

Electronic Supplementary Information

Photocatalytic synthesis of highly dispersed Pd nanoparticles on reduced graphene oxide and their application in methanol electro-oxidation

Haiyan Li,^a Guohui Chang,^a Yingwei Zhang,^a Jingqi Tian,^{a,b} Sen Liu,^a Yonglan Luo,^a

Abdullah M. Asiri,^{c,d} Abdulrahman O. Al-Youbi^{c,d} and Xuping Sun^{*a,c,d}

^aState Key Lab of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China

^bGraduate School of the Chinese Academy of Sciences, Beijing 100039, China

^cChemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

^dCenter of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

*To whom correspondence should be addressed. Tel/Fax: (+86) 431-85262065;

E-mail: sunxp@ciac.jl.cn

Experimental Section

Materials The 8,13-Bis(vinyl)-3,7,12,17-tetramethyl-21H,23H-porphine-2,18-dipropionic acid tin(IV) dichloride (SnP) (99.95%) was purchased from Frontier Scientific, Inc. (Logan, UT, USA). Solutions of SnP in ethanol was prepared as stock solutions in advance, and kept in a refrigerator in a light protected foiled vial. Graphite powder and H_2PdCl_4 were from Aladin Ltd. (Shanghai, China). Unless otherwise specified, other reagents involved were obtained commercially from the Beijing Chemical Reagent Plant (Beijing, China) and used as received without further purification. Solution of H_2PdCl_4 in water was prepared as stock solution in advance, the water used throughout all experiments was purified through a Millipore system, and the experiments were carried out at room temperature and humidity.

Preparation of GO GO was prepared from natural graphite powder through a modified Hummers' method.¹ In a typical synthesis, 1 g of graphite was added into 23 mL of 98% H_2SO_4 , kept stirring at room temperature for 24 h. then, 100 mg of NaNO_3 was introduced into the mixture and stirred for 30 min. Subsequently, the mixture was kept below 5 °C by ice bath, and 3 g of KMnO_4 was slowly added into the mixture. After being heated to 35-40 °C, the mixture was stirred for another 30 min. After that, 46 mL of water was added into above mixture during a period of 25 min. Finally, 140 mL of water and 10 mL of 30% H_2O_2 were added into the mixture

to stop the reaction. After the unexploited graphite in the resulting mixture was removed by centrifugation, as-synthesized GO was dispersed into individual sheets in distilled water at a concentration of 1 mg mL^{-1} with the aid of ultrasound for further use.

Preparation of PdNPs/RGO nanocomposites The RGO was first synthesized by a photocatalytic process. In a typical synthesis, 0.5 ml of 1 mg mL^{-1} GO, 40 μl of 200 mM SnP and 6 ml of 45 mM triethanolamine (TEA) were added to a glass reactor, cooling water was circulated outside the reactor to maintain the reaction temperature at $25 \text{ }^\circ\text{C}$, then irradiated with a 500 W xenon lamp (CHFXQ500W, Beijing) with a UV cutter filter ($\lambda > 400 \text{ nm}$) for 15 min under magnetic stirring. Next, 261 μl of 9.3 mM H_2PdCl_4 stock solution was added to the above solution, and then irradiated for 5 min to produce PdNPs on the RGO surface.

Characterization and measurements X-ray photoelectron spectroscopy (XPS) analysis was measured on an ESCALABMK IIX-ray photoelectron spectrometer using Mg as the exciting source. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 EM (Hitachi, Tokyo, Japan) with an accelerating applied potential of 200 kV. The sample for TEM characterization was prepared by placing a drop of the dispersion on carbon-coated copper grid and dried at room temperature. Electrochemical measurements are performed with a CHI

660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell was used, including a glassy carbon electrode (GCE, geometric area=0.07 cm²) as the working electrode, a Ag/AgCl (saturated KCl) electrode as the reference electrode, and platinum foil as the counter electrode. The potentials are measured with a Ag/AgCl electrode as the reference electrode. 2 μL of PdNPs/RGO nanocomposites (3.8 mg mL⁻¹) or commercial Pd/C (11 mg mL⁻¹) was dropped on the surface of GCE and the solvent was allowed to evaporate at ambient temperature before use. The Pd loading amount for as-synthesized PdNPs/RGO (0.059 mg cm⁻²) and commercial Pd/C (0.063 mg cm⁻²) were determined from their respective amounts present in the suspension assuming 100% utilization of the Pd precursor.

1. J. W. S. Hummers and R. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

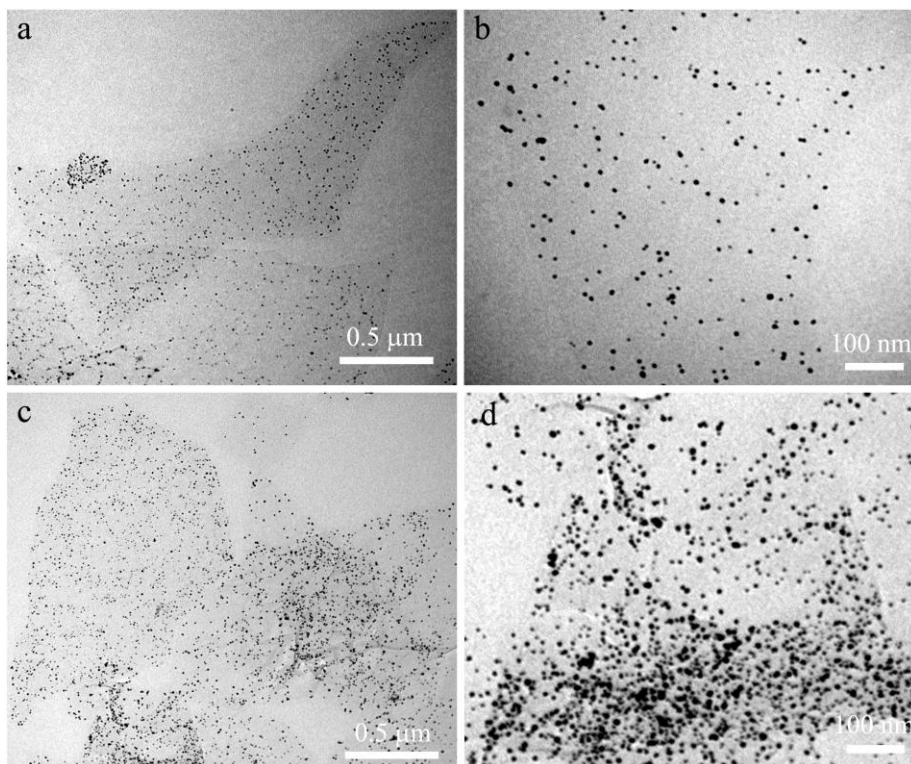


Fig. S1 Low and high magnification TEM images of PdNPs/RGO nanocomposites with irradiation time of (a) and

(b) 2 min, (c) and (d) 15 min.