Electronic Supplementary Information for Graphene-based Electrochromic Systems: the Case of Prussian Blue Nanoparticles on Transparent Graphene Film

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Experimental Section

All SEM images were taken using a FE-SEM (JSM6700F). The absorbance data were recorded using Ocean Optics USB4000 spectrometer. Cyclic voltammetry measurements were carried out using a CH instruments model CHI600 potentiostat. Conventional three electrodes assembly was used to record cyclo-voltammograms. The counter electrode was a platinum wire and Ag/AgCl (Ag/Ag⁺) was used as the reference electrode.

Preparation of Graphene: Following the procedure (basically based on the reported method by Ruoff, ref. 5 in text), a transparent graphene was prepared. It is noteworthy that this method resulted exclusively in the formation of single-layered graphene, as reported in ref. 5 in text. First, Cu foils (0.070 mm thickness, Wakopa Co.) were rinsed with dilute HF (10 v% in water) solution, methanol and acetone. After drying, the Cu foils (1 cm * 1 cm) were inserted into chemical vapour deposition chamber (Scientech Co.) and the temperature was increased from room temperature to 1000 °C for 1h with 10 sccm flow of hydrogen. Then, the temperature (1000 °C) was maintained for additional 1 h with 10 sccm flow of hydrogen. The mixture of gas (CH₄, 30 sccm and H₂, 10 sccm) was flowed for 1h to induce the graphene growth on Cu foil at 1000 °C. Then, the graphene film on Cu foil was rapidly cooled below 100 °C and then room temperature. Poly(methylmethacrylate), PMMA (Micro. Chem. M240004) was spin-coated (Intec Co. SP-7200GT, 500 rpm 3 s, 1000 rpm 27 s) on graphene. The Cu foils were etched for 30 min by dipping into the commercial etching reagent (Transene Co. CE-100). After washing with distilled water, the PMMA-graphene was transferred on glass and PMMA was removed with warm acetone (~50 °C). After washing with acetone, the graphene on glass was dried.

Preparation of P-40: The aqueous precursor solution containing 5.0 mM FeCl₃, 5.0 mM K₃Fe(CN)₆, 0.10 M KCl and 0.10 M HCl were prepared and then, PB nanoparticles were electrodeposited with 0.9 cm² area on graphene film (1 cm * 1 cm) through cyclic voltammetry. Fig. 1a shows the typical scanning electron microscopy (SEM) image of PB nanoparticles on graphene which prepared by 40 scans between $+0.30 \sim +0.80$ V with 100 mV/s scan rate. The electrochromic performance of PB nanoparticles on graphene was studied in aqueous 0.10 M KCl electrolyte solution by cyclic voltammetry, chronoamperometry and UV-vis absorption spectroscopy.

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Figure S1. Raman spectra at 6 spots on the prepared graphene on glass; The absence of D band (indicated by dotted line) and the relative intensity ratio between G and 2D bands support that the prepared graphene has a high-quality and mainly single or a few layers , which matches well with the result in literature (ref.5 in text, Science 2009, 324, 1312.).



Figure S2. (a) Absorbance of PB materials on ITO and graphene depending on the cycle number of cyclic voltammetry, (b) comparison of response times of PB materials on graphene and ITO with a same absorbance.



Figure S3. SEM images of PB materials on ITO depending on the cycle number of cyclic voltammetry.



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Figure S4. Thicknesses of PB nanoparticle-films on ITO and graphene.





Figure S5. The size distribution diagrams of PB nanoparticles on graphene (left) and ITO (right)