Supporting Information

Monolayer of close-packed Pt nanocrystals on reduced graphene oxide (RGO) nanosheet and its enhanced catalytic performance towards methanol electrooxidation

Lin-Nan Zhou,[a] Xiao-Ting Zhang, [a] Wen-Jin Shen, [a] Shi-Gang Sun,*[b] and Yong-Jun Li* [a]

[a]*State Key Lab of Chemo/Biosensing and Chemometrics, School of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China. E-mail: liyje@hnu.edu.cn*

[b]*State Key Lab for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, China. E-mail: sgsun@xmu.edu.cn*

Synthesis of Pt_{17}/RGO, Pt_{19}/RGO, Pt_{39}/RGO and Pt_{52}/RGO nanocomposites

Besides Pt_{24}/RGO described in the text, Pt_{17}/RGO, Pt_{19}/RGO, Pt_{39}/RGO and Pt_{52}/RGO were also synthesized by the same procedure except for the difference of the amount of H_2PtCl_6 and $NaBH_4$ added in the synthetic process. In all synthesis, the molar ratios of $NaBH_4$ to H_2PtCl_6 were kept to be 5. Table S4 shows the detailed information about the added amount of $NaBH_4$ and H_2PtCl_6. Pt contents of Pt_{17}/RGO, Pt_{19}/RGO, Pt_{39}/RGO and Pt_{52}/RGO were determined to be 17 wt%, 19 wt%, 39 wt% and 52 wt%, respectively, by an inductively coupled plasma-optical emission spectroscopy (ICP-OES).

All dry samples were redispersed into 5 mL of water for electrocatalysis and the corresponding concentrations were 3.306 mg/mL Pt_{17}/RGO, 2.958 mg/mL for Pt_{19}/RGO, 1.441 mg/mL for Pt_{39}/RGO and 1.081 mg/mL for Pt_{52}/RGO.

Fabrication of catalytic electrode

10 μL of Pt_{17}/RGO, Pt_{19}/RGO, Pt_{39}/RGO and Pt_{52}/RGO dispersions were applied over clean GC disks (diameter, 5 mm), respectively. After drying in the air at room temperature, 5 μL of Nafion alcohol solution (0.05 wt%) was applied over each electrode surface for solidification.

Table S1. Summary of C1s XPS analysis result.

	binding energy/eV (atomic percentage, %)			
Sample	C=C	C-O-	C=O	COOH
RGO	284.79 (58.60)	286.19 (14.06)	288.00 (18.57)	291.82 (8.77)
RGO/Pt	284.73 (61.22)	286.21 (17.14)	288.35 (16.32)	292.10 (5.32)

Table S2. Summary of O1s XPS analysis result.

	binding energy/eV (atomic percentage, %)		
Sample	C=O*-/-C=O*O-	C-O*/C=OO*-	adsorbed H_2O
RGO	530.96 (31.63)	532.60 (58.59)	534.96 (9.78)
Pt /RGO	530.70 (17.01）	532.08 (71.46)	535.44 (11.53)

*represents the type of oxygen.

Table S3. Summary of Pt4f XPS analysis result.

	binding energy/eV (atomic percentage, %)		
Sample	Pt(0)	Pt(II)	Pt(IV)
Pt nanoparticles	71.29&74.49 (85.53)	72.53&75.73 (7.25)	75.86&78.76 (7.22)
Commercial Pt/C	71.61&74.81 (67.10)	73.35&76.50 (18.99)	76.07&78.97 (13.91)
Pt_{24}/RGO	71.61&74.81 (44.60)	72.84&75.84 (34.73)	76.33&79.28 (20.68)

Table S4. Detailed information of Pt/RGO composites.

Samples	Volume (H_2PtCl_6)/mL[a]	Volume ($NaBH_4$)/mL[b]	$c_{Pt/RGO}$/mg·mL^{-1}	Pt wt%[c]	ECSA/m^2·g^{-1}	j_f/j_b
Pt_{17}/RGO	1.0	1.0	3.306	17	15.08	1.24
Pt_{19}/RGO	2.0	2.0	2.958	19	16.06	1.01
Pt_{24}/RGO	3.0	3.0	2.342	24	32.6	1.23
Pt_{39}/RGO	6.0	6.0	1.441	39	36.7	1.11
Pt_{52}/RGO	12.0	12.0	1.081	52	24.1	0.91
Pt/C	—	—	2.810	20	17.3	0.87

[a] The concentration of H_2PtCl_6 is 0.02 mol/L.

[b] The concentration of $NaBH_4$ is 0.10 mol/L.

[c] It was determined by ICP-OES.

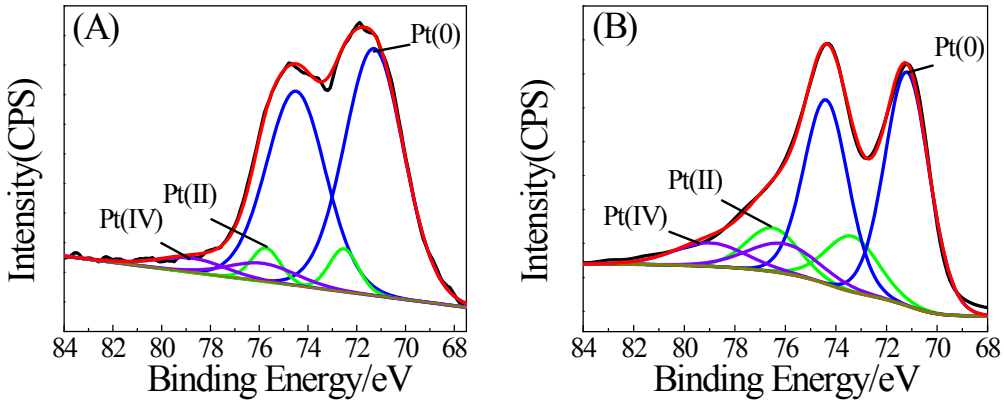

Fig. S1. Pt4f XPS spectra of Pt nanoparticles and the commercial Pt/C catalyst. Black curves are the original patterns; red curves are the simulated patterns by the curves of the deconveluted components marked in each figure.

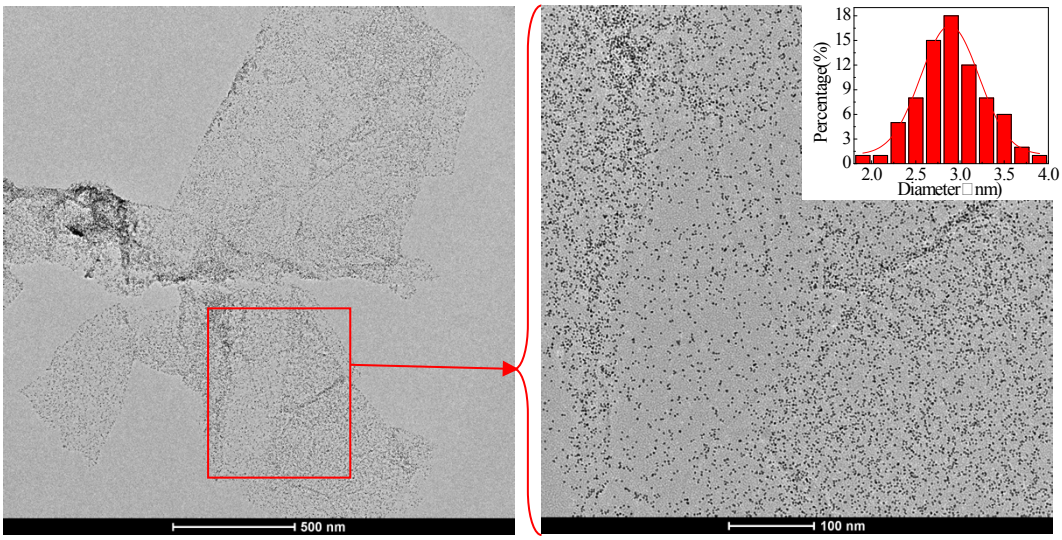

Fig. S2. TEM images of Pt_{17}/RGO with different magnifications. The inset is the particle size distribution and the diameter is 2.88 ± 0.02 nm.

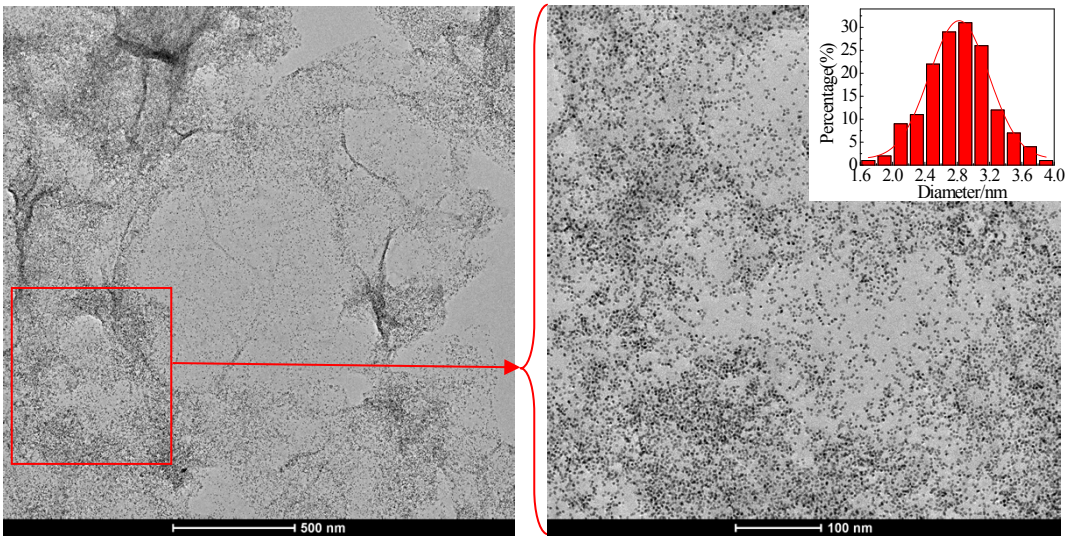

Fig. S3. TEM images of Pt_{19}/RGO with different magnifications. The inset is the particle size distribution and the diameter is 2.82 ± 0.02 nm.

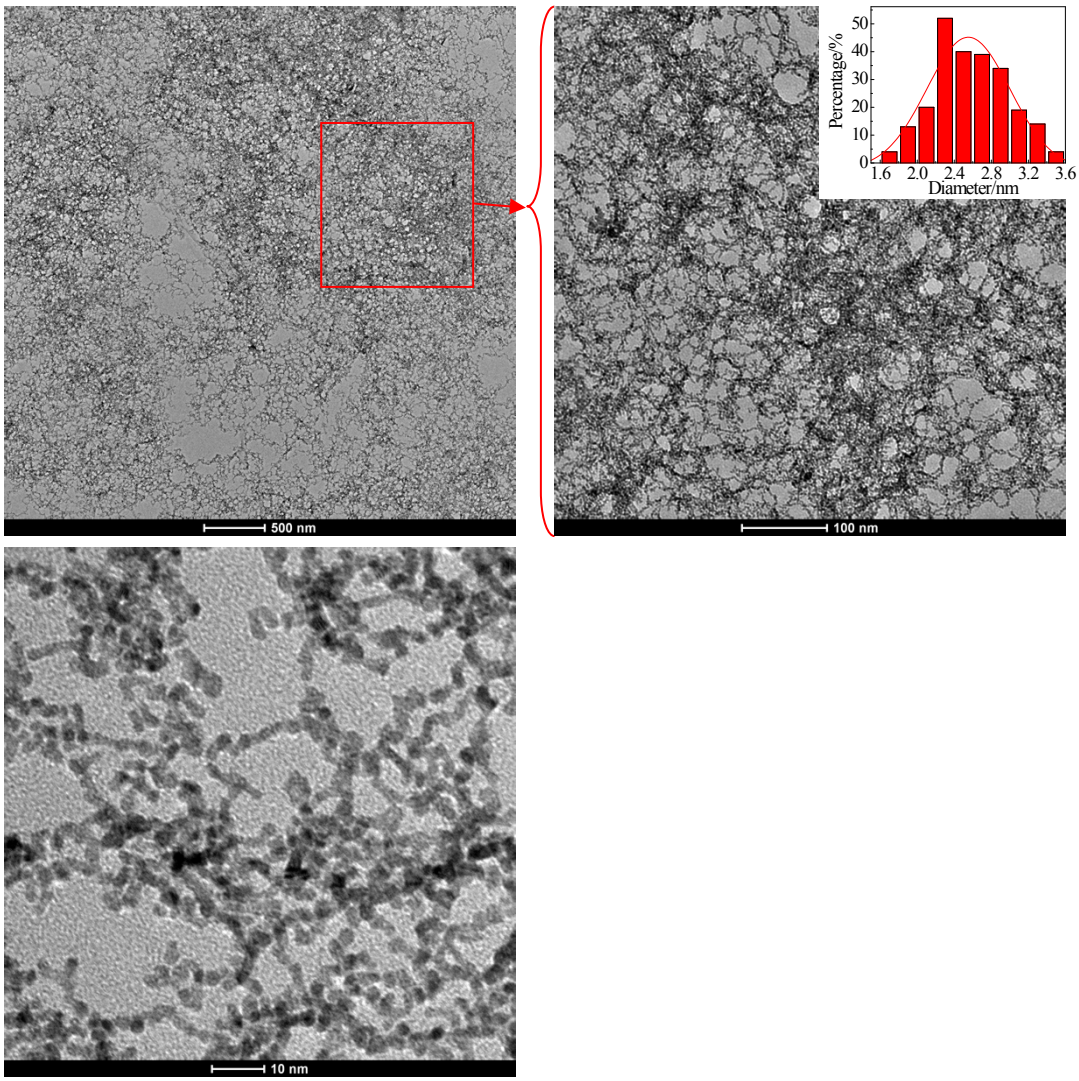

Fig. S4. TEM images of Pt_{39}/RGO with different magnifications. The inset is the particle size distribution and the diameter is 2.55 ± 0.04 nm.

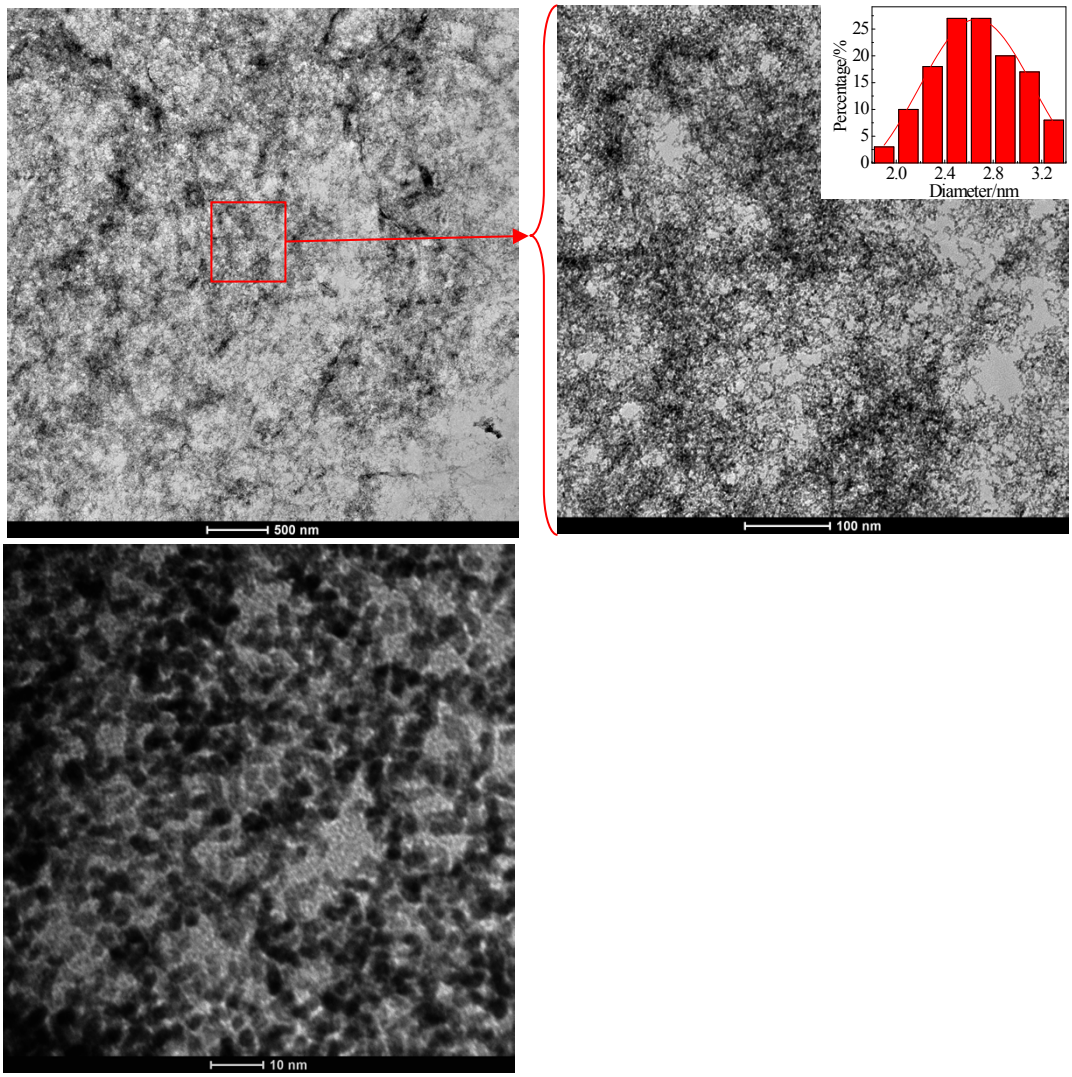

Fig. S5. TEM images of Pt_{52}/RGO with different magnifications. The inset is the particle size distribution and the diameter is 2.66 ± 0.02 nm.

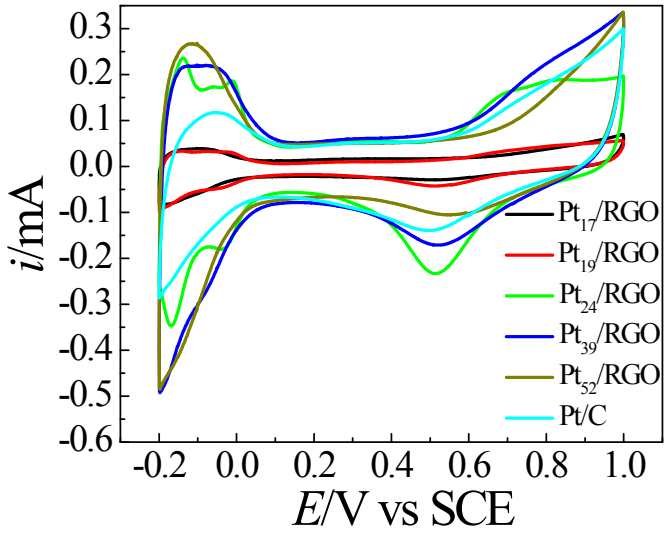

Fig. S6. Cycle voltammograms of five Pt/RGO composites and the commercial Pt/C in 0.5 mol/L H_2SO_4 at a scan rate of 50 $mV \cdot s^{-1}$.