrolyte solution resistance, R_{cat} is the inherent catalyst resistance, and R_{ct} is the charge transfer resistance. Both R_{cat} and R_{ct} are parameters that relate to ORR activity through charge transport towards oxygen. To consider the surface roughness and the uneven coating of the electrode, a constant phase element was used instead of capacitance to represent the interfaces within the electrocatalyst (Q_{cat}) and the catalyst-electrolyte interface (Q_{ct}).²

Among the three electrocatalysts, Ag/N-rGO contains the semicircle with the least radius which in turn produces the lowest R_{cat} followed by Ag/FNG and FNG (Table S-2) This means that Ag decoration improves materials electrical conductivity. Thus Ag/FNG exhibits the better conductivity than FNG. The lowest slope in the low-frequency region goes to Ag/FNG as followed by Ag/rGO and FNG which shows that Ag/FNG is more capable of charge transfer among the others, as reflected on their respective R_{ct} values. Therefore, the presence of the Ag/Fe₂O₃ heterojunction interface both enhances the conductivity and charge transport.

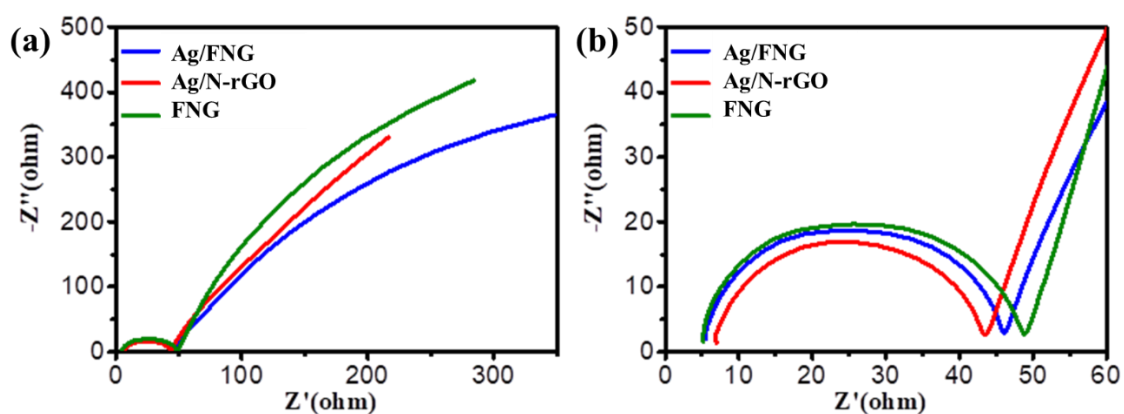
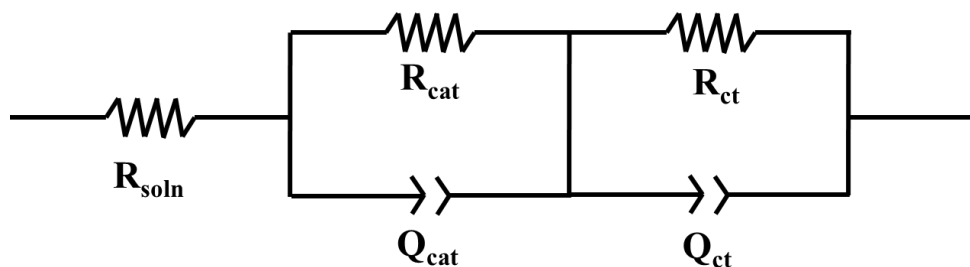


Fig. S3. The Nyquist plots generated based on the EIS measurements of the catalysts at 0.7 V vs. RHE. Plot (b) just expands the semicircle representing the high-to-medium potential frequency measurements in plot (a).



Scheme S2. The equivalent circuit for the Nyquist plot generated from the EIS measurement.

Table S1. The resistance of R_{cat} and R_{ct} based on the Nyquist plots. The values were generated from EIS fitting software ZSimpWin.

	$R_{cat}(\Omega)$	$R_{ct}(\Omega)$
Ag/FNG	40.1	1240
Ag/N-rGO	36.3	1514
FNG	43.6	1553

Table S2. The performance Ag/FNG as compared to similar electrocatalysts in literature.

Catalyst	Onset potential (RHE)	Potential of limiting currents [#] (RHE)	Electron transfer number (n)	Reference
Ag/FNG	0.92 V	0.6 V	~3.9	This work
FNG	0.86 V	No	3.1-3.8	This work
Fe ₃ O ₄ /N-GAs	0.78 V	No	3.7-3.9	[3]
Fe ₂ O ₃ /Ppy/ GO-800	0.90 V	No	3.5-3.9	[4]
Co ₃ O ₄ /rmGO	0.85 V	0.4 V	3.7-3.9	[5]

[#] The initial potential of limiting current of LSV curves

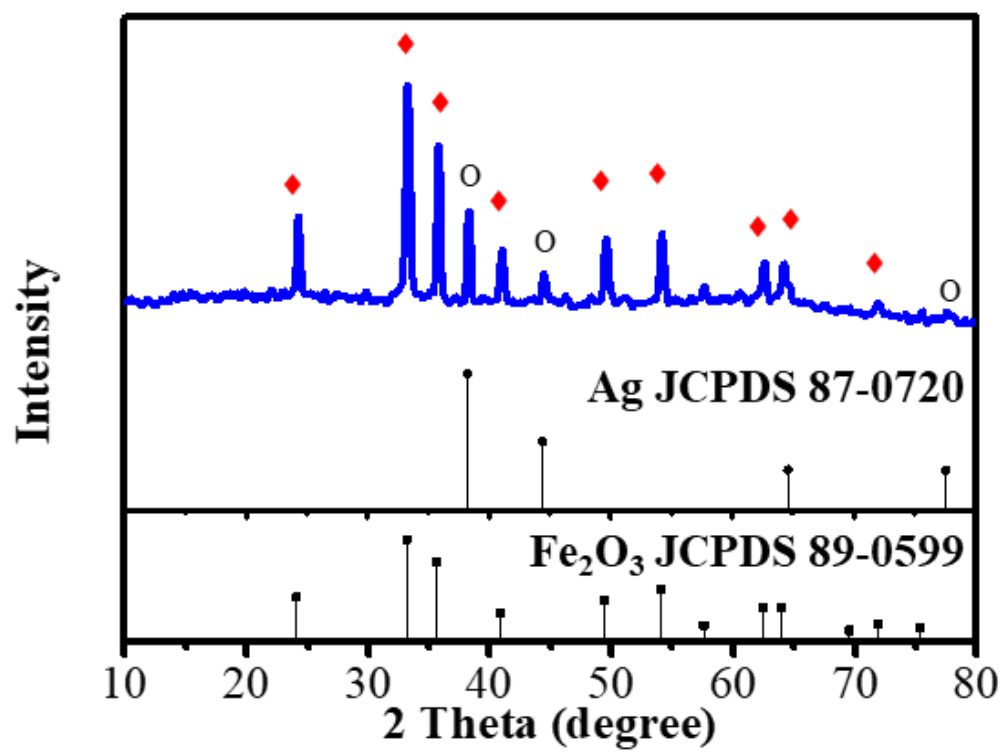


Fig. S4. The XRD patterns of the heterojunction-free sample. The diamond-labelled peaks correspond to Fe₂O₃ (hematite) while the circle-labelled peaks correspond to Ag.

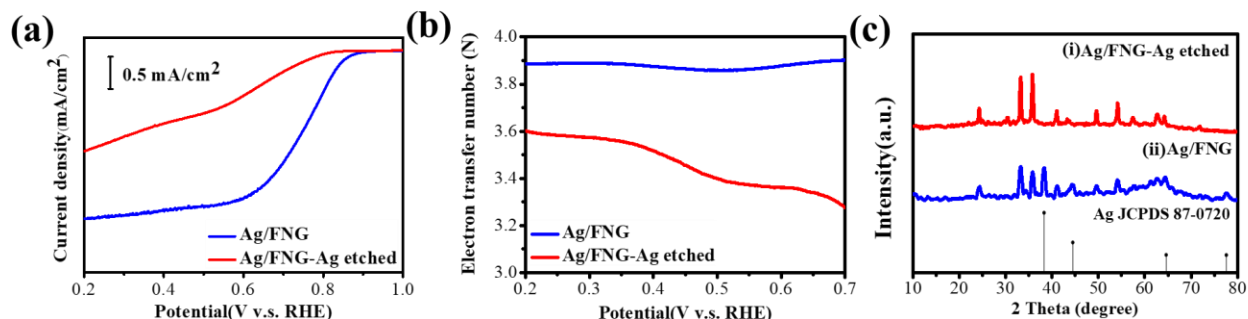


Fig. S5. The comparison of Ag/FNG before and after etching in terms of their (a) RDE and (b) electron transfer number plots. (c) The XRD pattern comparison of Ag/FNG before (blue pattern) and after etching (red pattern). It is clear to see the absence of Ag signals after the etching process.

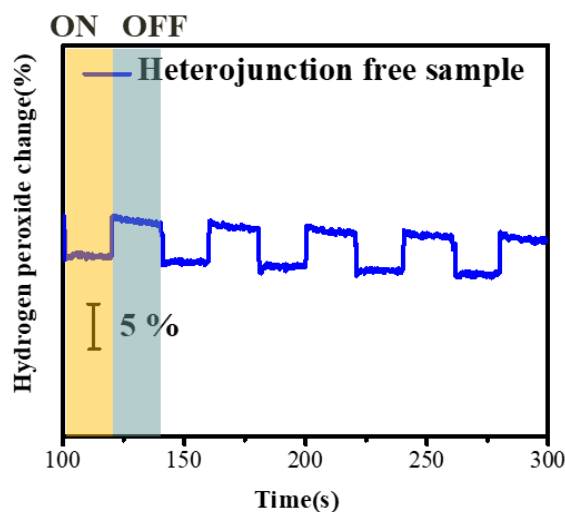


Fig. S6. The change in hydrogen peroxide yield on the heterojunction free sample under cyclic on/off conditions

References:

1. C.-H. Chen, S. Hu, J.-F. Shih, C.-Y. Yang, Y.-W. Luo, R.-H. Jhang, C.-M. Chiang and Y., Jr. Hung, *Sci. Rep.* 2017, **7**, 3908.
2. C. Jin, F. Lu., X. Cao, Z. Yang and R. Yang, *J. Mater. Chem. A*, 2013, **1**, 12170-12177
3. Z. S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng and K. Mullen, *J. Am. Chem. Soc.* 2012, **134**, 9082-9085.
4. S. Ren, S. Ma, Y. Yang, Q. Mao and C. Hao, *Electrochim. Acta.* 2015, **178**, 179-189.
5. Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.* 2011, **10**, 780-786.