Graphene sheets fabricated from disposable paper cups as a catalyst support material for fuel cells

Hong Zhao and T.S. Zhao*

Department of Mechanical Engineering, the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon SAR, China

E-mail: *metzhao@ust.hk*

Tel. +852-23588647; Fax: +852-235886471543

Experimental Section

Preparation of the graphene sheets and Pt/graphene sheets. In a typical synthesis, a disposable paper-cup was cut into small pieces and put in KOH aq％(1M/L), stirring for 72 h. The solid was separated by several washing/centrifugating cycles with distilled water until neutral, the K^+-doped paper-cups pulp were obtained. For preparation of the M^{n+}-loaded pulp, dispersed the solid into $(NH_4)_2FeSO_4$ (1M/L), $FeCl_3$(1M/L), $CuCl_2$(1M/L) and $NiCl_2$ (1M/L) aqueous solution, respectively, stirring for 48 h under the protection of nitrogen, then the solid was separated by centrifugation. This procedure was repeated three times. The corresponding composite named M^{n+}-pulp was then carbonized at 1100 ℃ under N_2 atmosphere for 45 min. Then, the obtained sample was treated in hydrochloric acid for 12 h to remove the metal catalyst. The obtained solids were separated by several washing/centrifugating cycles with distilled water until neutral and dried in a vacuum oven at 60℃. Thus, the graphene sheets and other carbon materials were obtained, respectively. It is great that about 2g graphene sheets can be obtained using one discarded paper-cup. When no complete removing the Fe specials, dispersed the Fe-graphene solid in distilled Pt $(NH_3)_4Cl_2$ (6mM) water solution reaction system with ultrasound assisted for 6 hours, after the mixture was filtered and dried, thus Pt/graphene sheets were obtained.

Characterizations. Transmission electron microscopy (TEM) images were obtained by using a high-resolution JEOL 2010F TEM system operating with a LaB6 filament at 200 kV. Carbon-coated nick grids were used as sample holders for TEM analysis. AFM images were recorded on a Seiko SPA 400 with a Nanonavi Probe Station in tapping mode (dynamic force mode). Commercially available Si cantilevers with a force constant of 20 N/m were used as substrate.

The valence state of the prepared samples was carried out by the X-ray photoelectron spectroscopy (XPS) technique, which is equipped with a Physical Electronics PHI 5600 multi-technique system using Al monochromatic X-ray at a power of 350 W. Raman measurement was performed with a Jobin Yvon HR 800 micro-Raman spectrometer at 633 nm. The laser beam was focused onto the sample with a 50×objective. The X-ray diffraction (XRD) patterns were obtained with a Philips powder diffraction system (model PW 1830) using a Cu Ka source operating at 40 keV at a scan rate of $0.025^{o}S^{-1}$. The electrical conductivity (r) of the graphene films was calculated using the simple relation r = 1/Rt, where R is the surface resistivity and t is the film thickness. The surface resistivity was measured by the four-point probe method and the thickness was estimated by micrometer caliper. Electrochemical measurements were carried out by cyclic voltammetry (CV) using a potentiostat (EG&G Princeton, model 273A). A conventional, three-electrode cell consisting of glassy carbon electrode (GCE) was used as the working electrode, Pt foil was employed for the counter electrode and Ag/AgCl $HClO_4$ (1.0 M) was used as the reference electrode. The working electrode was modified with the catalyst layer achieved by dropping a suitable amount of catalyst on the GCE.

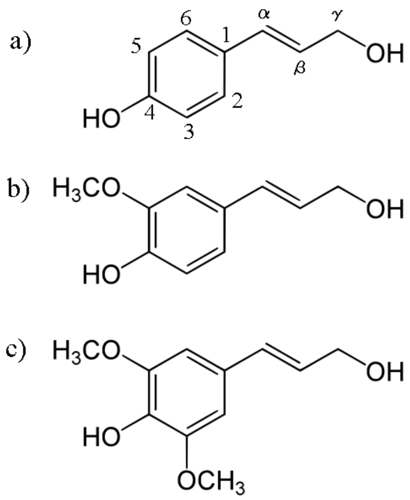

Fig. S1 The three common monolignols: paracoumaryl alcohol (a), coniferyl alcohol (b) and sinapyl alcohol (c).

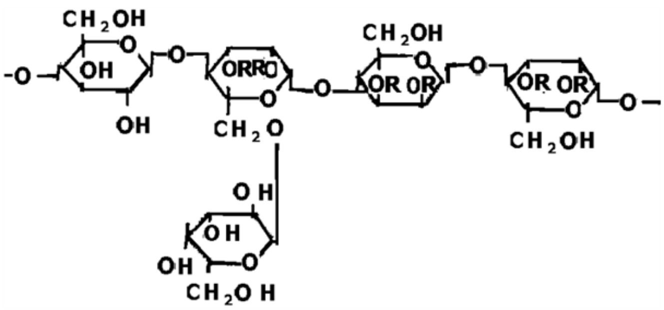

Fig. S2 An example for molecular structure of hemicellulose.

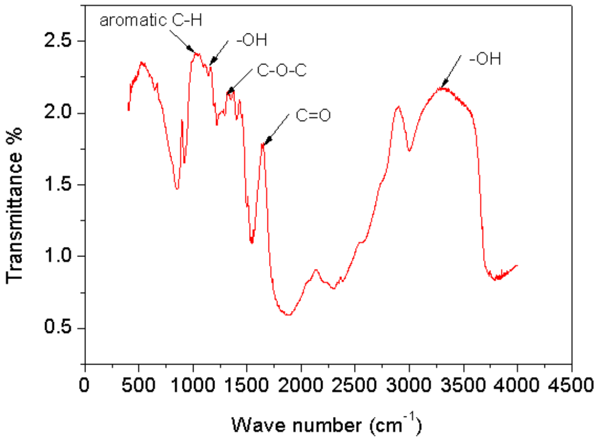

Fig. S3 FTIR spectrum of paper-cups pulp.

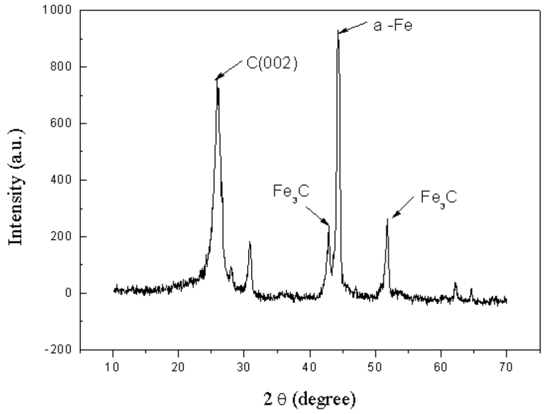

Fig. S4 XRD curve of the sample of Fe^{2+}-C after heat treatment.

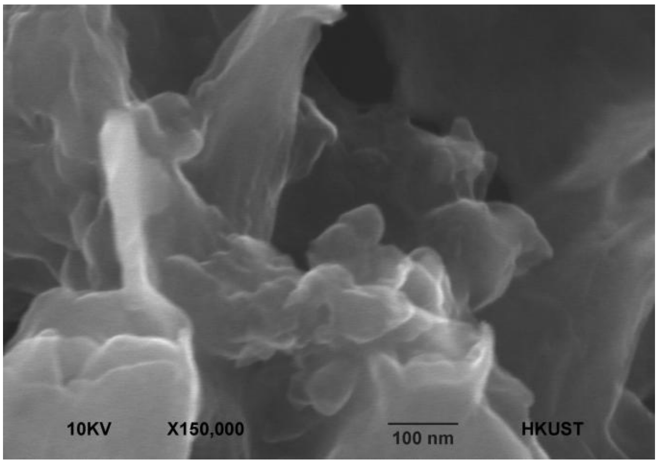

Fig. S5 SEM of the conglomerated graphene sheets.

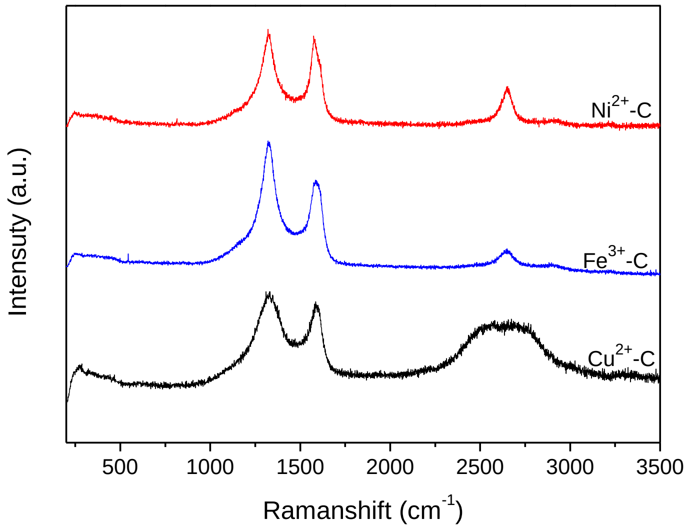

Fig. S6 Raman spectra of different metal-carbon systems.

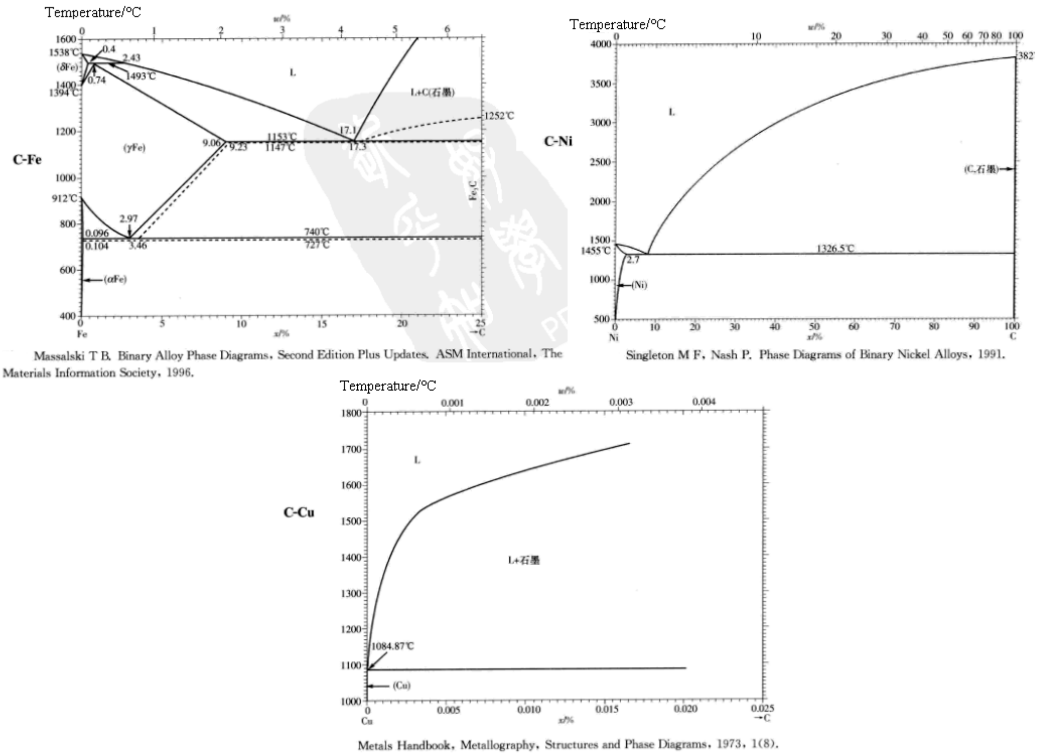

Fig. S7 Phase diagrams of metal-carbon systems. (from internet)

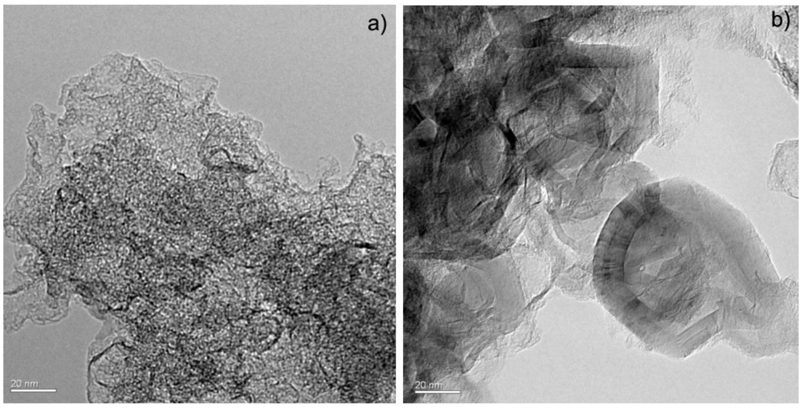

Fig. S8 TEM images of carbon nanostructures of samples Ni^{2+}-C (a) and Fe^{3+}-C (b).

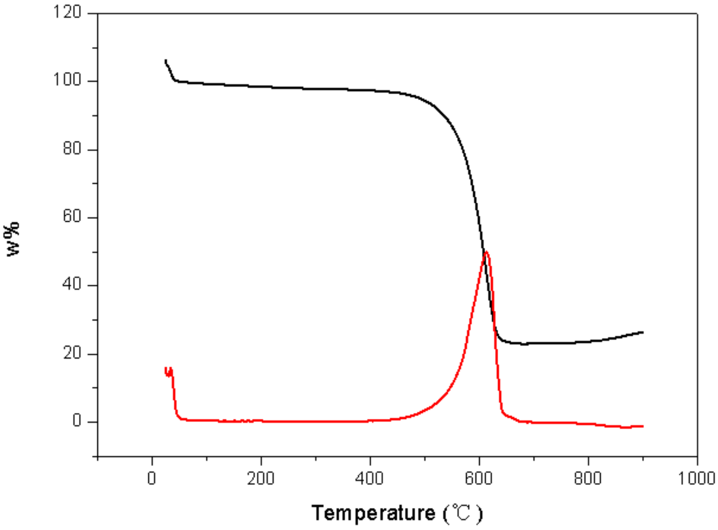

Fig. S9 TG curves of Pt/graphene sheets.