Electronic Supplementary Information for

Continuous synthesis of graphene sheets by spray pyrolysis and their uses as catalysts for fuel cells

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Experimental Section

Preparation of graphene sheets (GNS) : The mixture of carbonyl and pyridine was injected into a quartz reactor at a flow rate of 5 mL min^{-1}. Meanwhile, N_2 was supplied at a flow rate of 600 L h^{-1}. The resultant sample was collected in a glass bottle connected with the quartz reactor (Fig. S1). In order to remove iron particles, the as-prepared sample was mixed with excess ammonium chloride (NH_4Cl) and heated at 800 °C for 30 min in a quartz tube. The heated sample was then washed and filtered in water and finally dried for future uses.

Preparation of Pt/GNS catalysts: Pt/GNS catalysts were prepared by ethylene glycol reduction. In a typical process, GNS were sonicated in ethylene glycol to form a suspension. Then, the mixed solution of chloroplatinic acid (CPA) and ethylene glycol was added slowly into the GNS suspension. The Pt loading on GNS was ~25 wt.%. The mixture solution was refluxed at 130 °C for 3 h. After cooling to room temperature, the catalysts were filtered, washed with deionized water until no Cl^- could be detected, and subsequently vacuum-dried for 24 h.

Electrochemically testing of Pt/GNS in 0.5M H_2SO_4 and GNS Pt-free catalyst in 0.1 M KOH: Electrochemically-accelerated durability testing (ADT) was employed to evaluate the long-term performance of catalysts in a three-electrode cell using a CHI618D instrument at a constant temperature. This temperature was controlled to be within 25±2 ºC in a water bath in order to minimize the effect of ambient temperature variation from winter to summer or from day to night time. A saturated calomel electrode (SCE) and a Pt foil were used as reference and counter electrodes, respectively. All the potential in this work were referred to normal hydrogen electrode (NHE). A rotating disk electrode (RDE, Pine, AFMSRCE 3005) with a diameter of 5.6 mm was used as the working electrode for the oxygen reduction reaction (ORR) test.

In the experiment of testing Pt/GNS catalyst in 0.5 M H_2SO_4, the working electrode was prepared as follows: 4 mg Pt/GNS catalyst was dispersed in a mixture of methanol and 5 wt.% Nafion solution with a weight ratio of 50:1. The mixture was agitated by ultrasonication for 30 min to form an ink. A given amount of this ink was then dropped on the electrode and dried to yield a thin-film electrode. The Pt loading on the RDE was ~23 μg cm^{-2}. Cyclic Voltammetry curves (Fig. S8) were recorded in N_2–saturated 0.5 M H_2SO_4 solution at 25 °C with a scan rate of 100mV s^{-1}. Polarization curves were obtained in O_2-saturated 0.5 M H_2SO_4 solution at 25 °C with a scan rate of 5mV s^{-1} and a rotation rate of 1600 rpm. For the durability study, the RDE was subjected to a potential cycling from 0.6 to 1.2 V (vs. NHE) at a rate of 100 mV s^{-1}. ORR curves were recorded at each set of 1000 cycles. For comparison, a commercial Pt/C catalyst from Johnson Matthey Co. (JM) was tested with the same procedures.

In the test of Pt-free GNS catalyst in 0.1 M KOH, the working electrode was prepared as follows: 5 mg G2 was dispersed in a mixture of methanol and 5 wt.% Nafion solution with a weight ratio of 50:1. The mixture was agitated by ultrasonication for 30 min to form an ink. Then a given amount of this ink was dropped on the electrode and dried to form a thin-film electrode. The G2 loading on the RDE was controlled to be 0.71 mg cm^{-2}. The ORR polarization curves were recorded in an O_2–saturated 0.1 M KOH solution, with a scan rate of 5 mv s^{-1} and a rotation rate of 1600 rpm. For the durability test, the electrode was scanned from -0.2 to 0.4 V (vs. NHE) at a rate of 100 mV s^{-1}. ORR curves were recorded at each set of 1000 cycles. For comparison, JM catalyst was tested with the same procedures.

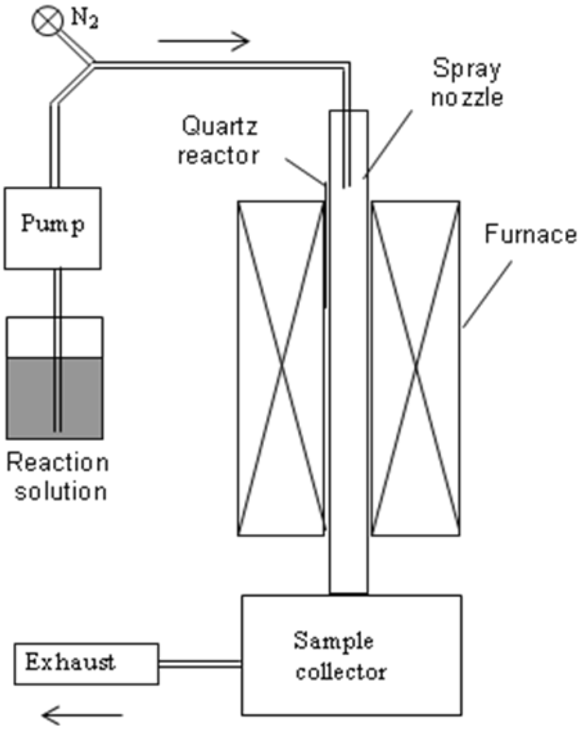

Fig. S1. Experimental setup for the present spray pyrolysis.

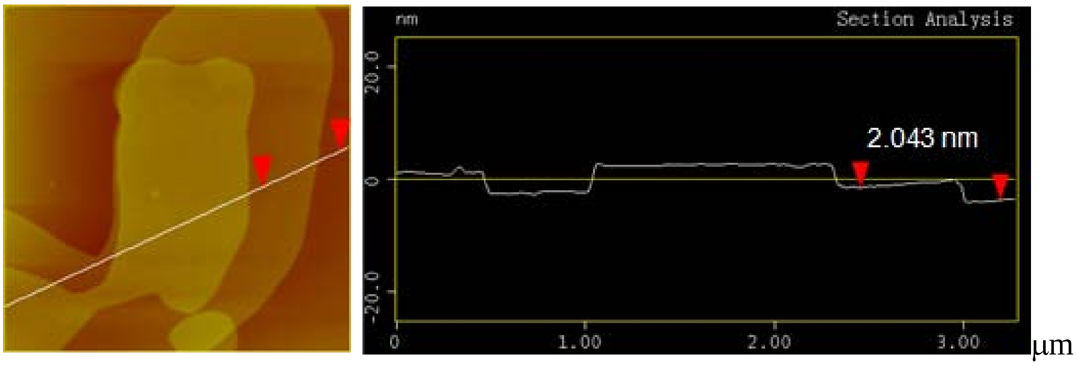

Fig. S2. A typical tapping mode AFM image of G2 sample deposited on a mica substrate from aqueous dispersion, and the corresponding height cross-sectional profile. (scanning area: 3×3μm).

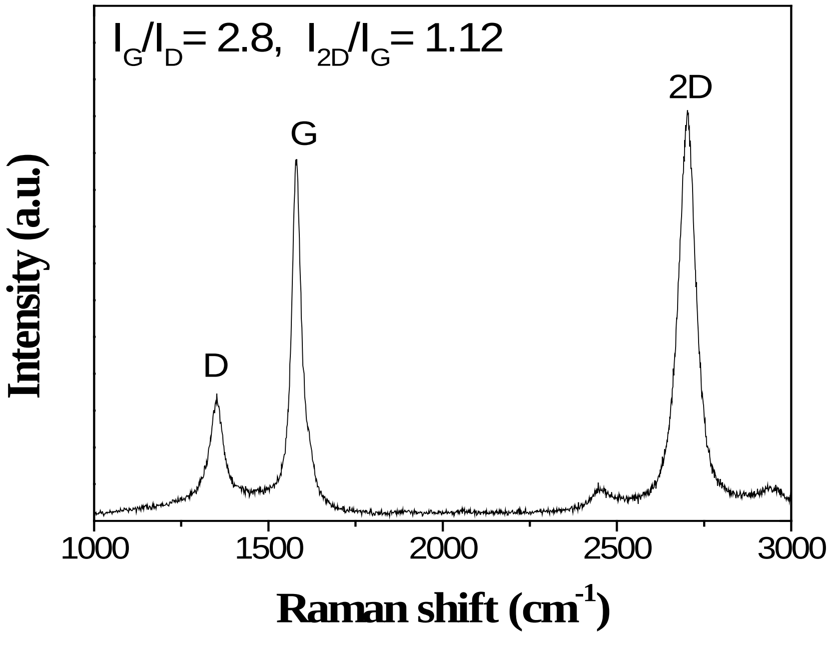

Fig. S3. Raman spectrum for the sample of G2.

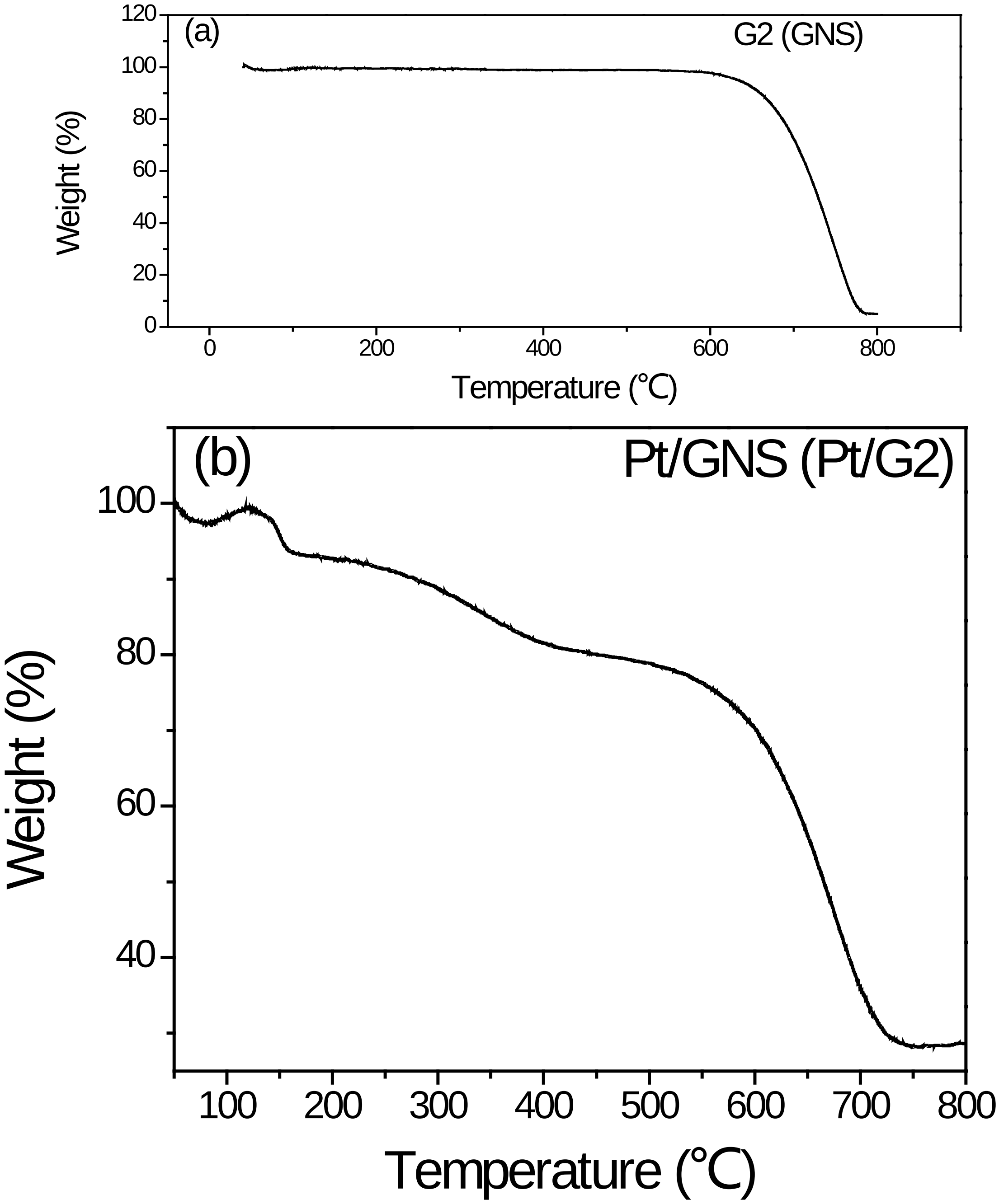

Fig. S4. TGA curves of GNS sample (a) and Pt/GNS catalyst (b). (Atmosphere: air; heating rate:10°C min^{-1}; temperature range: 40-800°C).

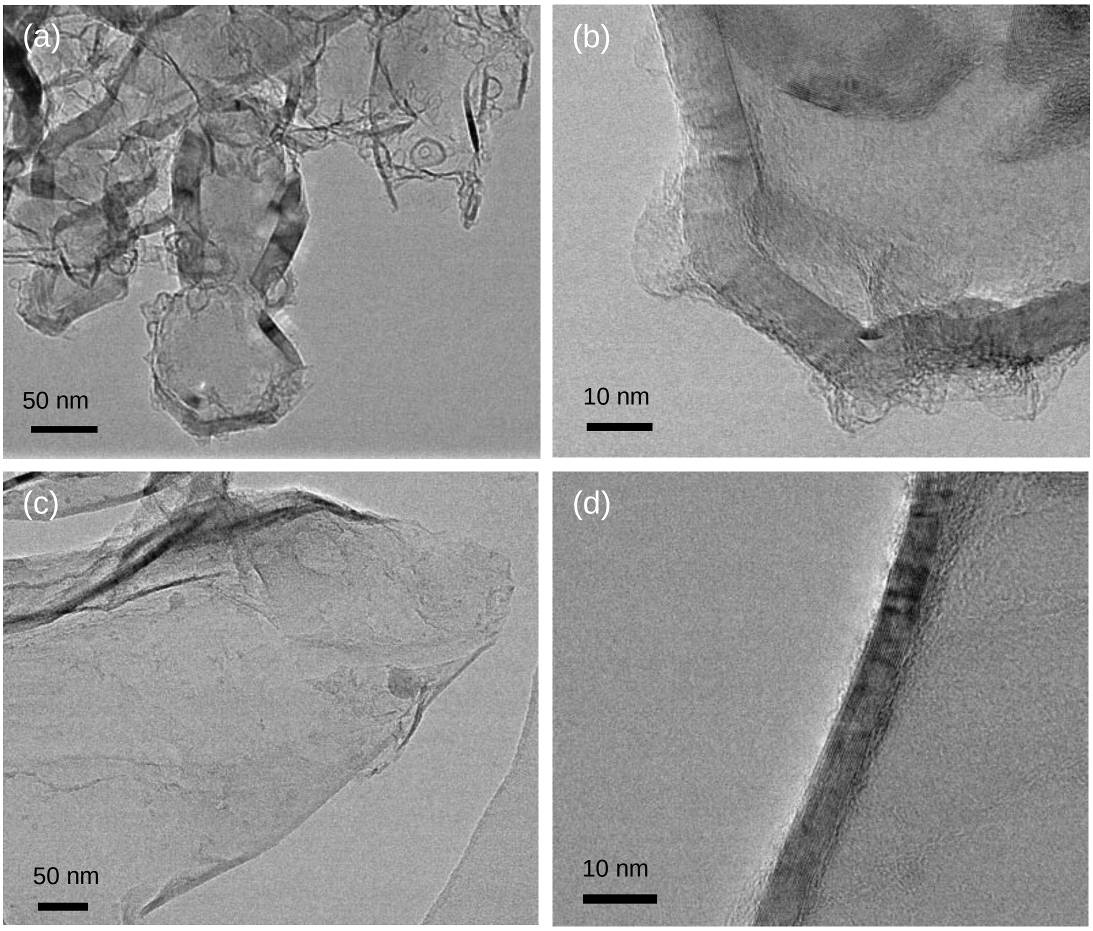

Fig. S5. TEM images of G3 (a, b) and G4 (c, d).

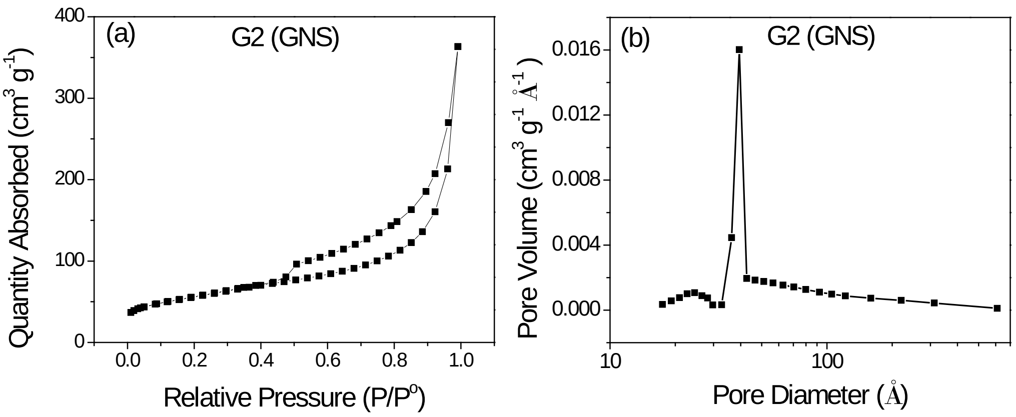

Fig. S6. N_2 adsorption/desorption isotherms (a), and mesopore size distribution (b) of G2 sample.

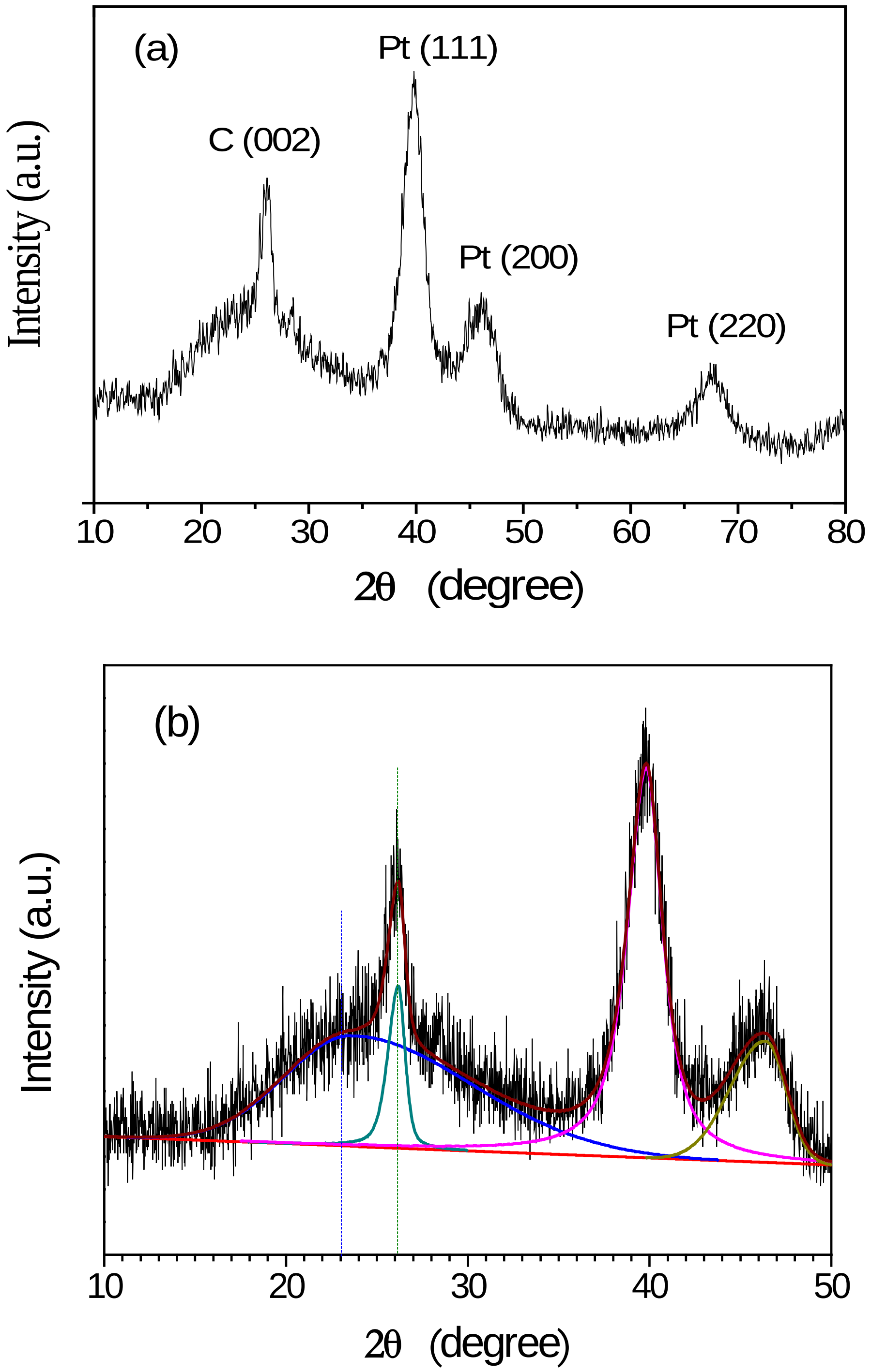

Fig. S7. XRD pattern of Pt/GNS catalyst (a), and the deconvolution of the peak at about 26° into two peaks (b). The sharp peak at 2θ=26.16° (green) may be ascribed to a small amount of multi-layered graphene sheets with a well-developed graphitic structure, and the broad one at about 23° may be attributed to few-layered graphene sheets.

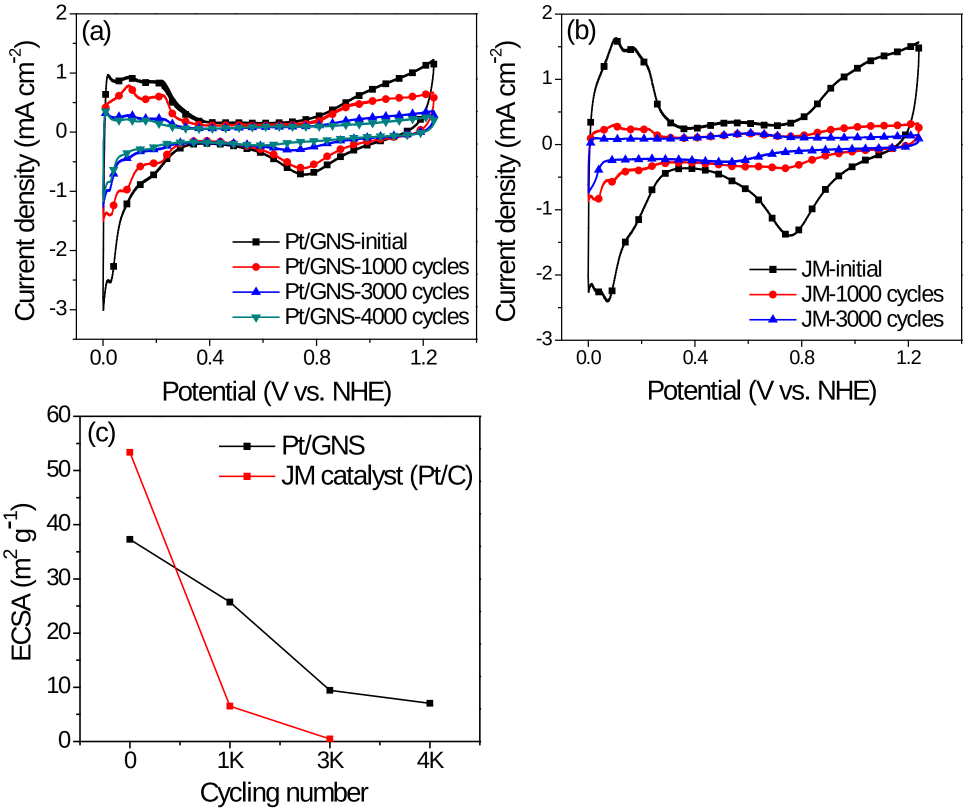

Fig. S8. CV curves of Pt/GNS (a) and JM catalysts (b) in N_2-saturated 0.5M H_2SO_4 (scan rang: 0-1.24 V vs. NHE; scan rate: 100 mV s^{-1}) and the variation of ECSA with the cycling number (c).

The electrochemical surface area (ECSA) was calculated according to the following equation (W. Wang and Z. Ma, Acta Phys.-Chim. Sin, 2012, 28, 2879-2884):

$$\mathrm{ECSA}=\frac{Q_H}{(m\cdot\beta)}$$

where, Q_H is the charge for hydrogen desorption (mC cm^{-2}), m the quantity of Pt used, and β the charge required to oxidize a monolayer of H_2 to bright Pt (=0.21 mC cm^{-2}).

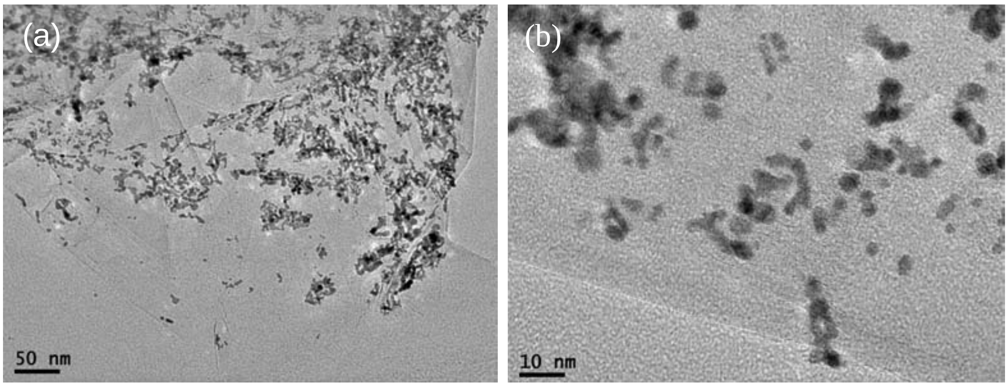

Fig. S9. TEM images of Pt/GNS after 4000 potential cycles.