Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Atmospheric plasma reaction synthesised Pt_xFe_{1-x}/graphene and TiO_2 nanoparticles/graphene for efficient dye-sensitized solar cells

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1. Experiment

1.1. Electrode preparation

To prepare the Pt_xFe_{1-x}/G CE for DSSCs, 0.2 g of the obtained Pt_xFe_{1-x}/G powders were suspended in 2 mL ethanol by sonication and magnetic stirring; then 0.86 mL terpineol and 1.1 mL ethyl cellulose in ethanol (10 wt%) were dipped into the mixture solution one by one, followed by again stirring and sonication. The resulting paste was coated onto the FTO (Fluorine doped Tin Oxide) glass (Sigma-Aldrich, R = 7 Ω/sq) via spin coating method at 4000 rpm for 30 s. Afterwards, the CEs were annealed at 450 ºC in Ar for 30 min. Moreover, the commercial Pt CE purchased from Dalian HepatChroma solar-Tech Co., Ltd was used as a reference.

TiO_2 nanoparticles/G paste was prepared by the following method. Prepared nanoparticles were well ground, and it was mixed along with diluted acetic acid followed by addition of deionized water and was ground in a mortar until the paste attains homogeneity. Further 5% ethyl cellulose in ethanolic solution was added to the paste, and it was ground well. Finally, terpinol was added and it was further stirred until the paste attains homogeneity and in-order to remove ethanol from the mixture it was kept in a water bath at 90 ºC for 10 min. The final prepared paste was coated over 40 mM $TiCl_4$ treated FTO by doctor blade method using the template spacers (an active surface area of 0.25 cm^2 and the total thickness of about 11 μm was optimized).

The prepared photoanodes were further annealed at 450 ºC for 30 min in a programmable furnace at the rate of 10 ºC/min. After cooling at room temperature, the TiO_2 nanoparticles/G photoanodes were took out and immersed in a 0.50 mM ethanol solution of N719 dye for 24 h. Finally, the dye-sensitized TiO_2 nanoparticles/G photoanodes were took out from dye solution and washed with anhydrous ethanol.

1.2. Fabrication of DSSCs

Each DSSC device was fabricated by combining a dye-sensitized TiO_2 nanoparticles/G photoanode and a CE sandwiched with I_3^-/I^- based liquid electrolyte. The whole assembled arrangement was clamped. The liquid electrolyte was prepared by dissolving 10 mM of LiI, 1 mM of I_2, and 0.1 mM of $LiClO_4$ in acetonitrile.

1.3. Characterization and measurements

The crystallographic structure was characterized by X-ray diffraction (XRD) on an X-ray powder diffractometer (Rigaku SmartLab9, Japan) using Cu Ka radiation (λ = 1.5406 Å). Raman spectroscopy was measured on a LabRAM HR 800 Raman Spectrometer (HORIBA Jobin Yvon) with the green line of an argon-ion laser (514 nm) as the excitation source, and the Raman bands were collected in the wavelength range of 200 – 3000 cm^{-1}. The morphology of nanopowders was characterized by using a scanning electron microscopy (SEM, Zeiss Supra 35VP, Berlin, Germany). High-resolution transmission electron microscopy (HRTEM) images were acquired using a JEOL HRTEM (JEM-1400 electron microscope) with an acceleration voltage of 120 kV. The chemical states were analyzed via X-ray photoelectron spectroscopy (XPS) using a Thermo-ESCALAB 250XI (Thermo, USA) instrument with non-monochromated Al Kα 1486.6 eV radiation. The room-temperature photoluminescence (PL) spectra were measured on a Fluorolog3 photoluminescence spectrometer (Horiba Jobin Yvon, Japan), and the excited wavelength of 340 nm was chosen.

Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) measurements were conducted with each CE on a conventional Electrochemical Workstation (CHI600E, Shanghai Chenhua Co.). CV plots were recorded at a scan rate of 50 mV s^{-1} from –0.3 to 0.6 V in a three electrode setup: A FTO coated with

Pt_xFe_{1-x}/G served as the working electrode, a Pt electrode served as the working electrode and an Ag/AgCl electrode served as reference electrode respectively. The diluted electrolyte for CV consisted of 10 mM LiI + 1 mM I_2 + 100 mM $LiClO_4$ in acetonitrile. The EIS were carried out in the frequency range of 10^{-2} Hz to 10^6 Hz in a two-electrode system (CE/electrolyte/CE). The magnitude of the alternative signal was 5 mV. The Tafel measurement was applied in the potential range of −0.6 V to +0.6 V. The current density-voltage (J-V) curves of the assembled DSSCs were measured on an Electrochemical Workstation (CHI600E) under simulated AM 1.5 sunlight at 100 mW cm^{-2} irradiance generated by a solar light simulator (Xe Lamp Oriel Sol^3A™ Class AAA Solar Simulators 94023A, USA).

2. Characterization of the TiO_2 nanoparticles/G composite

Before assembling the DSSCs, the newly developed TiO_2 nanoparticles/G was characterized by XRD, Raman, FESEM and TEM; the results are shown in Fig. S1 and Fig. S2. In the XRD full spectrum (Fig. S1a), the diffraction peak of TiO_2 at 25.3°, 37.8°, 47.9°, 54.0°,54.9°, 62.5° and 70.3° corresponded to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4) and (2 2 0) crystal faces of anatase TiO_2 planes, respectively. The diffraction peaks corresponding to the planes match well with the peaks corresponding to the anatase phase of TiO_2 (JCPDS Card No: 21-1272, shown as vertical lines in Fig. S1a). It could be seen that there are similar peaks for TiO_2 and TiO_2 nanoparticles/G.

Raman spectra were measured to explore the crystal structure and surface compositions of G and TiO_2 in the composite structures (Fig. S1b) of TiO_2 and TiO_2 nanoparticles/G. The pure TiO_2 displayed four obvious bands located at 142.5, 392.9, 511.3, and 636.4 cm^{-1}, which were consistent with the specifically characteristic peaks of anatase TiO_2 phase. The Raman peaks of TiO_2 nanoparticles/G showed all peaks of the anatase TiO_2 and G, which demonstrated the successful integration of TiO_2 on G.

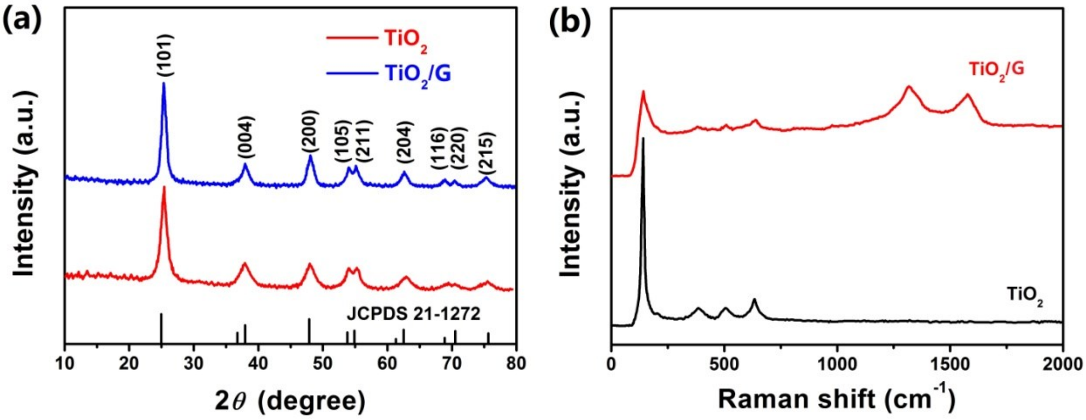
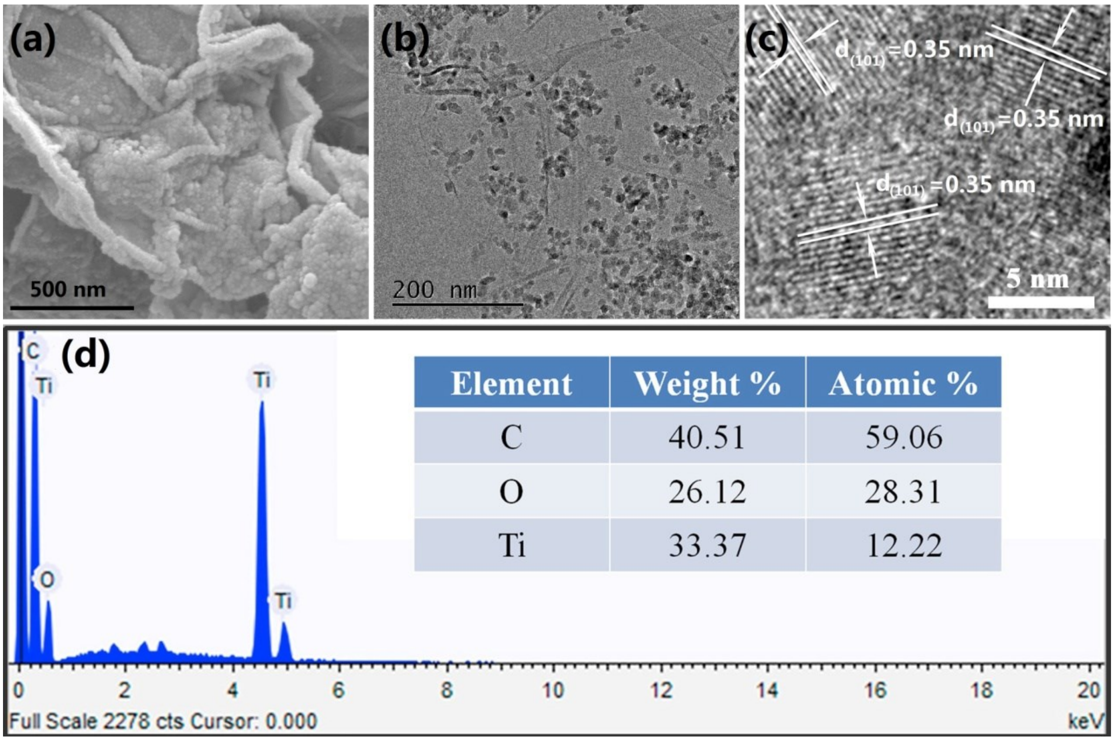


Fig. S1. (a) XRD patterns of pristine TiO_2 and TiO_2 nanoparticles/G. (b) Raman spectra of pristine TiO_2 and TiO_2 nanoparticles/G.

As shown in Fig. S2(a and b), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the TiO_2 nanoparticles/G composite show the typical morphology and internal structure of the products. A FESEM image (Fig. S2a) clearly revealed complete and uniform coating of TiO_2 nanoparticles onto the G sheets. TEM image (Fig. S2b) further revealed the nature of the ultrathin sheet and the fact that TiO_2 nanoparticles with the size of ~20 nm are homogeneously packed on the sheet, which perfectly fitted the images from FESEM. High-resolution TEM data (HRTEM) (Fig. S2c) indicated a wide variety of TiO_2 nanoparticles are supported on the G sheets. They have a defined crystal structure with a lattice distance (0.35 nm) equivalent to the crystal structure of anatase (1 0 1) plane. Fig. 1c shows the energy dispersive X-ray spectrometer (EDS) spectrum of a wide area of the TiO_2 nanoparticles/G composite and demonstrated that the sample is made up of C, O, Ti elements, and the corresponding atomic ratios are 59.06%, 28.31% and 12.22%, respectively. These results deduced that TiO_2 nanoparticles were efficiently dispersed on the G sheets.



Element	Weight %	Atomic %
C	40.51	59.06
O	26.12	28.31
Ti	33.37	12.22

Fig. S2. FESEM (a) and TEM (b) of TiO_2 nanoparticles/G composite. (c) The corresponding EDS spectrum.

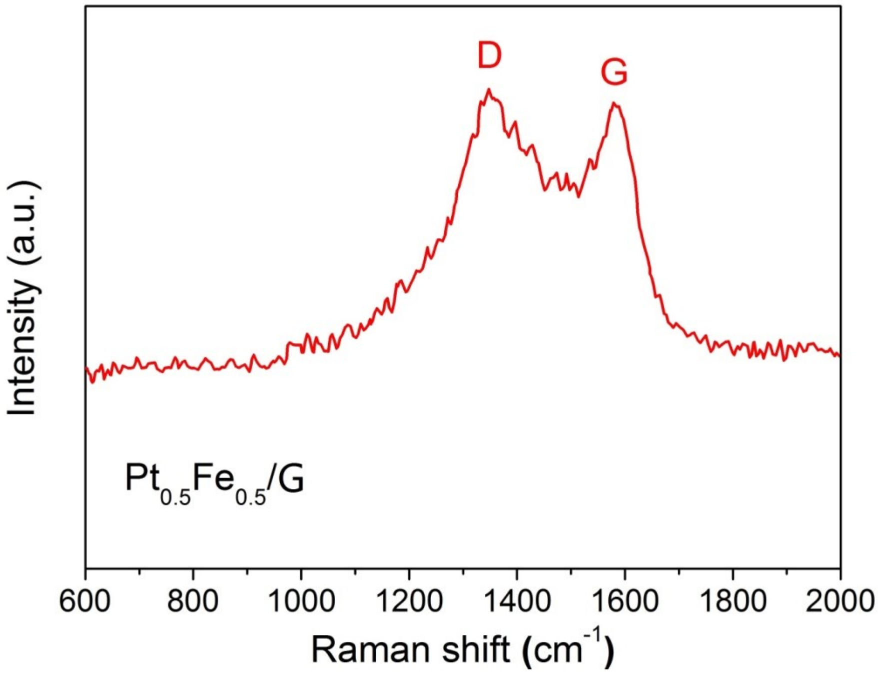


Fig. S3. Raman spectra of the $Pt_{0.5}Fe_{0.5}$/G.

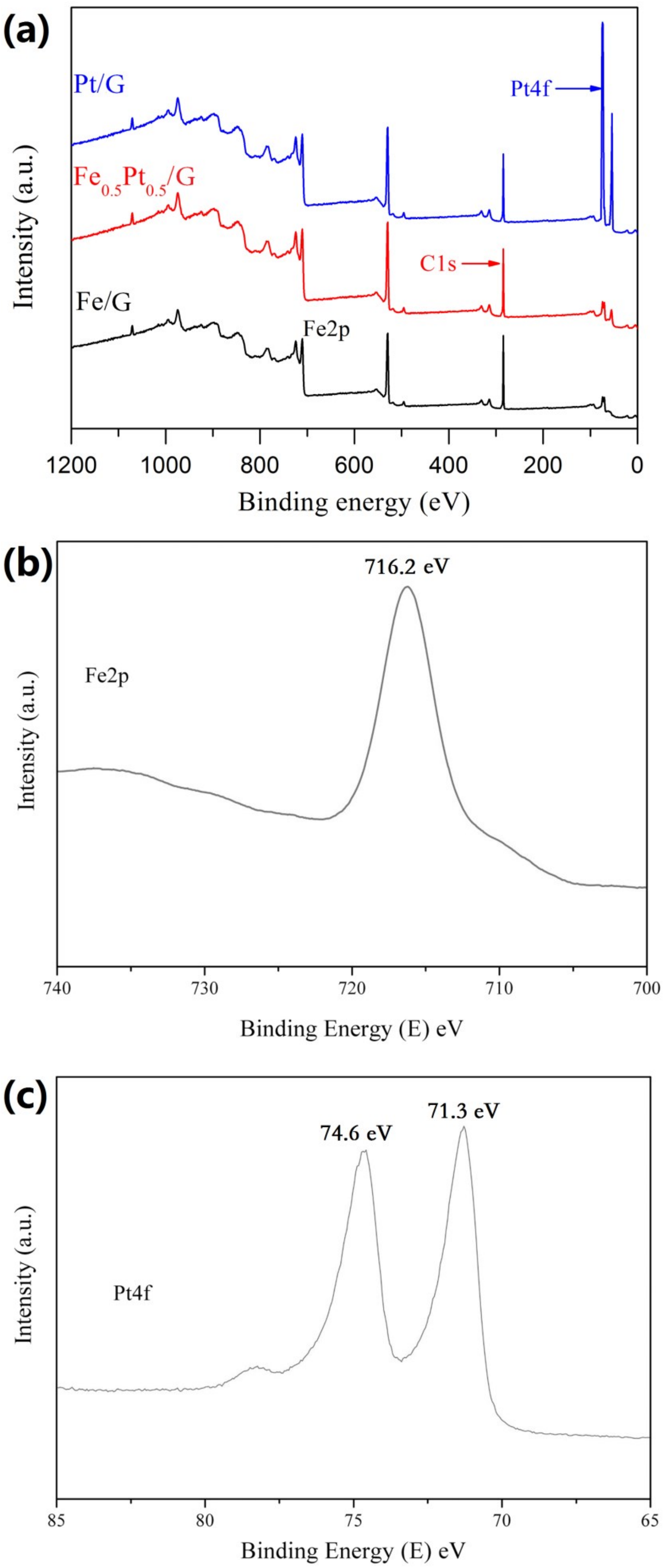


Fig. S4. (a) XPS spectra of the Pt/G, $Pt_{0.5}Fe_{0.5}$/G, and Fe/G CEs. XPS spectra of (b) Fe2p and (c) Pt4f.

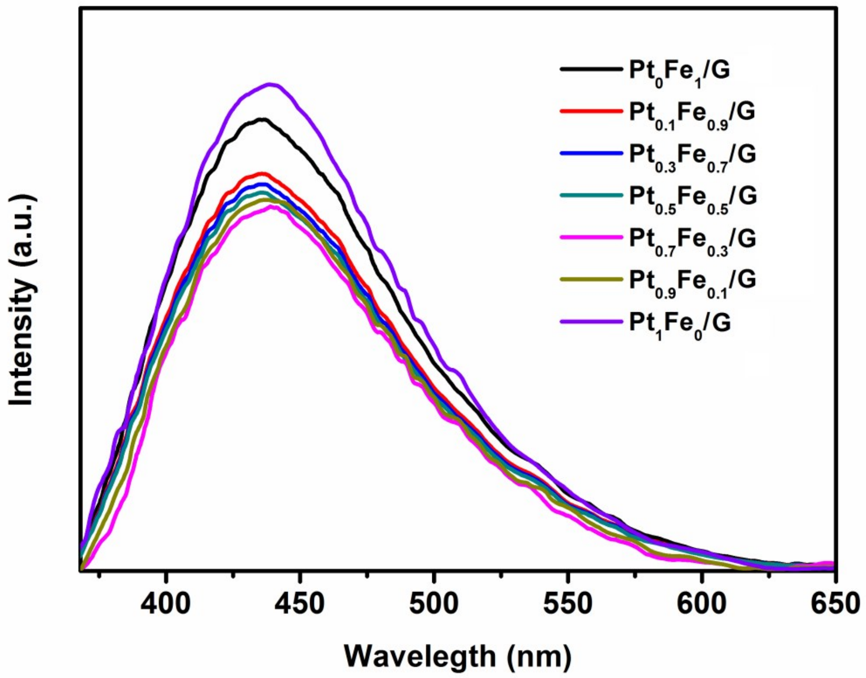


Fig. S5. Photoluminescence spectra of the Pt_xFe_{1-x}/G nanocomposites (Excitation wavelength: 340 nm).

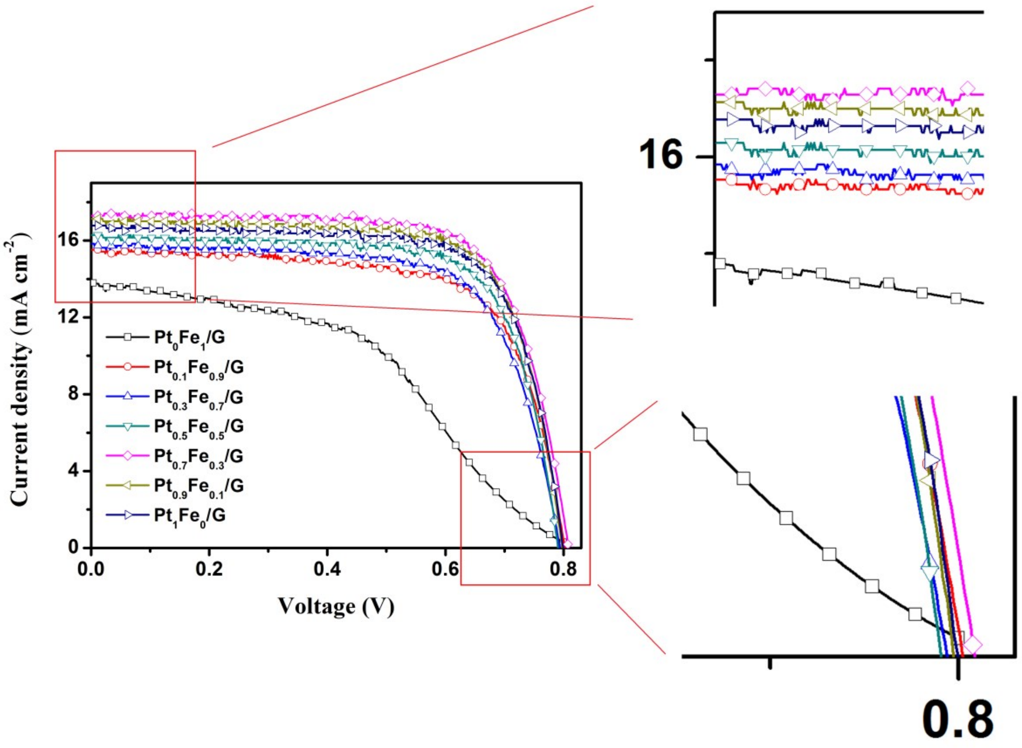


Fig. S6. The local magnification figures of Fig.6a.

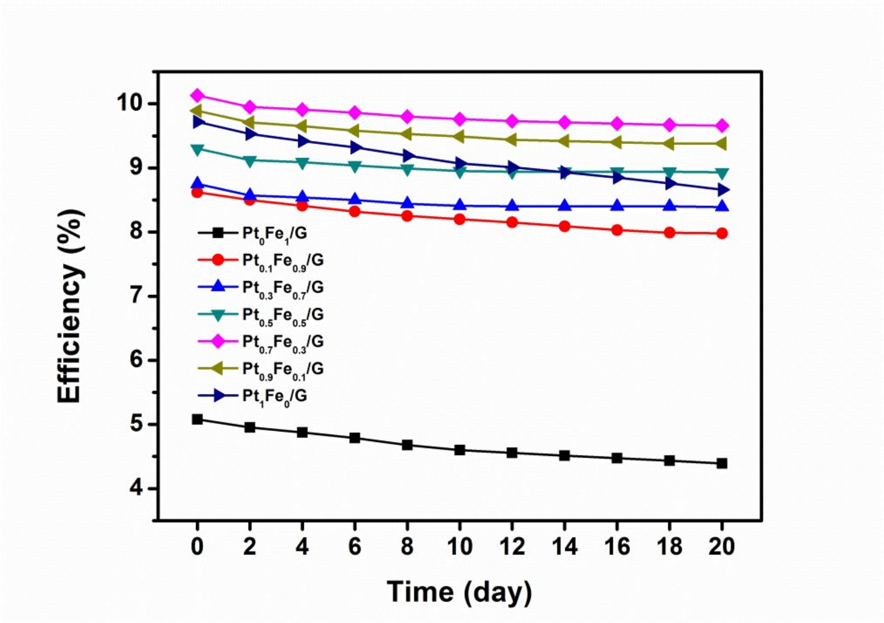


Fig. S7. Long-term stability of DSSCs with Pt_xFe_{1-x}/G CEs for 20 days.

Table S1. XPS parameters of Pt_xFe_{1-x}/G electrodes

Counter electrode	Atomic percentage		Pt:Fe
	Pt	Fe	
Pt_1Fe_0/G	1.60	-	1.00:0.00
$Pt_{0.9}Fe_{0.1}$/G	1.88	0.20	0.89:0.11
$Pt_{0.7}Fe_{0.3}$/G	1.93	0.42	0.82:0.18
$Pt_{0.5}Fe_{0.5}$/G	2.22	0.55	0.80:0.20
$Pt_{0.3}Fe_{0.7}$/G	1.46	1.13	0.56:0.44
$Pt_{0.1}Fe_{0.9}$/G	1.18	1.56	0.43:0.57
Pt_0Fe_1/G	-	1.75	0.00:1.00