

Supporting information

Fast Electrochromic Display: Tetrathiafulvalene- Graphene

Nanoflake as Facilitating Materials

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Preparation method of Graphene Oxide (GO)

GO was synthesized from natural graphite powder by the modified Hummers method¹. Before going for GO preparation, an extra step of preoxidation of graphite powder was performed. The 2g graphite powder was put into 75 °C solution of 8 mL concentrated H₂SO₄, 3g of K₂S₂O₈, and 3g of P₂O₅. The resultant precipitate in the solution was allowed to cool to room temperature over a period of 10 hours. The solution was then carefully diluted with distilled water, filtered, and washed until the rinse water became neutral. The product was dried at ambient temperature over 24 hours. This preoxidized graphite was then put into cold (0 °C) concentrated H₂SO₄ (45 mL). NaNO₃ (1 g) was added. KMnO₄ (6 g) was added successively with continues stirring while maintaining mixture temperature below 12 °C for next 1 hour. The mixture was then stirred at room temperature for 6 h and left for overnight. DI water around 90 mL was added to the mixture which improves temperature to 75 °C, wait for 15 min, then end the reaction by adding large

amount of DI water (300 mL) and 30% H₂O₂ solution (5 mL), within few second color of the mixture changed into light yellowish. Finally the mixture was filtered and swilled with DI water diluted (1:10) hydrochloric acid solution (250 mL) for the removal of metal ions, then after again rinsed it with a large amount of distilled water and at last dry it in vacuum.

Preparation method of Graphene nanoflakes (GNFs)

The solution of GO in DMF having concentrations of 70 mg/5 ml was ultrasonicate for 30 minutes. The GO/DMF solution was transferred to a Teflon lined autoclave (50 mL) and heated at 180°C for 6 h. After this reaction, the autoclave was cooled to room temperature naturally. The product contained black precipitates with brownish suspension. The precipitate can be acquired out by centrifuge and at last evaporate the solvent.

Step-wise recipe to fabricate electrochromic device

Polyethylene oxide (PEO, MW = 100,000) and ethyl viologen diperchlorate (EV) were purchased from Sigma-Aldrich and used as received. GNFs were prepared by the above-mention revised hummer method. Step-wise recipe to prepare the EC-Gel is as follows:

Step 1: Prepare solution of 4wt% ethyl viologen diperchlorate in acetonitrile: solution A (say)

Step 2: Prepare solution of 5wt% PEO in acetonitrile: solution B (say)

Step 3: Prepare GNFs powder as per details given below seperately.

Step 4: 5 ml of solution A + 5 ml of solution B + 0.06 mg of GNFs powder (designated “electrolyte”): Solution C (say)

Step 5: Solution C mixed properly using vortex for 10 minutes.

Step 4: Filter solution after step5 through a 0.75 μm PTFE filter: Solution D (say).

Step 5: Affix a transparent double-sided tape, pattern with desired text, on an FTO coated glass.

Step 6: Spin coat solution D with 1000 rpm for 120 sec on substrate prepared in step 5.

Step 7: Stack second FTO coated glass on to the film coated substrate prepared in step 6. The double-sided tape, used in step 5, will keep the two FTO coated substrates attached with each other with EC-Gel (solution D) layer sandwiched as patterned on the tape. The two FTO coated glass allows the biasing of the device.

*****End of Recipe*****

Additional discussion on role of TTF and GNFs in the EC-Gel

TTF is known as an electron donor material (*Olaya et al, J. Am. Chem. Soc., 133, 12115, 2011; Kaminska, ACS Appl. Mater. Interface, 04, 5386, 2012*) hence was selected as one of the components in the EC-Gel with viologen as the color changing agent which changes color on reduction at the cost of TTF oxidation. To confirm the same, its redox process has been studied by carrying out the CV measurements as shown in Figure S1 below. Figure S1 (a) shows the typical CV of viologen (EV) alone showing double reduction (negative current peaks) while scanning in the direction shown by arrow mark. The reduction is reversible as the reduced species get oxidized back to its EV^{2+} state when the CV cycle completes as can be seen as two peaks in the positive currents in figure S1(a). Figure S1 (b) shows the CV curve for TTF alone with the arrows showing the direction of scan. Two peaks in the CV curves in positive potential window correspond to the oxidation of TTF (*Kaminska, ACS Appl. Mater. Interface, 04, 5386, 2012*). This oxidation is also reversible as can be seen as peaks in negative current direction during the reverse scan in the same cycle. The same redox behavior of TTF and EV is expected when are present in combination as can be seen in Figure S1(c). The curve in Figure S1(c) looks as if the two curves in (a) and (b) have been superimposed onto each other which means the redox activity of the two species remain intact. Which means that during the reduction of EV,

electrons were accepted by EV to form EV^+ and EV^0 (evident as two peaks shown inside blue circle in Figure S1c) and later these were used during oxidization of EV^0 and EV^+ (evident as two peaks shown inside red circle in Figure S1c) to eventually return back to EV^{2+} .

To understand the effect of GNF, the CV curve in Figure S1(c) has been compared with the CV curve in Figure S1 (d) which has been obtained from the EC-Gel which contains GNF along with EV and TTF. The comparison shows that the EV reduction peaks are present even in the presence of GNFs (the two peaks shown inside blue circle in Figure S1d) that means the electrons are being accepted by EV as supplied by the cell. The important observation is the absence of any peak (red circle in Figure S1d) when the bias is decreased after the viologen reduction. Instead of peaks, zero current is observed that means the electrons released by oxidizing EV^+ and EV^0 on reversing the bias is being absorbed by the GNFs present in the EC-Gel as this is the only extra component which has been added to the material which resulted in the CV curve in Figure S1(c). A comparison of the CV curves from EC-Gel (Figure S1d) and EC-Gel sans GNF (Figure S1c) establishes the role of GNFs in the EC-Gel used in the ECD presented in the manuscript. This property of GNF has also been reported by bridewell et al, ACS Sensors, 01, 1203, 2016 (ref number 25 in the manuscript).

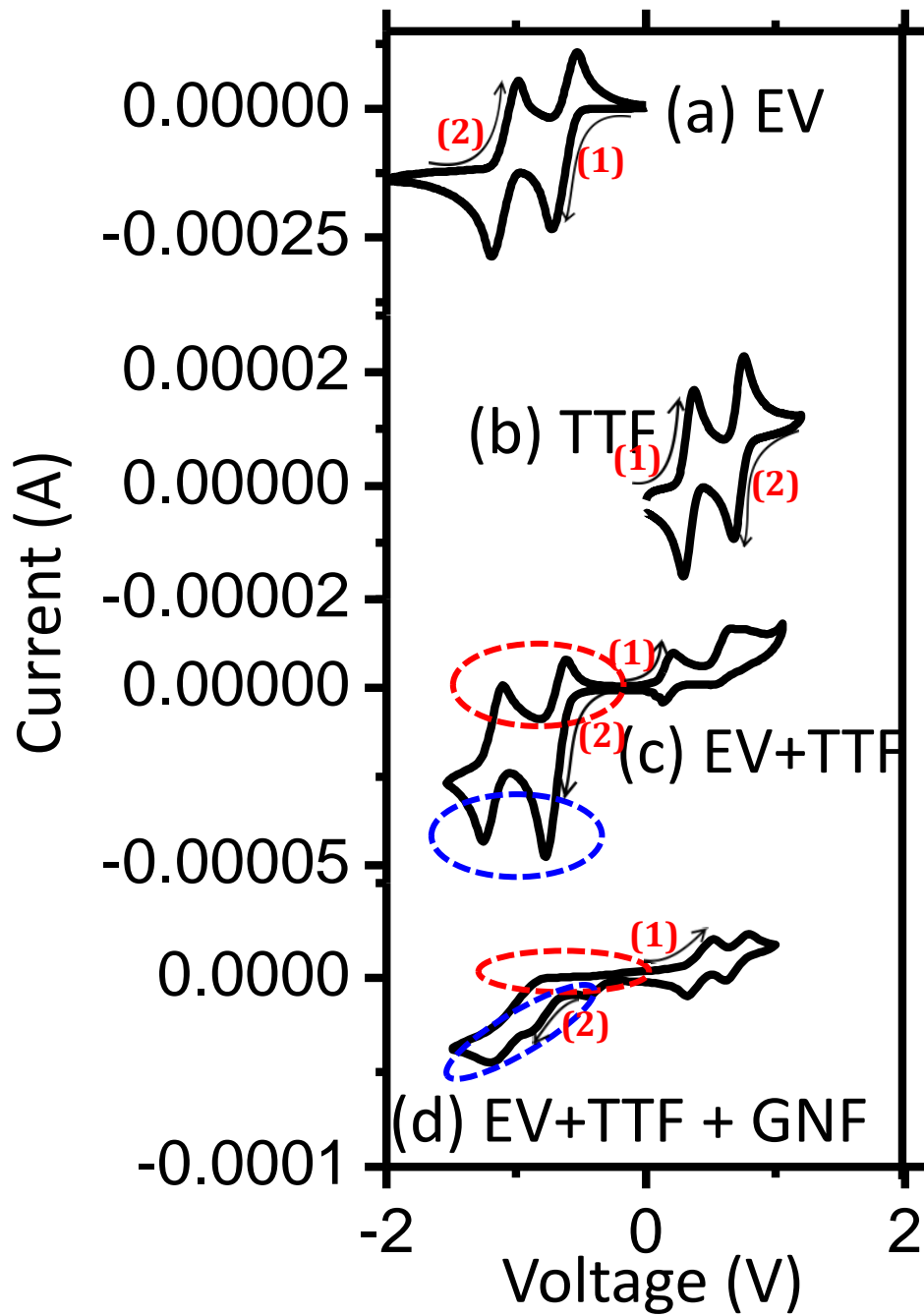


Figure S1: Three electrode CV curves for (a) only EV, (b) only TTF, (c) EV+TTF and (d) EC-Gel (containing EV+TTF+GNF)

Schematic of device operation

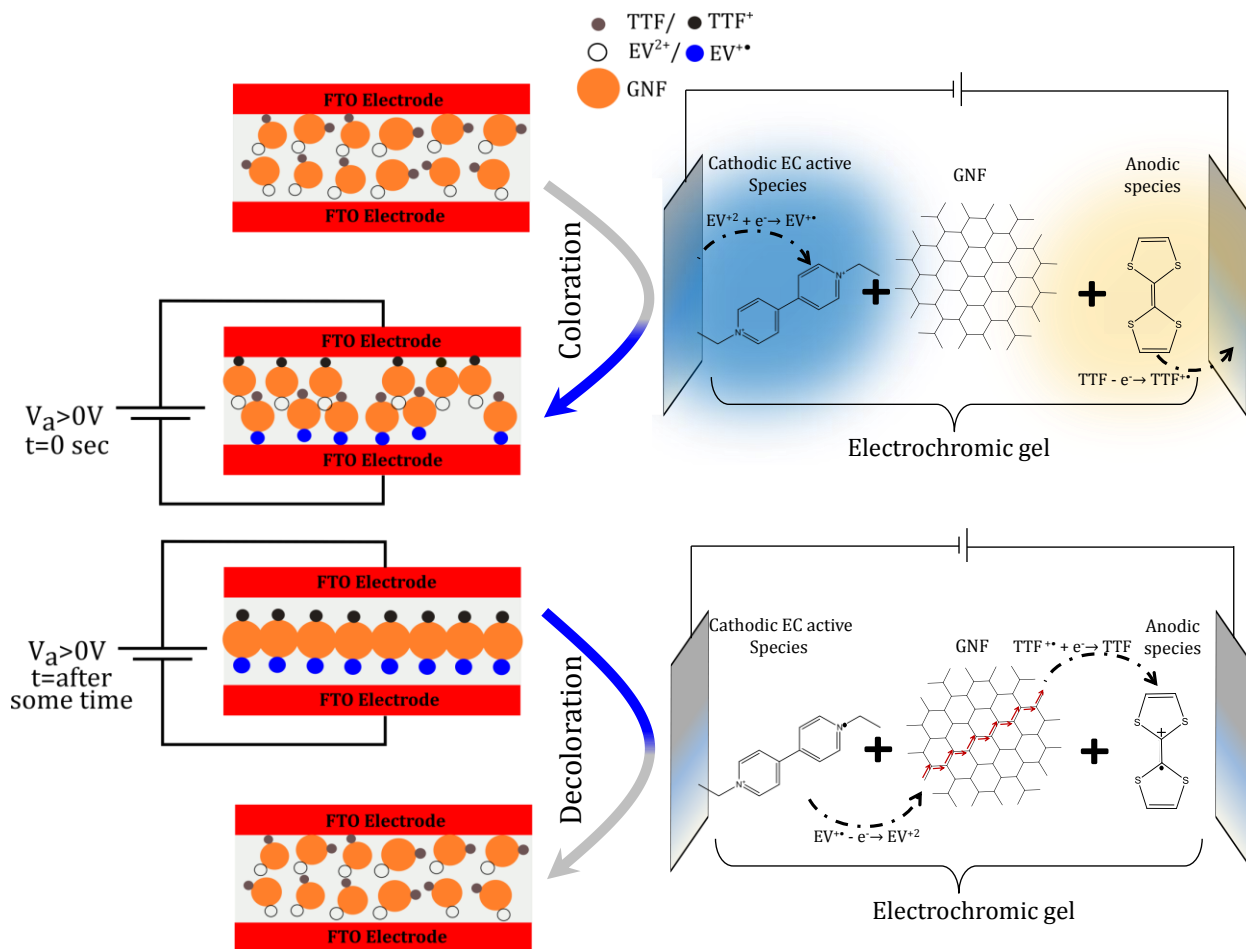


Figure S2: Schematic representation of redox induced coloration-decoloration process (left panel) along with electron movement during coloring and bleaching of the device (right panel).

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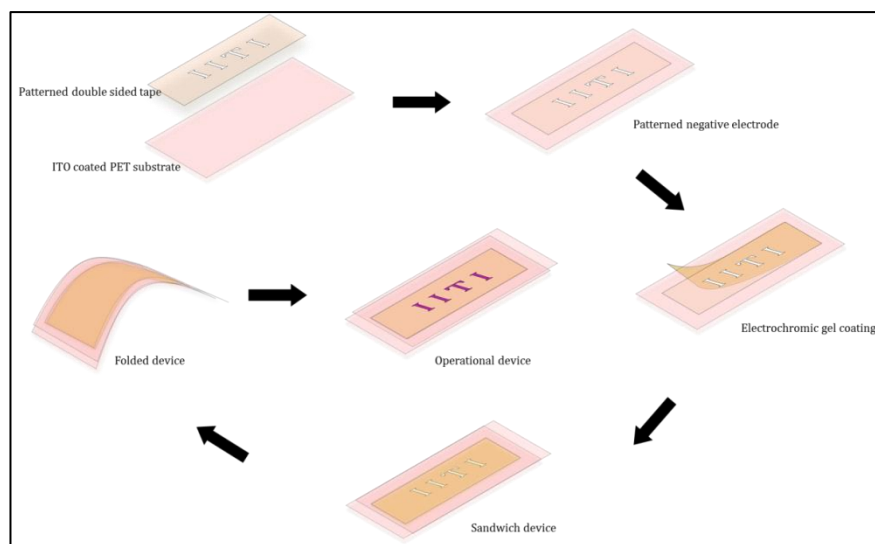


Figure S3: Schematic portraiture of step by step fabrication process of ECD. The reduction and oxidation process was conducted by applying -1.6 and 0.0 V, respectively.