Supporting Information

Nonvolatile Resistive Memory of Ferrocene Covalently Bonded on Reduced Graphene Oxide

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Synthesis of ferrocenylphenylamine (FPA):

Ferrocenylphenylamine was synthesized following the literature.[1,2] Ferrocenylphenylamine was synthesized from ferrocene as the starting material. Arylation of ferrocene by a diazonium salt under phase transfer conditions gave nitropheneylferrocene. Reduction of the nitropheneylferrocene with tin under acidic conditions produced ferrocenylphenylamine. ^1H NMR ($CDCl_3$ 300 MHz): δ 7.28 (d, J = 4.5 Hz, 2 H), 6.64 (d, J = 8.4 Hz, 2 H), 4.54 (s, 2 H), 4.2 (s, 2 H), 4.0 (s, 5 H), 3.63 (s, 2 H). IR (powder, cm^{-1}): 3436, 3356, 1620, 1607, 1529, 1454, 1103, 999.

Synthesis of Graphene Oxide:

GO was prepared from natural graphite powder (Bay Carbon, SP-1 graphite) using the modified Hummers method with H_2SO_4, $NaNO_3$ and $KMnO_4$.[3,4] In a pretreatment step that ensures complete oxidation, concentrated H_2SO_4 (50 ml) was heated to 90°C in a 300 ml beaker. $K_2S_2O_8$ (10 g) and P_2O_5 (10 g) were added with stirring until the reactants were completely dissolved. The mixture was then cooled to 80 °C. Graphite powder (12 g) was then added to the H_2SO_4 solution, resulting in bubbling that subsided within 30 minutes. The mixture was maintained at 80 °C for 4.5 hours using a hot plate, after which the heating was stopped and the mixture was diluted with 2 L of DI water and left overnight. On the following day, the mixture was filtered and washed using filter paper to remove all traces of acid. The solid was transferred to a drying dish and left overnight under ambient conditions. For oxidation, H_2SO_4 (460 ml) was placed into a 3 L Erlenmeyer flask and chilled to 0 °C using an ice bath. The pretreated graphite was added to the acid and stirred. $KMnO_4$ (60 g) was added slowly and allowed to dissolve, closely monitoring the temperature so that it did not get higher than 10 °C. This mixture was then allowed to react at 35 °C for 2 hours, after which distilled water (920 ml) was added in 20-30 ml aliquots. Since the addition of the water caused the temperature of the mixture to rapidly increase, this step was performed in an ice bath to limit the temperature to not higher than 50 °C. As more water was added, the mixture became less reactive until a final ~700 ml of water was added with no observable increase in temperature. After adding all of the 920 ml of DI water, the mixture was stirred for 2 hours, at which point an additional 2.8 L of DI water was added. Shortly after this dilution, 50 ml of 30% H_2O_2 was added to the mixture, resulting in a bubbling, brilliant yellow solution. The mixture was allowed to precipitate for at least a day, after which the clear supernatant was decanted. The remaining mixture was centrifuged and washed with a total of 5 L of 10% HCl solution, followed by 5 L of DI water to remove the acid. The resulting solid was dried in air and diluted to a 2% w/v dispersion that was dialyzed for two weeks to remove any remaining metal. The solution was sonicated for half an hour, followed by centrifuged at 4000 rpm for 30 min. The obtained supernatant was dried via evaporation under vacuum. Then, the solid was again dispersed in water (1.5 mg/mL) via ultrasonication for 2 h and centrifuged at 10,000 rpm for 15 min to further remove aggregates. Finally, the supernatant was collected and air-dried.

Synthesis of ferrocenylphenyl-NHCO-GO

For the chemically-functionalized GO active layer of MIM-type devices, functionalized GOs were synthesized via the carboxyl group on the side of GO and the amino group in the ferrocenylphenylamine, which formed amide bonding to obtain ferrocenylphenyl-NHCO-GO (FPAGO). The functionalized GOs were prepared by sonicating a solution of GO (50 mg), ferrocenylphenylamine (100 mg), and *N, N'*- dicyclohexylcarbodiimide (DCC, 100 mg) in DMF (100 ml) for 30 min and then vigorously stirring the solution at 50^{o}C for 24 hours. The remainder of the ferrocenylphenylamine and other impurities were removed by washing with acetone several times.

Fabrication of MIM device using FPArGO:

The ITO/FPArGO/Al device was successfully fabricated by applying spin-coating, thermal annealing, and an e-beam evaporator. The ITO glass substrate was cleaned by applying a typical ultrasonic cleaning process using acetone, DI water, piranha solution, and ethanol. The ITO glass substrate was spin-coated using the FPArGO solution described above at 500-4,000 rpm, followed by drying in a vacuum oven for 24 h. Finally, the FPAGO-coated ITO substrate was thermally annealed at 200^{o}C using a rapid thermal anneal system (RTA). By using a shadow mask, aluminum top electrodes with 100-nm-thickness were deposited on top of the active layer.

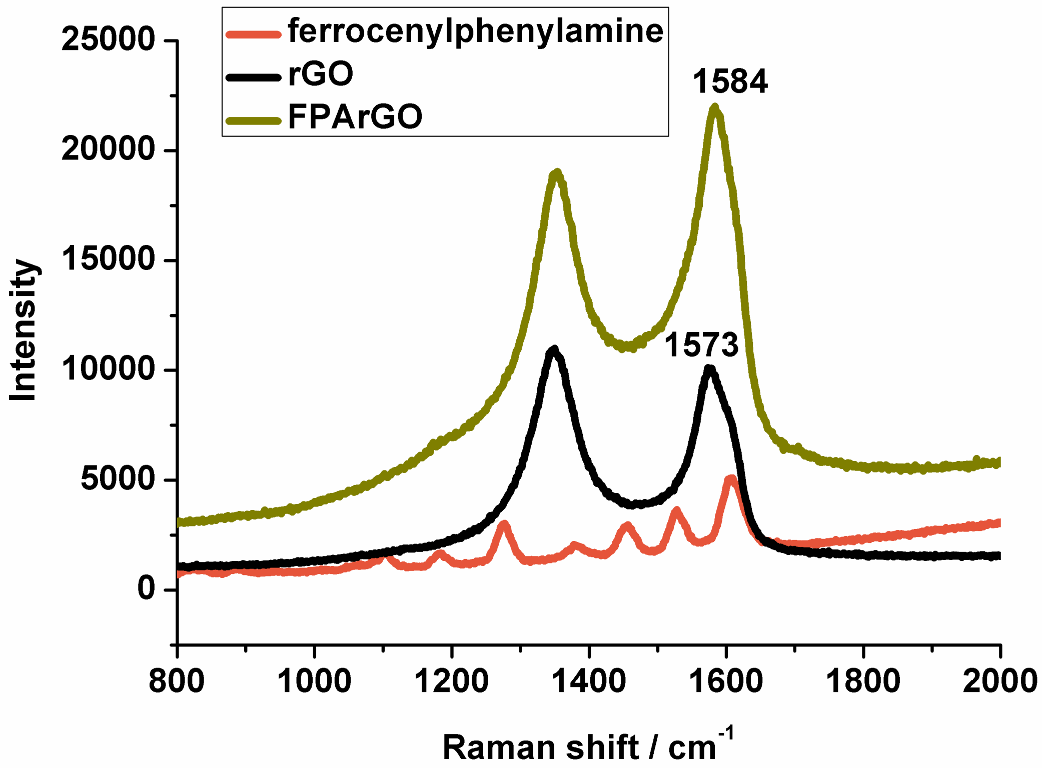

Figure S1. Raman spectra of ferrocenylphenylamine, FPArGO, and rGO (annealed at 200 °C). The G band of rGO annealed at 200 °C was observed at 1,573 cm^{-1}, and that of the FPArGO peak was observed at 1,584 cm^{-1}. These bands indicate that ferrocene acting as an electron acceptor led to a blue shift in the G-band position, and the carboxylate groups of the GO induced by acid treatment provided a functionalization site for the amine functional groups. The D/G ratio of GO covalently functionalized with ferrocenylphenylamine (0.86) was lower than that of rGO (1.09), implying a decreased area of the sp^3 domains on the chemically modified GO.

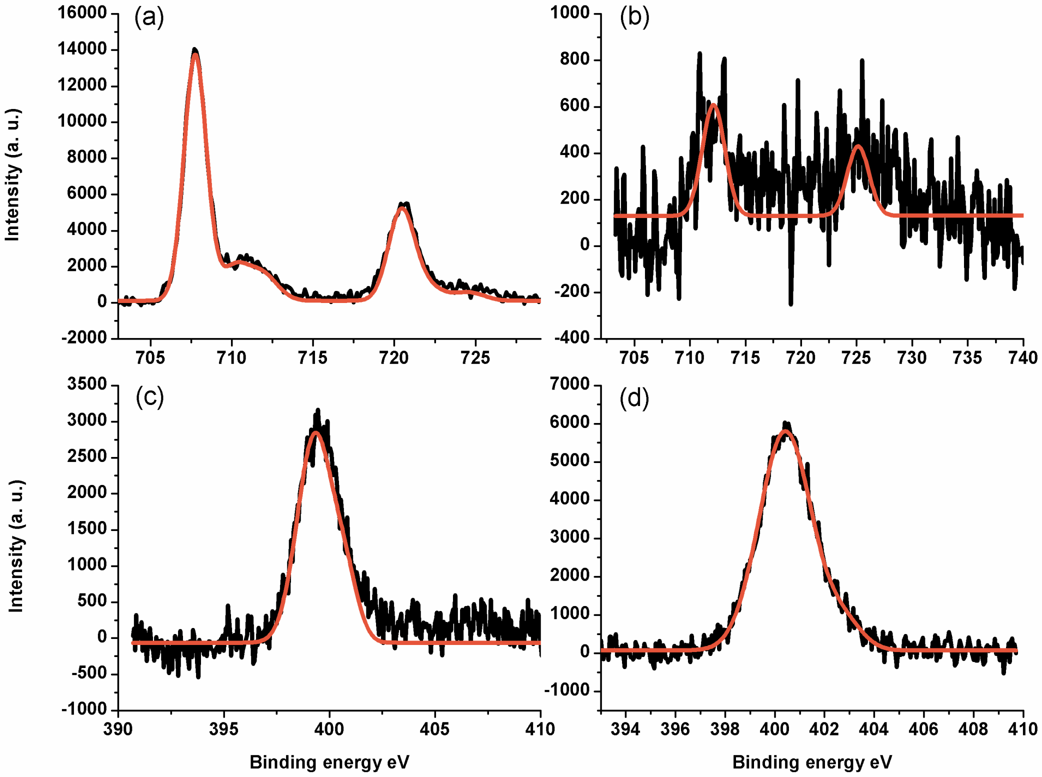

Figure S2. XPS analysis of (a) Fe2p1/2, Fe2p3/2 spectra of ferrocenylphenylamine, (b) Fe2p1/2, Fe2p3/2 spectra of FPArGO, (c) N1s spectra of ferrocenylphenylamine, and (d) N1s spectra of FPArGO. The XPS analysis further revealed the surface compositions of FPArGO. The nitrogen and iron signals were continually monitored, as shown in Figure S2. The N1s XPS spectrum of ferrocenylphenylamine clearly indicates that the peak of nitrogen functionality appeared at 399.3 eV (N in C-N bonds). In contrast to ferrocenylphenylamine, the peak at 400.4 eV corresponding to N bonded to the carbonyl C (NH-C=O) was observed in the N1s XPS spectrum of FPArGO. Also, specific Fe2p1/2 and Fe2p3/2 peaks were observed in the FPArGO spectrum, indicating that ferrocenylphenylamine molecules were bonded to GO.

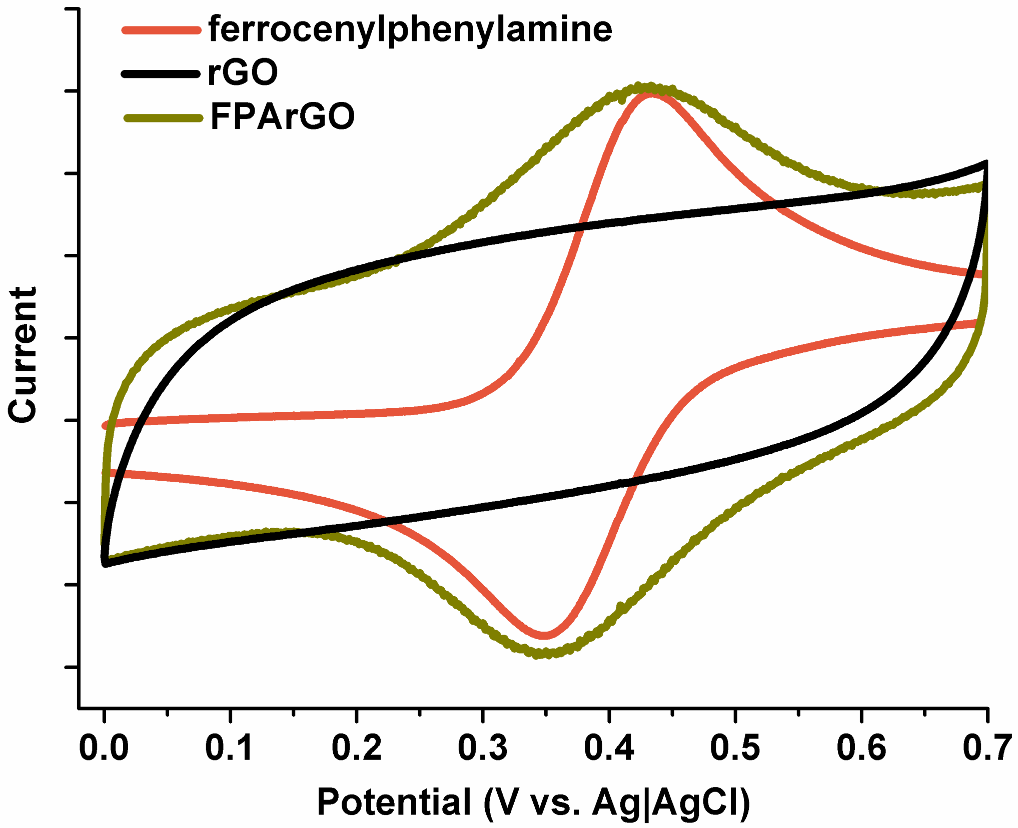

Figure S3. Cyclic voltammetry of ferrocenylphenylamine, rGO(200 ^{o}C) and FPArGO.

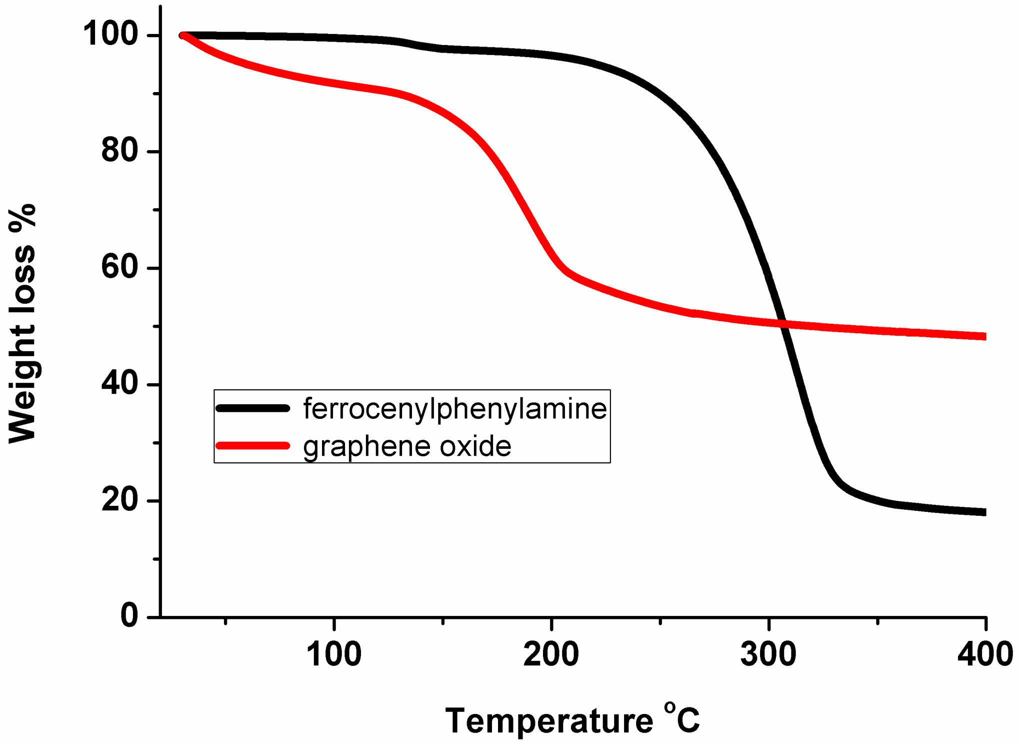

Figure S4. TGA analisys of graphene oxide (red line) and ferrocenylphenylamine (black line) shows that partially reduced graphene oxide at 200 °C did not decompose the ferrocenylphenylamine.

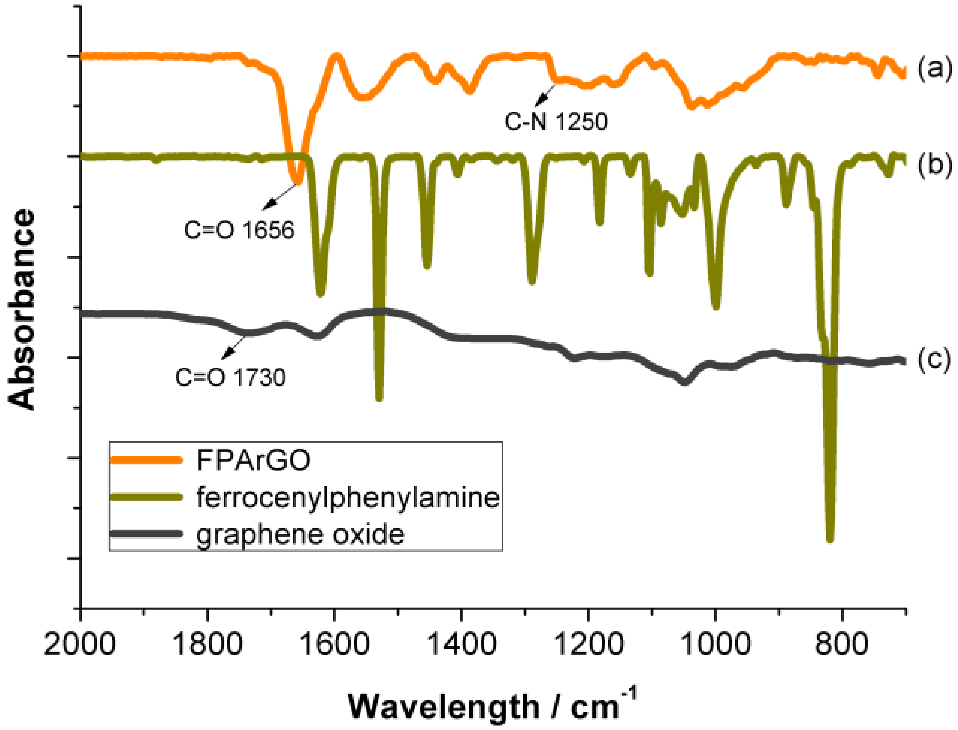

Figure S5. FT-IR data of (a) FPArGO. The band emerged at 1656 cm^{-1} corresponds to the C=O stretch of the amide group, indicating that the ferrocenylphenylamine molecules were covalently bonded to the graphene oxide by an amide linkage. (b) ferrocenylphenylamine and (c) graphene oxide.

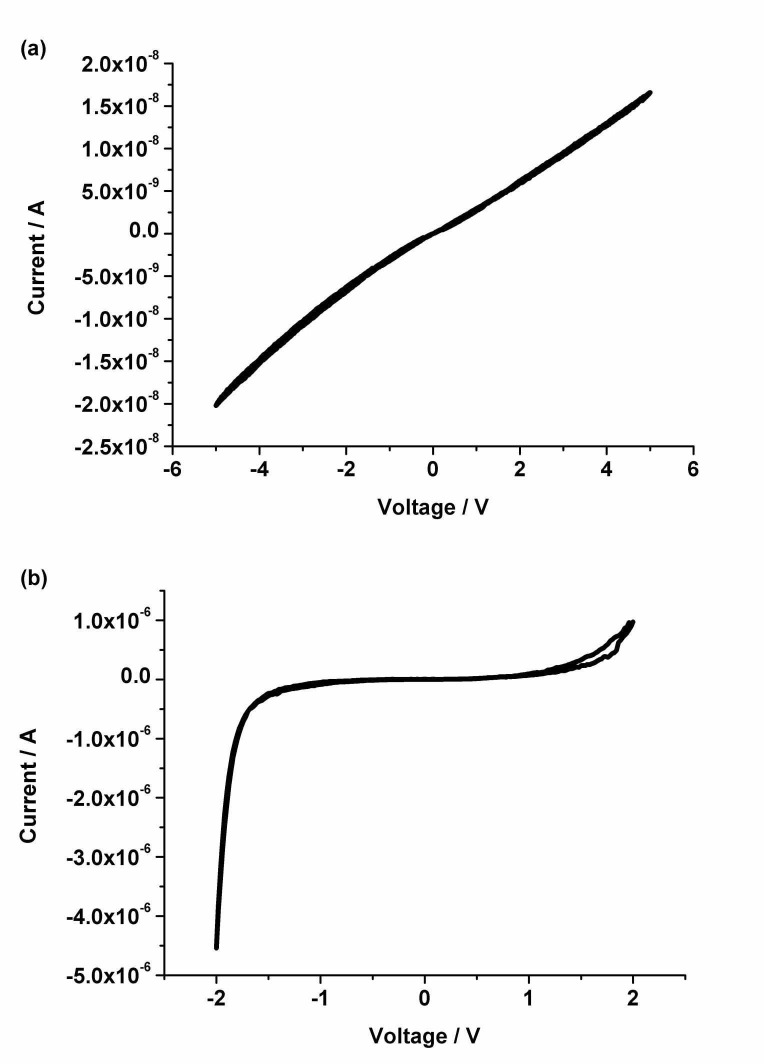

Figure S6. The MIM-type device (ITO/organic layers/Al). I-V characteristics with (a) GO annealed at 200 ^{o}C, (b) ferrocenylphenylamine for the control experiments.

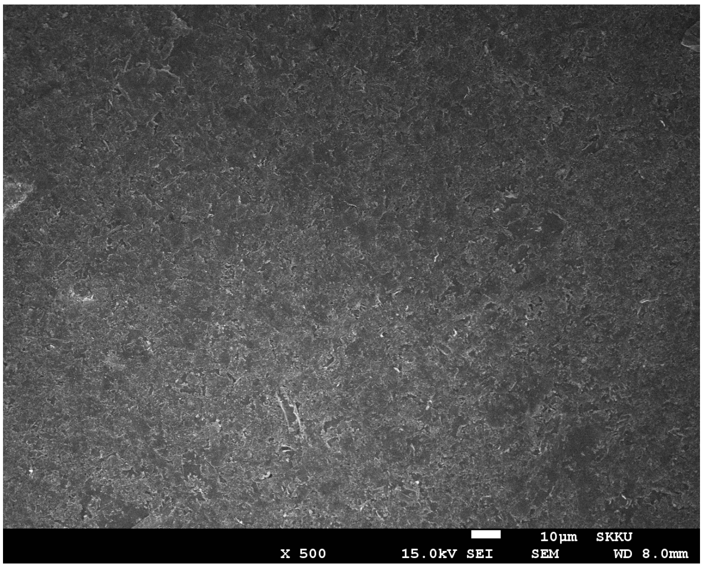

Figure S7. SEM image of FPArGO thin film.

The morphology of the SEM image of FPArGO thin film showed a uniformity that was prepared by spin-coating technique.

Supporting Reference

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