

Pd_xAg_y alloy nanoparticles supported on reduced graphene oxide as efficient electrocatalyst for ethanol oxidation in alkaline medium

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Supplementary Information

Experimental Details

Catalyst preparation: GO was prepared from natural graphite (Sinopharm Chemical Reagent Co., Ltd) according to the Hummers method.¹ 0.5 mg mL⁻¹ GO brown suspension was obtained by ultrasonication in deionized water. In a typical synthesis of Pd₁Ag₁ catalyst, 1 ml PVP (MW ≈ 50 000, Sinopharm Chemical Reagent Co., Ltd) solution (0.01 mol L⁻¹) and 1 ml HCHO (Sinopharm Chemical Reagent Co., Ltd) solution were added into 9.6 ml GO suspension, subsequently, 9.9 ml Pd(NO₃)₂ (Sinopharm Chemical Reagent Co., Ltd) solution (1.5×10⁻³ mol L⁻¹) and 0.15 ml AgNO₃ (Sinopharm Chemical Reagent Co., Ltd) solution (0.1 mol L⁻¹) were added into the solution while stirring. The mixture was sealed in a Teflon-lined stainless steel autoclave and maintained at 105 °C for 6 h, and cooled to ambient temperature. The resultant product was collected by centrifugation, washed with deionized water and ethanol to remove the residual impurities, and then dried in a vacuum oven at 50 °C for 24h. The obtained catalysts were denoted as Pd_xAg_y/RGO where x to y stands for the nominal atomic ratio of Pd to Ag. For comparison, Pd/RGO catalyst was also prepared with the same procedure. Furthermore, bare RGO was also synthesized under the same conditions in the absence of both Pd(NO₃)₂ and AgNO₃.

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Electrochemical investigation: All the electrochemical measurements were performed on a CHI660D electrochemical workstation at room temperature. The working electrode was prepared by dropping 15 μL electrocatalyst ink ($0.6\text{mg}\cdot\text{mL}^{-1}$) onto glassy carbon electrode with a micropipette and then dried at room temperature. The ink was prepared by ultrasonically mixing 10 μL electrocatalyst sample in 5 μL Nafion solution (DuPont, 1 wt% in isopropanol). A Pt foil and Hg/HgO electrode were used as the counter and reference electrodes, respectively. The solutions were deaerated by bubbling ultrapure N_2 for 20 min and protected with a nitrogen atmosphere during the entire experimental procedure.

Materials characterization: Structure and morphology of the $\text{Pd}_x\text{Ag}_y/\text{RGO}$ nanocomposite were investigated using X-ray diffraction (XRD, Bruker D8 advance X-ray diffractometer, Cu-K α radiation, $\lambda = 0.154059\text{ nm}$ at 40 kV and 40 mA, 2θ range of $30\text{-}80^\circ$, scan rate $4^\circ\cdot\text{min}^{-1}$) and transmission electron microscopy (TEM, JEM100CXII). Composition analysis of the sample was obtained on HITACHI S-3500N scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDX, OXFORD 7021).

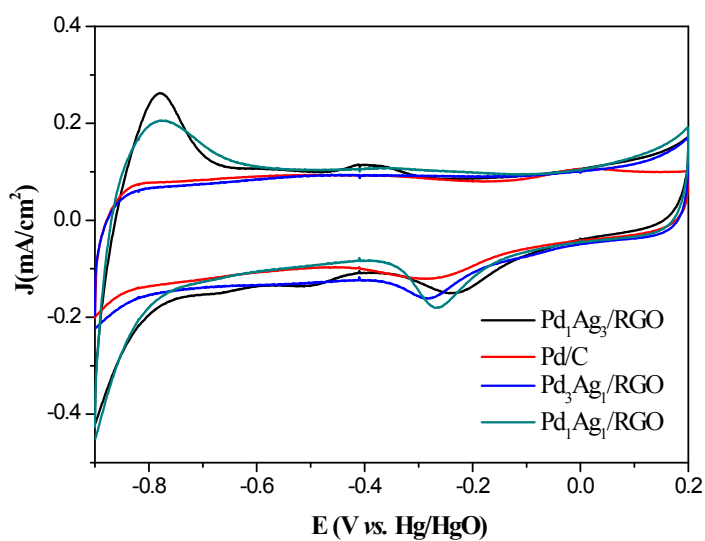


Figure S1 CVs of the Pd_xAg_y/RGO catalysts and commercial Pd/C in 1.0 mol L⁻¹ KOH solution.

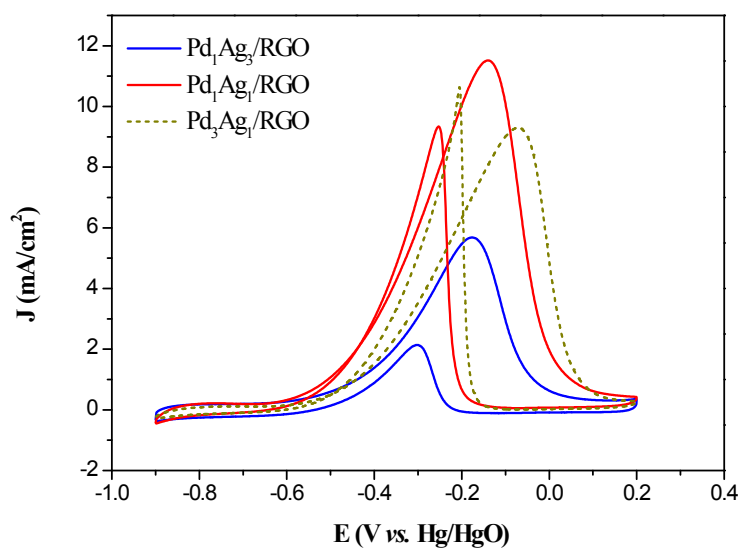


Figure S2 CVs of the Pd_xAg_y/RGO catalysts in 1.0 mol L⁻¹ KOH solution containing 1.0 mol L⁻¹ ethanol.

Table S1 The calculated lattice parameter and atomic percentage of Ag in the Pd_xAg_y/RGO catalysts.

Samples	A_{fcc} (Å)	y_{Ag} (at.%)
Pd ₁ Ag ₃ /RGO	4.0442	81.4
Pd ₁ Ag ₁ /RGO	3.9857	51.7
Pd ₃ Ag ₁ /RGO	3.9302	22.3

Table S2 Results of the cyclic voltammetric study on the Pd_xAg_y/RGO catalysts.

Samples	E_s (V)	E_p (V)	J_p (mA·cm ⁻²)
Pd ₁ Ag ₃ /RGO	-0.66	-0.17	5.7
Pd ₁ Ag ₁ /RGO	-0.68	-0.14	11.5
Pd ₃ Ag ₁ /RGO	-0.65	-0.07	9.3

Reference

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