

Supporting Information

Boosting ethanol electrooxidation via photothermal effect over palladium/ reduced graphene oxide

Yongmeng Wu,^a Shuhe Han,^a Yi Huang,^a Yanmei Shi,^a and Bin Zhang^{*ab}

^aTianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China. E-mail: bzhang@tju.edu.cn

^bCollaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

* Corresponding Author: bzhang@tju.edu.cn

1. Experimental Details

1.1 Synthesis of Pd/RGO.

Graphene oxide (GO) was prepared according to a modified Hummer's method. In a typical synthesis of Pd/RGO, homogeneous GO suspension (10 mL 0.5 mg mL⁻¹) and K₂PdCl₆ (1mL 10 mM) aqueous solution were mixed, then 10mg sodium citrate was added. After stirring for 30 minutes, 5 mL 0.1M NaBH₄ was injected in ice bath. The black as-prepared precipitates were collected and washed several times with distilled water and ethanol.

1.2 Synthesis of pure Pd nanoparticles.

In a typical preparation of pure Pd nanoparticles, 0.0729g CTAB dissolved in the mixed

solution of 7.5 mL H₂O and 30 mL ethylene glycol. Then 7.5 mL K₂PdCl₆ (10 mM) added to above solution and stirring for 30 min. The black as-prepared precipitates were collected and washed several times with distilled water and ethanol.

2. Materials Characterizations

The scanning electron microscope (SEM) images are obtained by Hitachi S-4800. Powder X-ray diffraction (XRD) data is acquired on a Bruker D8 Focus Diffraction System with a Cu K α radiation ($\lambda = 0.154178$ nm). Transmission electron microscopy (TEM) is taken on JEOL-2100F system. X-ray photoelectron spectroscopy (XPS) measurements are performed with a Perkin Elmer PHI 1600 Versa Probe with Al K α as the excitation source. Raman spectra were recorded on a RENISHAW inVia reflex Raman Microscope at excitation laser wavelength of 532 nm. Inductively coupled plasma mass spectrometry (ICP-MS) was carried out on an Agilent 7700x gas chromatograph equipped with an Auto sampler Injector. The ultraviolet-visible (UV-Vis) absorption spectra are collected in 200-1200 nm against BaSO₄ reflectance standard. The infrared imagines are obtained by FLIR E4 thermal imaging infrared camera.

3. Electrochemical Measurements

Electrochemical measurements were carried out in a typical three-electrode cell consisting of a working electrode, a Pt plate counter electrode, and a Hg/HgO electrode performed using an electrochemical workstation (CHI 660D, CH Instruments, Austin, TX). A “L” shape glassy carbon electrode (diameter $d = 3$ mm, Tianjin Incole Union Technology Co.Ltd) was used as the working electrode. All potentials, if not specified, were recorded according to reversible hydrogen electrode (RHE) in this work. For Pd/RGO and Pd catalysts working electrode, 2 mg Pd/RGO and pure Pd nanoparticles were dispersed in 2 mL of a mixture solvent (the volume ratio of H₂O: isopropanol: 5% Nafion is 4 : 1 : 0.025), and the mixture was sonicated for 30 min to get a homogeneous ink.

Specifically, cyclic voltammetrys (CVs) were performed in 1 M N₂-purged KOH solution at a scan rate of 50 mV s⁻¹. For ethanol, glycerol and ethylene glycol oxidation, CVs were

recorded in N₂-purged 1 M KOH + 1 M ethyl alcohol, 1 M KOH + 1 M glycerol and 1 M KOH + 1 M ethylene glycol, respectively, at a scan rate of 50 mV s⁻¹.

The light illumination is obtained by passing light from a 300 W Xenon lamp (Beijing China Education Au-light Co., Ltd) with a convex lens and the power intensity of the incident light is calibrated to 0.1, 0.2, 0.4 and 0.8 W cm⁻² at the surface of the working electrode. The effect of irradiation wavelengths on EOR performance is investigated under a monochromatic light which are obtained by using a band-pass filters of 500 nm.

Chronoamperometry was carried out in 1 M KOH + 1 M ethanol, 1 M KOH + 1 M glycerol and 1M KOH +1 M ethylene glycol at 0.85 V (vs. RHE) for 3600s.

For CO stripping, high-purity CO was bubbled into 1M KOH for 30 min. Dissolved CO was then purged out of the electrolyte by bubbling N₂ for 30 min. Two consecutive CVs were recorded for the catalysts between 0.1 and 1.3 V (vs. RHE) at a scan rate of 50 mV s⁻¹.

4. Additional Characterizations and Measurements

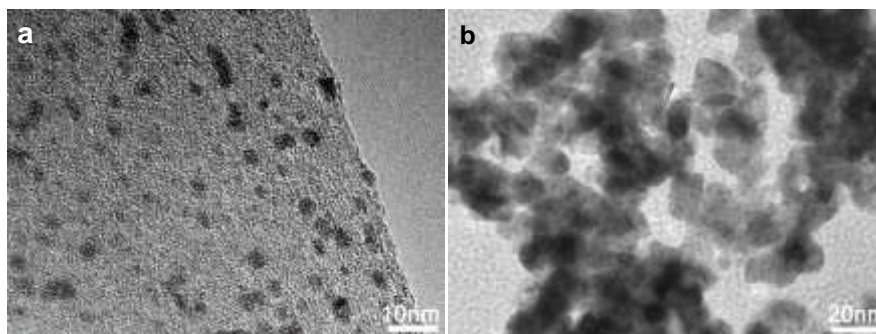


Fig. S1 TEM images of (a) Pd/RGO and (b) pure Pd nanoparticles.

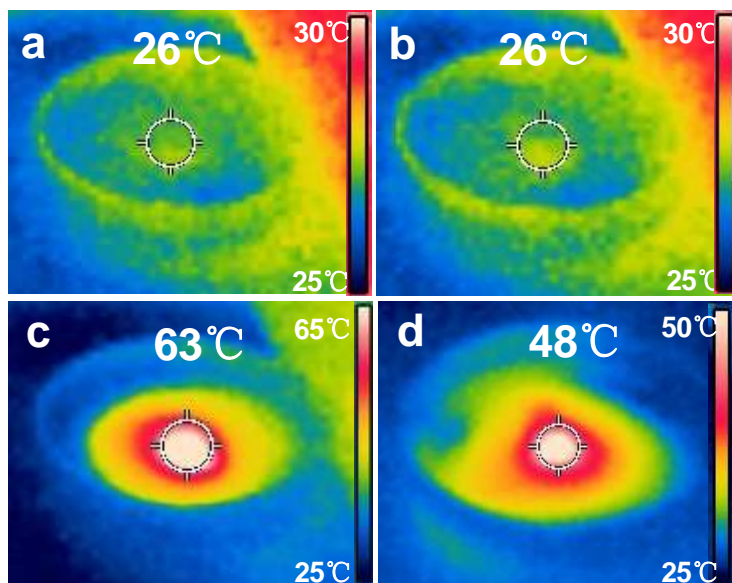


Fig. S2 Infrared photograph without light irradiation of (a) Pd/RGO and (b) pure Pd nanoparticles ; infrared photograph at the light irradiation of 0.8Wcm^{-2} at 1 minute of (c) Pd/RGO and (d) pure Pd nanoparticles.

For infrared thermography test, a certain amount of catalysts of Pd/RGO and pure Pd nanoparticles were coated on a double-sided tape and pasted on a glass slide of $1\times 1\text{ cm}^2$. The as-prepared samples were putted in a watch glass(diameter=8 cm) contained 20 mL electrolyte. A 300 W Xe lamp used as light source, the infrared photographs were taken by the infrared camera.

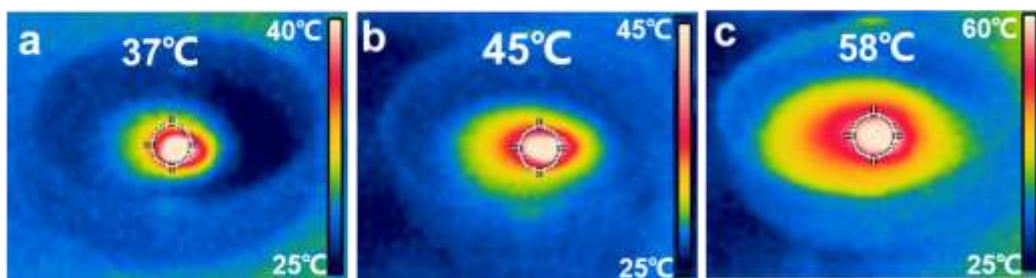


Fig. S3 Infrared photograph at the light irradiation of 0.1 Wcm^{-2} , 0.2 Wcm^{-2} and 0.4 Wcm^{-2} of Pd/RGO.

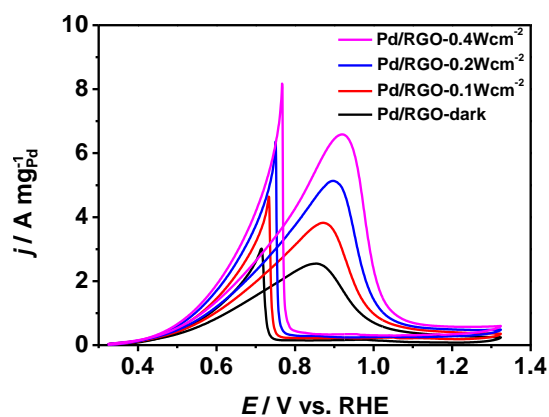


Fig. S4 The CV curves of EOR in the light illumination of 0.1Wcm⁻², 0.2Wcm⁻² and 0.4Wcm⁻² of Pd/RGO.

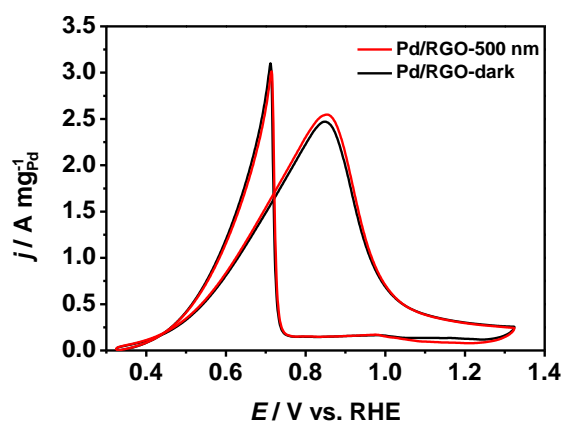


Fig. S5 The CV curves of EOR in the monochromatic light illumination of 500 nm of Pd/RGO.

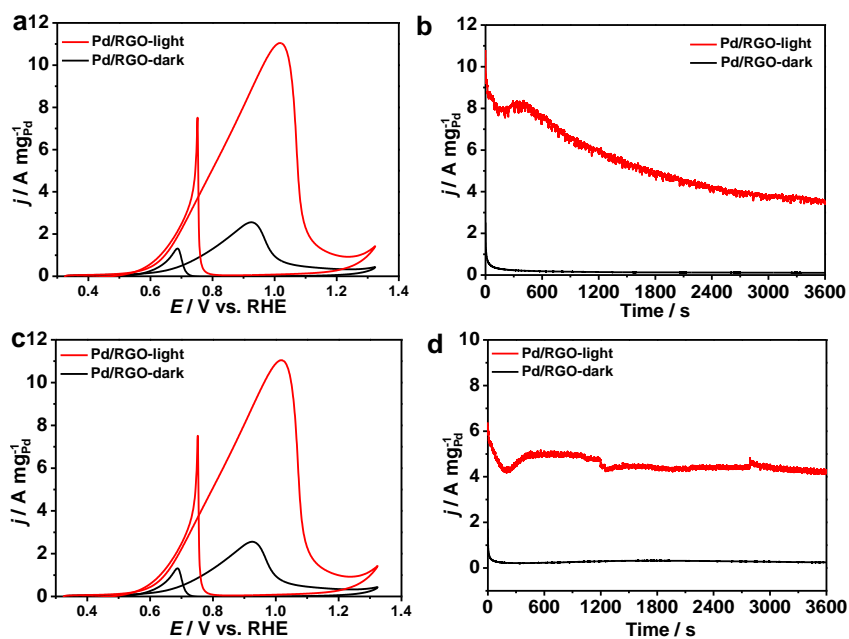


Fig. S6 The CV curves and chronoamperometry curves of (a, b) EGOR and (c, d) GOR.