

Electronic Supplementary Information (ESI) for:

**Soft Nano Wrapping on Graphene Oxide by Metal-organic
Network Composed of Tannic Acid and Fe Ions**

H. Ozawa,^{*a} and M. Haga^{*a}

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University,

1-13-27 Kasuga, Bunkyo-ku, Tokyo, Japan.

E-mail: mhaga@kc.chuo-u.ac.jp

Experimental

All starting materials and reagents were purchased from commercial suppliers and used without further purification. The graphite flake (natural, -325 mesh, 99.8%) was also purchased from Alfa Aesar and used as received. Ultraviolet–visible spectroscopy (UV-Vis) absorption and Raman spectra were recorded on an Agilent 8453 UV-Vis spectrophotometer and Lambda Vision MicroRAM-200 spectrometer, respectively. Zeta potential measurements were conducted by Otsuka electronics ELSZ-1000ZS. FT-IR spectra were recorded on an JASCO FT/IR-4200 FT-IR Spectrometer. Thermogravimetry (TG) analysis was carried out by RIGAKU Thermo plus EVO2 with a heating rate of 5°C/min in a N₂ atmosphere. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Kratos-Shimadzu AXIS HIS-165. Atomic force microscopy (AFM) images of the samples were recorded using an Agilent 5500. SEM images and energy-dispersive X-ray spectroscopy elemental mapping were observed using a field-emission type scanning electron microscopy (SEM) (S-5500, Hitachi High-Technologies) operated at 5 kV. Transmission electron microscopy (TEM) images were observed using Hitachi HT 7700 operated at 100 kV.

Preparation of graphene oxide

Graphene oxide (GO) was prepared according to the modified Hummers method.¹

Fabrication of TA-Fe/GO sheet in water

Graphene oxide (1.5 mg) and tannic acid (TA) (4mg) were added to 10 ml of water, and the mixture was sonicated for 2 min. FeCl₃·6H₂O (2mg) was added to the mixture solution and stirred for 1 min. The suspension was centrifuged (1000 G, 5 min) and the supernatant was removed to remove the excess TA, Fe ions, and TA-Fe complex which were not used for the wrapping on GO surface. The remaining solid was washed with water and centrifuged (1000 G, 5min). The obtained solid was dispersed into 10 ml of water by sonication.

Reduction of TA-Fe/GO sheets by hydrazine vapor

The TA-Fe/GO sheet on glass or silicon substrates were placed in a Petri dish containing 5 mL of hydrazine monohydrate. The substrate in the petri dish was heated to 100°C for 1 h. The obtained sheets were rinsed with MeOH and dried under air. The TA-Fe/GO sheets changed color after hydrazine vapor treatment, from dark gray to metallic gray, indicating reduction of the material.

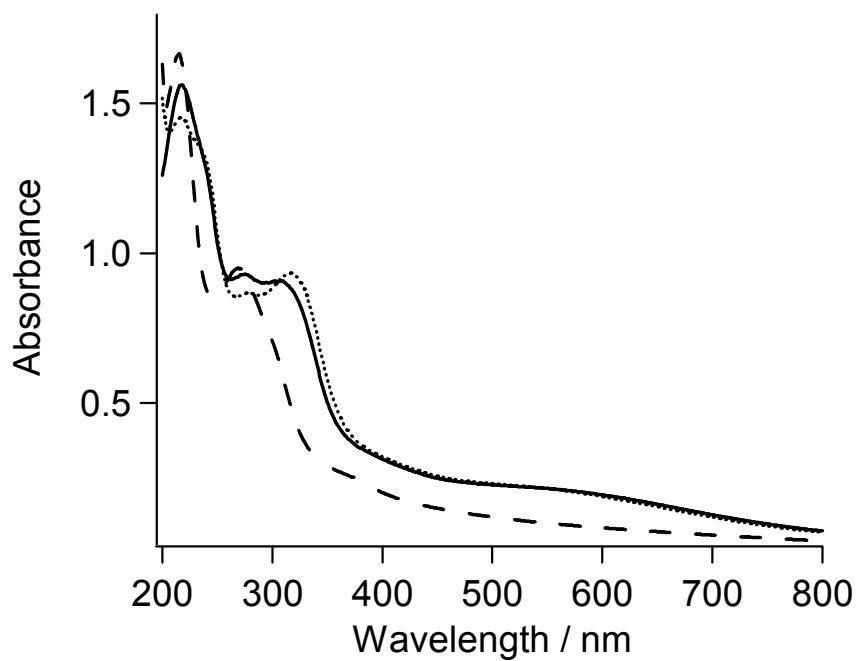


Figure S1. UV-Vis absorption spectra of TA-Fe/GO sheets in aqueous solution under neutral (solid line), basic (dotted line, addition of 1N NaOH), and acidic (broken line, addition of the HCl) conditions.

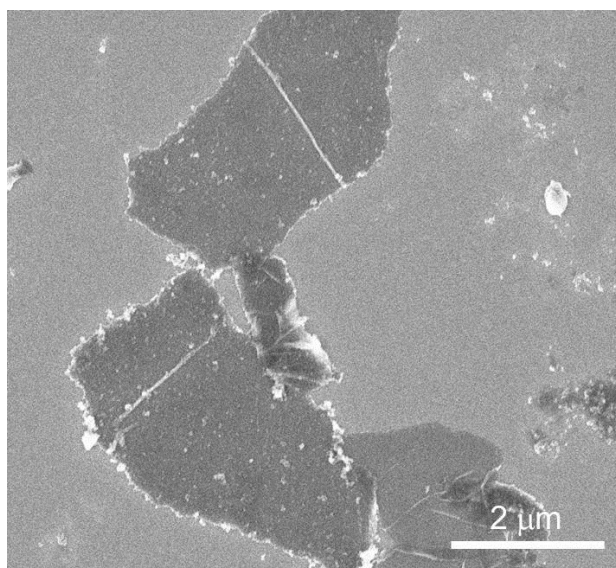


Figure S2. SEM image of TA-Fe/GO sheet on silicon substrate.

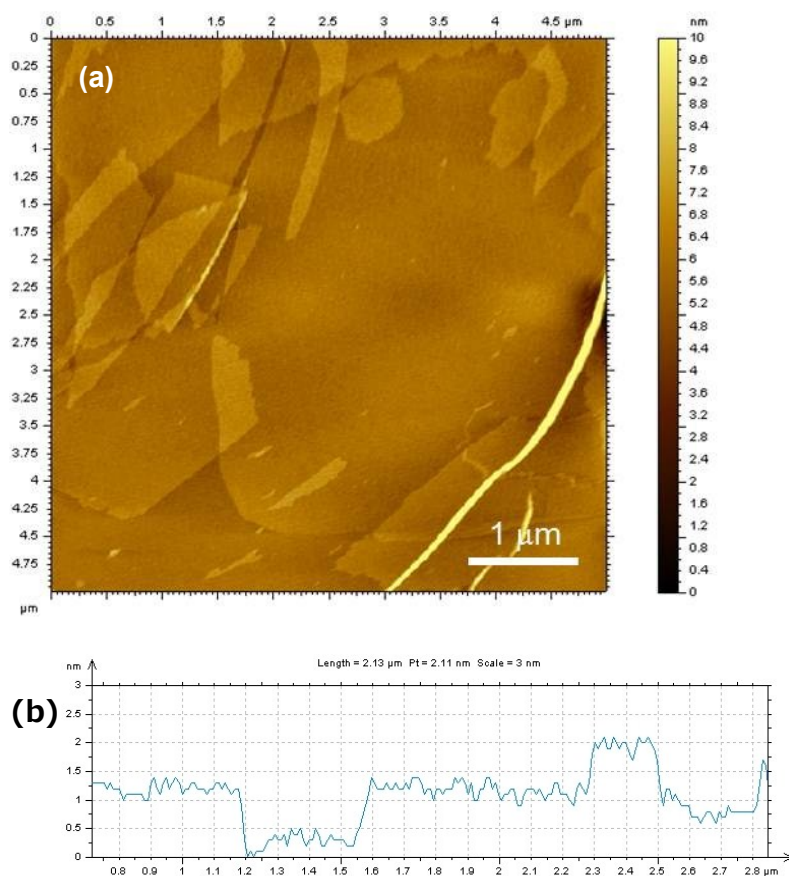


Figure S3. (a) AFM image and (b) cross section analysis of GO sheet.

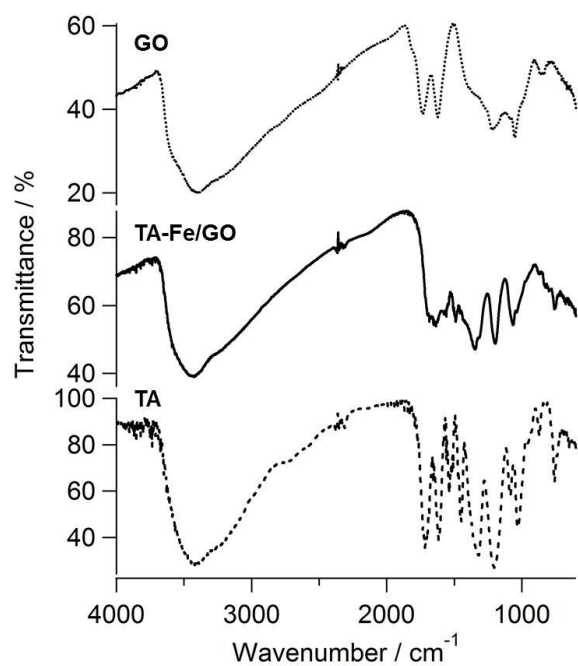


Figure S4. FT-IR spectra of GO (dotted line), TA-Fe/GO (solid line), and TA (broken line) in KBr pellet.

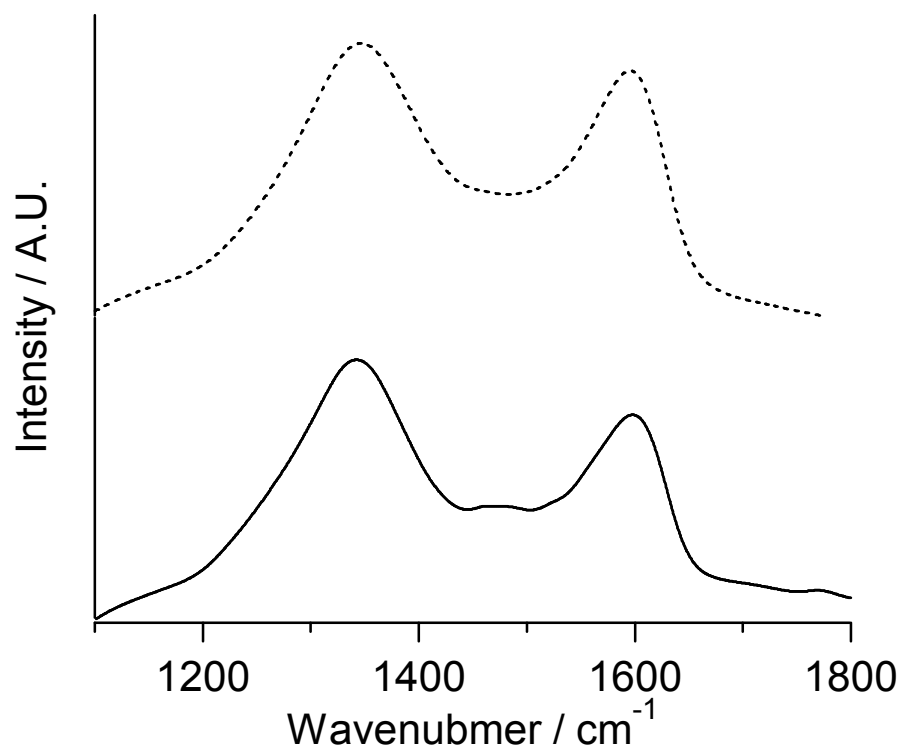


Figure S5. Raman spectra of TA-Fe/GO (solid line) and GO (dotted line) on silicon substrate.

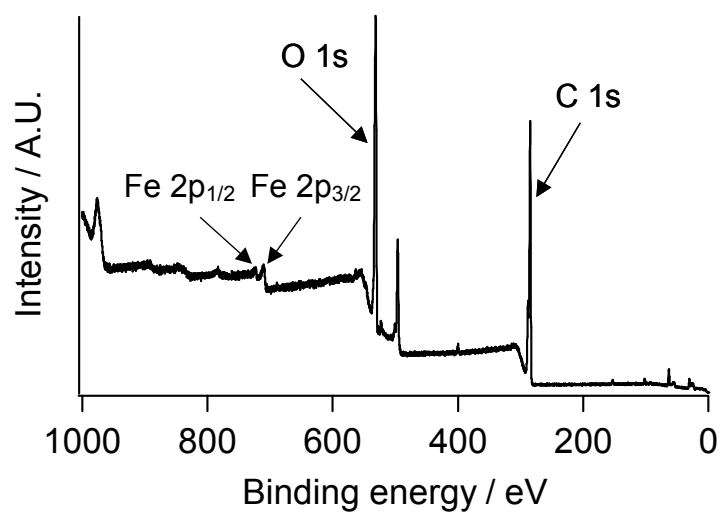


Figure S6. XPS spectra of TA-Fe/GO sheets.

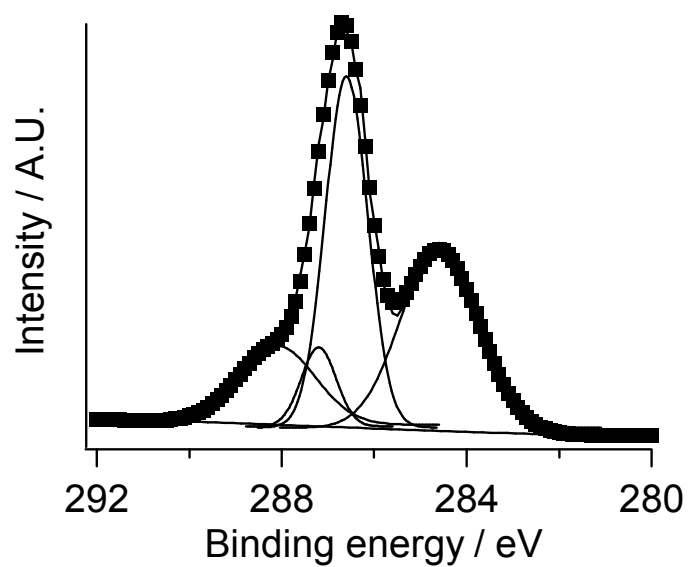


Figure S7. XPS of C1s spectra of GO. Deconvolution curves are also shown.

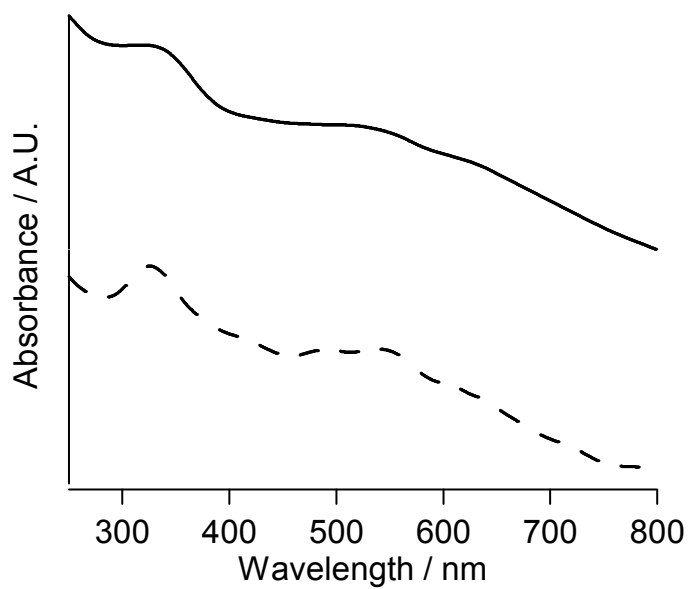


Figure S8. UV-Vis absorption spectra of TA-Fe/GO (solid line) and TA-Fe/rGO (broken line) sheets on quartz substrate.

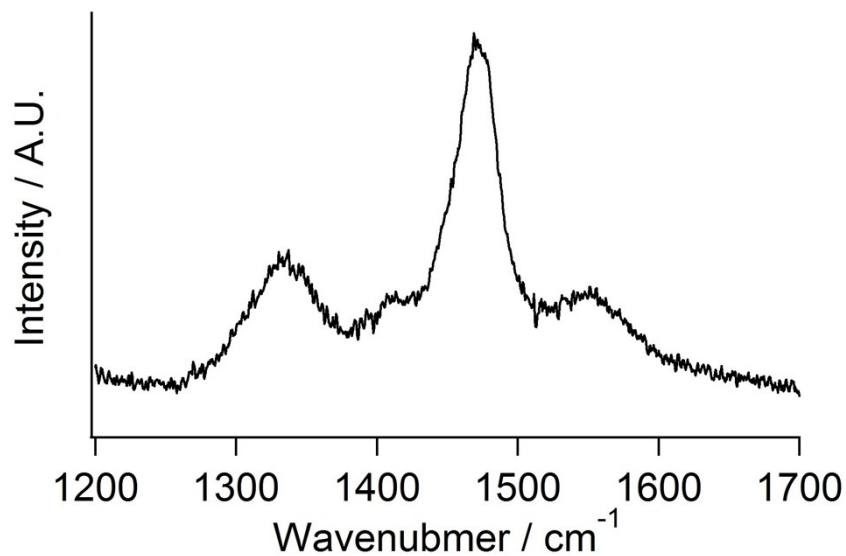


Figure S9. Raman spectrum of TA-Fe films on a silicon substrate.

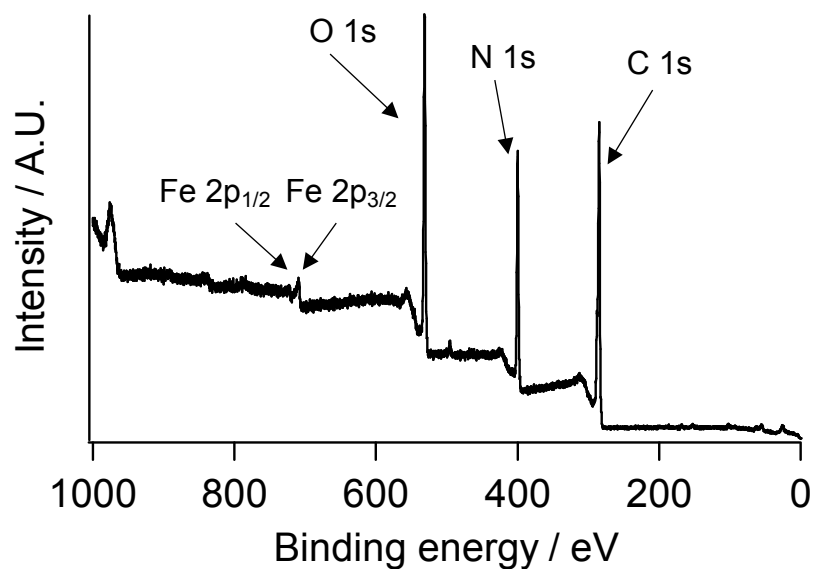


Figure S10. XPS spectra of TA-Fe/rGO sheets on silicon substrates. Peak at 399.9 eV corresponds to hydrazine. N 1s peak derived from residual hydrazine and reacted GO with hydrazine.

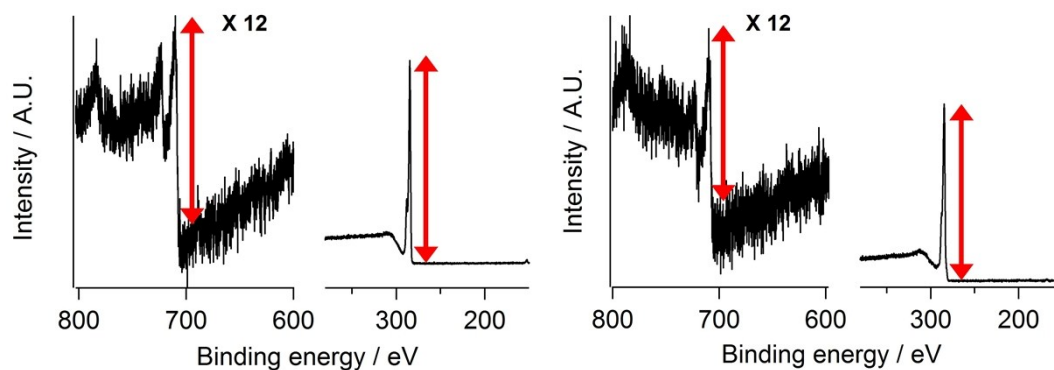


Figure S11. The ratios of both intensities between $I(\text{Fe } 2p_{3/2})$ and $I(\text{C}1s)$ of TA-Fe/GO before (left) and after (right) reduction.

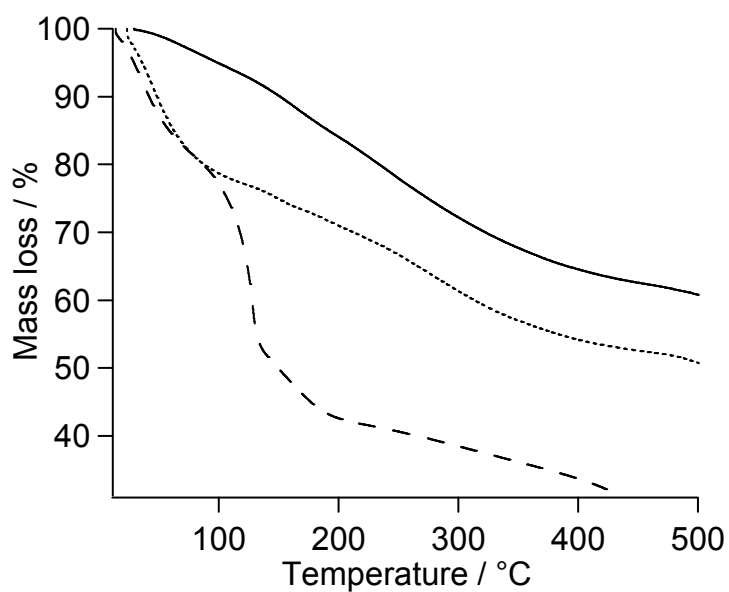


Figure S12. TGA curves of TA-Fe/rGO (solid line), TA-Fe/GO (dotted line), and GO (broken line) sheets with heating rate of $5^\circ\text{C}/\text{min}$ in nitrogen gas atmosphere.

References

1. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, **2010**, *4*, 4806-4814.