Electronic Supplementary Information (ESI)

FeP Nanoparticles Grown on Graphene Sheets as Highly Active Non-Precious-Metal Electrocatalyst for Hydrogen Evolution Reaction

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Experimental Section

Chemicals. Graphite was purchased from Alfa Aesar. N,N-Dimethylformamide (DMF) was purchased from Beijing Chemical Reagent Factory (Beijing, China). Tetraethylene glycol (TEG), NaH_2PO_2 and iron (III) acetylacetonate ($Fe(acac)_3$) were purchased from Aladdin Aladdin Industrial Inc. (Shanghai, China). All the reagents were used as received without further purification. All aqueous solutions were prepared with Milli-Q water (>18.2MΩ.cm) from a Milli-Q Plus system (Millipore).

Apparatus. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. X-ray diffraction (XRD) spectra was obtained on a D8 ADVANCE (Germany) using Cu Kα (1.5406 Å) radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a TECNAI G_2 high-resolution transmission electron microscope (Holland) with an accelerating voltage of 200 kV and Hitachi H600 electron microscope (Japan) with an accelerating voltage of 100 kV. The sample for TEM characterization was prepared by placing a drop of prepared solution on carbon-coated copper grid and drying at room temperature.

Preparation of GO. The graphite oxide was synthesized from natural graphite powder according to the literature.[1] The graphite oxide was dispersed in DMF at a concentration of 2 mg/ml by sonication in a low power bath ultrasound (80 W, 90% amplitude) for 2 hours. Then, exfoliation of graphite oxide into graphene oxide (GO) was achieved by sonication of the dispersion for 60 min (950 W, 70% amplitude) with horn probe sonic tip. The obtained balck dispersion was then subjected to centrifugation at 3,000 r.p.m for 10 min with a rotor radius of 8 cm in order to remove any unexfoliated graphite oxide. Finally, a homogeneous GO dispersion was obtained.

Synthesis of Fe_3O_4-GS and FeP-GS. Fe_3O_4-GS was synthesized by solvothermal route. In a typical synthesis, 10 mL TEG and 100 mg $Fe(acac)_3$ were added to 20 mL GO dispersion under magnetic stirring. After 30 min of stirring, a clear solution was obtained. The mixture was transferred to a Teflon-lined stainless steel autoclave for solvothermal reaction at 180 °C for 2 h. After the solvothermal treatment was completed, the autoclave was cooled and the final product was collected by centrifugation and washed with water. Then, the Fe_3O_4-GS dispersion was frozen by liquid nitrogen (-196 °C), and then the frozen sample was dried in a bulk dryer. After sublimation of ice, Fe_3O_4-GS was generated. The obtained Fe_3O_4-GS was transferred into a tubular furnace for phosphidation under N_2 flow. 20 mg Fe_3O_4-GS and 100 mg NaH_2PO_2 were put at two separate positions in a fused silica tube with NaH_2PO_2 at the upstream side of the tubular furnace. Then the Fe_3O_4-GS was annealed in N_2 up to 350°C for 2 h with a heating rate of 3 °C/min. Black FeP-GS powder was obtained after cooled to ambient temperature under N_2.

In addition, we further prepared Fe_3O_4 nanoparticles (NPs) and FeP NPs for comparison. Fe_3O_4 NPs were synthesized according to the literature.[2] FeP NPs were obtained similarly by replacing Fe_3O_4-GS with Fe_3O_4.

Electrochemical Measurements: Electrochemical measurements were performed with a CHI 660A electrochemical analyzer (CH Instruments, Inc., Shanghai). Electrochemical measurements were performed in a conventional three-electrode system using glassy carbon (Ø 3 mm) modified with the catalysts as the working electrode, saturated calomel electrode (SCE) as the reference electrode and carbon rod as the counter electrode. The potential, measured against a SCE electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) according to $E_{vs\ RHE} = E_{vs\ SCE} + 0.242 + 0.059pH$. Prior to the experiments, the glassy carbon electrode was polished on a polishing cloth using alumina pastes to obtain a mirror-like surface, followed by ultrasonic cleaning in ethanol and water. To make working electrodes, a stock solution of Fe_3O_4-GS at 10 mg/mL in water was prepared. 2 μL of this solution was drop-casted onto a GCE, and it was left to dry in air to obtain a catalyst loading of ~0.28 mg/cm^2. 3μL of 0.5% Nafion solution in ethanol was drop-casted on top to protect the film. Before the electrochemical measurement, the electrolyte (0.5 M H_2SO_4, pH=0) was degassed by bubbling argon for 30 min.

For comparison, the electrocatalytic activities of graphene, FeP NPs and Pt wire were measured under similar conditions.

References

1. V. C. Tung, L. M. Chen, M. J. Allen, J. K. Wassei, K. Nelson, R. B. Kaner and Y. Yang, *Nano Lett.*, 2009, **9**, 1949-1955.
2. L. Xiao, J. Li, D. F. Brougham, E. K. Fox, N. Feliu, A. Bushmelev, A. Schmidt, N. Mertens, F. Kiessling, M. Valldor, B. Fadeel and S. Mathur, *Acs Nano*, 2011, **5**, 6315-6324.

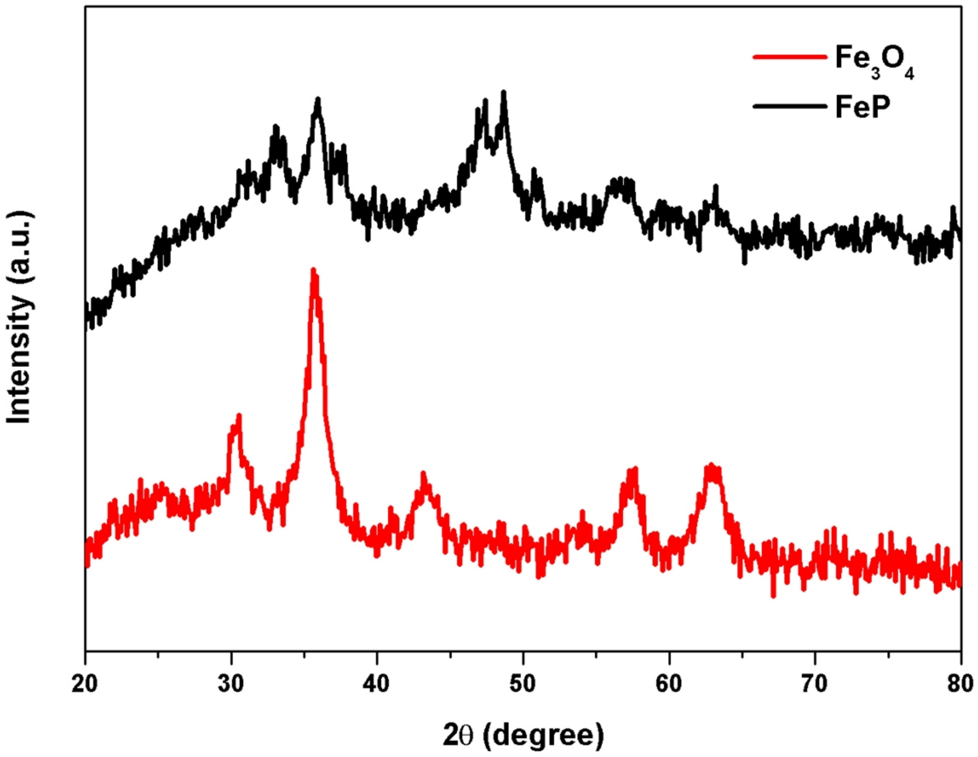

Figure S1. XRD patterns of Fe_3O_4 NPs and FeP NPs.

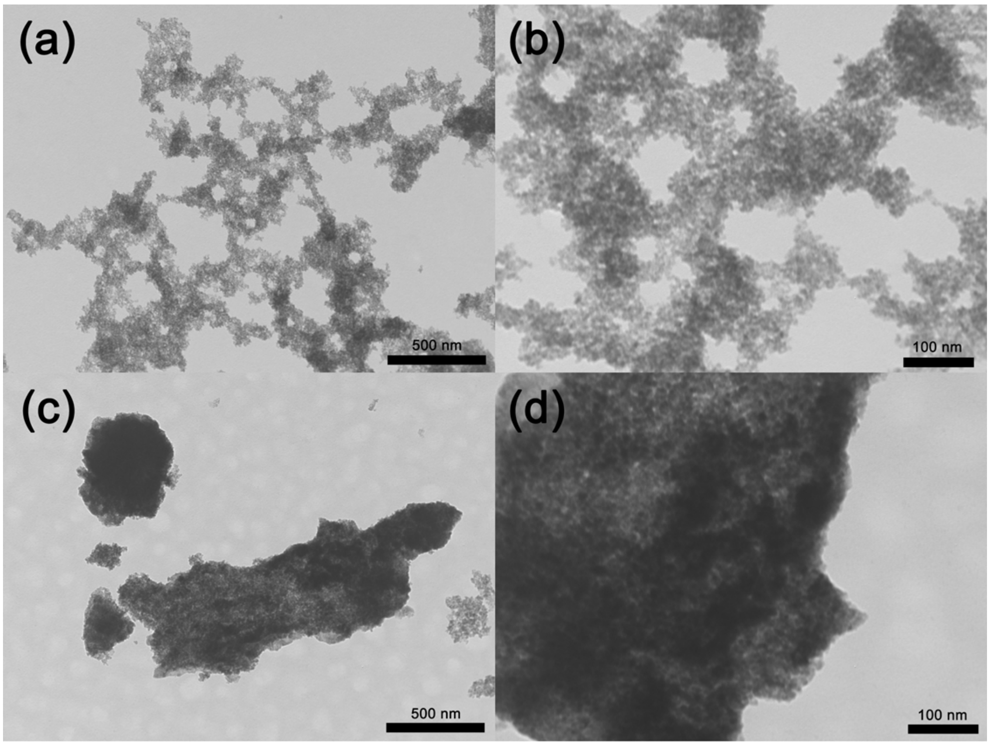

Figure S2. TEM images of Fe_3O_4 NPs (a, b) and FeP NPs (c, d) at different magnifications.

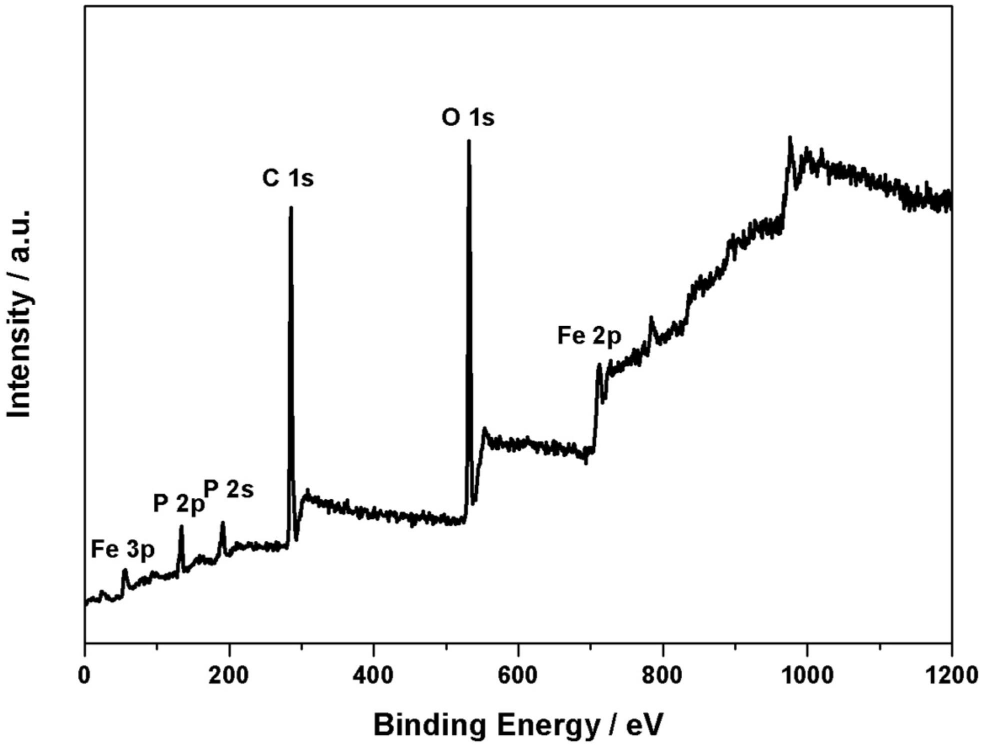

Figure S3. XPS survey spectrum of FeP-GS.

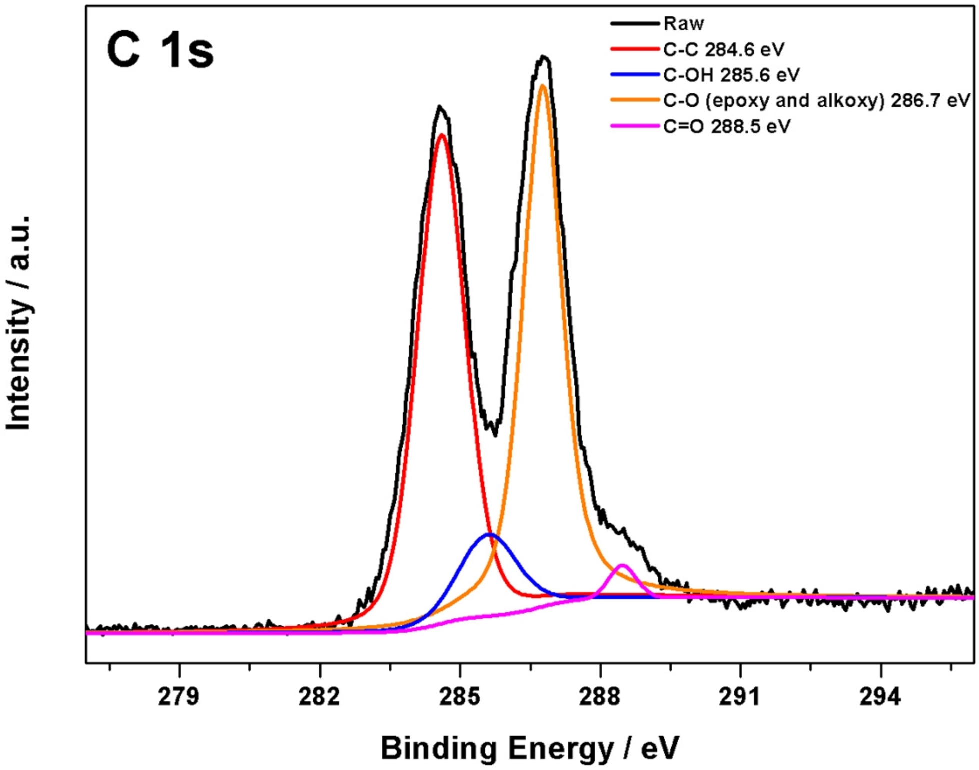

Figure S4. XPS spectrum in the C 1s region for graphite oxide.

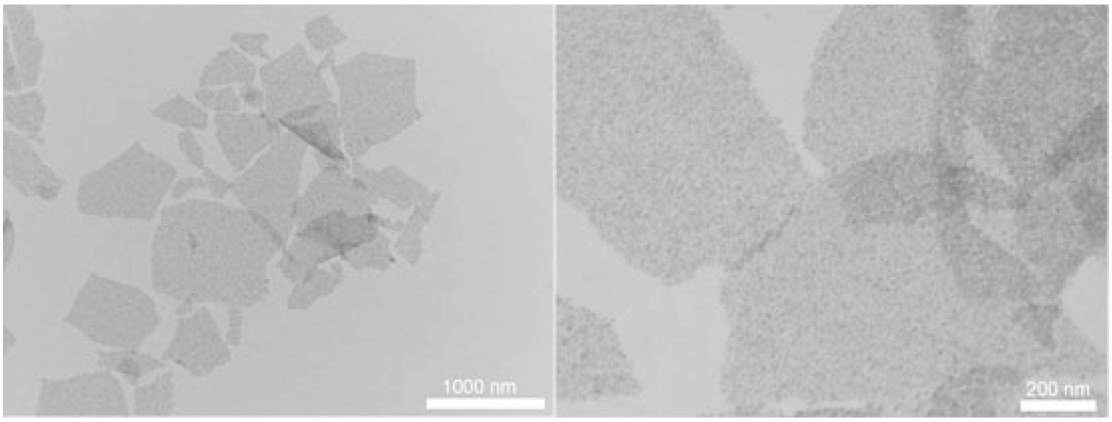

Figure S5. TEM images of Fe_3O_4-GS at different magnifications.

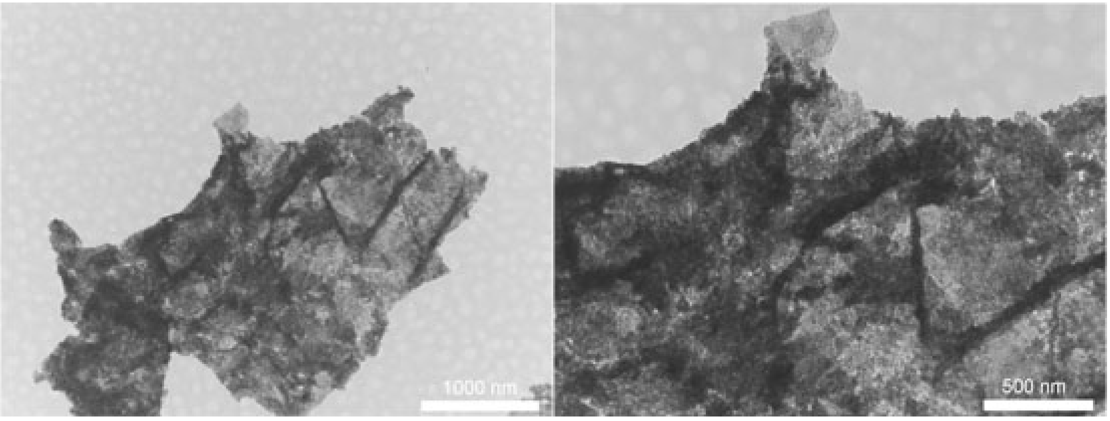

Figure S6. TEM images of FeP-GS at different magnifications.

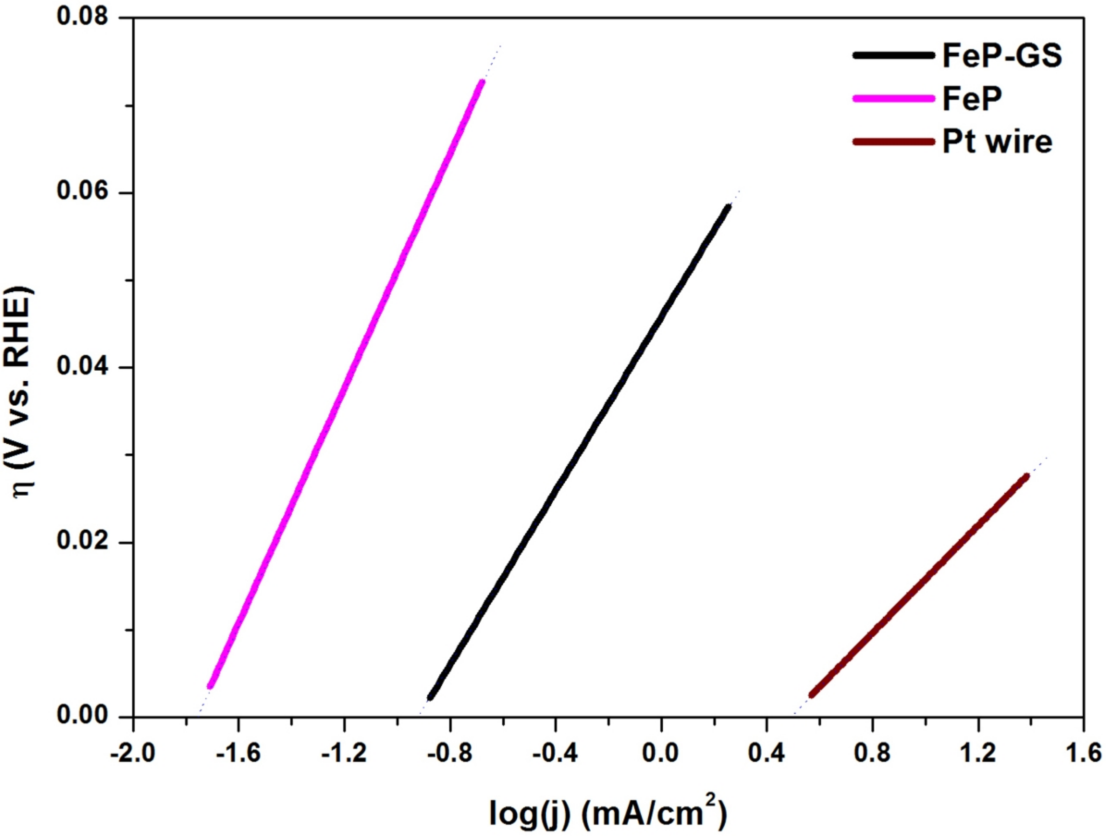

Figure S7. Calculation of exchange current density of FeP, FeP-GS and Pt wire.

The exchange current density (j_0) was calculated using extrapolation methods. When the η is 0, the log(j) values for FeP, FeP-GS and Pt wire are -1.76, -0.92 and -0.50, respectively. Based on Tafel equations, j_0 for FeP, FeP-GS and Pt wire was calculated to be 1.7×10^{-2}, 1.2×10^{-1}, and 3.2 mA/cm^2, respectively.

Table S1 Comparison of HER performance in 0.5 M H_2SO_4 electrolytes for FeP-GS with other HER electrocatalysts.

Catalyst	**Current density (*j*, mA/cm^2)**	**η at the corresponding *j* (mV)**	**Exchange current density (mA/cm^2)**	**Ref.**
FeP-GS	10	123	0.12	This work
CoP-CNT	10	122	0.13	[24]
FeP nanosheets	10	～240	--	[26]
Ni_2P nanoparticles	20	～130	0.033	[27]
MoP	30	180	0.034	[29]
MoS_2/RGO	10	150	--	[43]
defect-rich MoS_2	13	200	0.00891	[10]
$NiMoN_x$/C	2	170	0.24	[13]
Bulk MoB	1	～150	0.0014	[14]
Mo_2C/CNT	10	152	0.014	[15]
$Co_{0.6}Mo_{1.4}N_2$	10	200	0.23	[17]
$MoSe_2$ nanofilms	10	250	0.00038	[18]

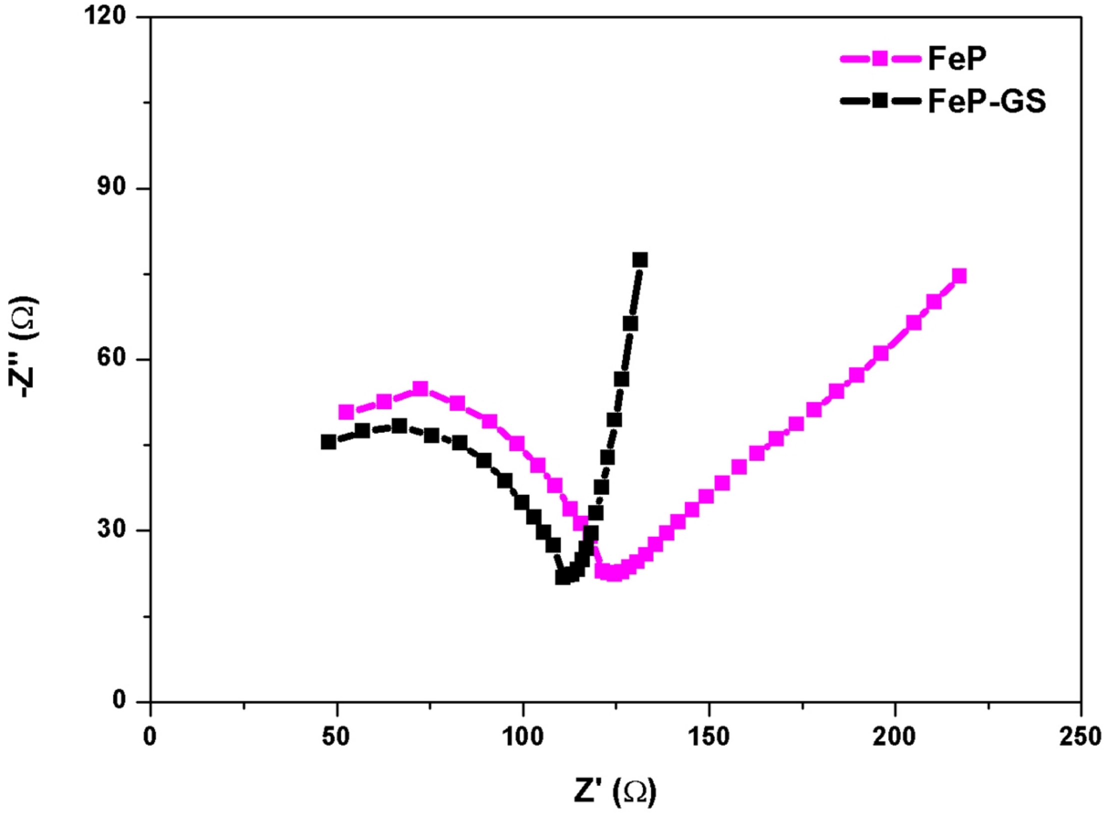

Figure S8. Nyquist plots of electrochemical impedance spectra of FeP and FeP-GS at η=200 mV.