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## Graphene-based electrochromic systems: the case of Prussian Blue nanoparticles on transparent graphene film†

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**Prussian Blue nanoparticles were electrodeposited on transparent graphene film, which showed a promising electrochromism with response times in the range of 3.3–38 s.**

Electrochromism, a reversible color change of materials through a supply of voltage, can be applied for diverse purposes *e.g.* in display devices, mirrors, smart windows and military camouflage.<sup>1</sup> Especially, electrochromic mirrors and windows have been commercialized in devices of cars and airplanes.<sup>1</sup> In addition to the color diversity and memory effect, the response time of materials is an important factor in device applications. For example, while display devices require a fast response time, a relatively slow response time is acceptable in smart windows or military camouflage.<sup>1,2</sup> Thus, information on the response time of materials in certain systems will be valuable.

Recently, graphene has emerged as a new conductive platform for diverse electronic devices.<sup>3</sup> The quality of graphene has been gradually increased by advances in synthetic methods. A large amount of graphene can be prepared by the reduction of graphene oxide in solution by the Hummers method.<sup>4</sup> However, the remaining oxygen contents often limit the electrochemical properties. Recently, a chemical vapor deposition (CVD) method using a copper catalyst afforded high-quality graphene films.<sup>5</sup> However, more explorations are definitely required to ensure the real merits of this new material. For example, a slow electron transfer in high-quality graphene has been recently reported by Banks *et al.*, and thus its application as electrode materials for sensor devices has been questioned.<sup>6</sup> However, carbon-based electrode materials have been believed to show unique physical properties such as flexibility,<sup>7</sup> which facilitates further exploration of graphene-based devices. Moreover, as far as we are aware, no study has investigated the electrochromic performance on graphene.

Prussian Blue (PB),  $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ , is an interesting material in terms of its electrochemical and magnetic properties.<sup>8</sup> In addition, it has been used as a pigment<sup>8a</sup> due to its intense

color and also as an electron-mediator<sup>9</sup> in sensing devices. Moreover, it can be diversified into sub-family materials *via* incorporation of diverse transition metals instead of iron.<sup>10</sup> Very recently, Wang's group prepared the graphene composites of PB nanoparticles for sensor devices.<sup>9a</sup> In their work, graphene was prepared by a wet-chemical method from graphite *via* a modified Hummers method. The PB nanoparticles were deposited on graphene by mixing the graphene suspension with a precursor solution of PB nanoparticles.

Our research group has continued the development of new organic and inorganic electrochromic systems for smart window and display applications.<sup>11</sup> In this work, we report the electrochromic performance of the electrochemically deposited PB nanoparticles on transparent graphene film. Especially, considering the slow electron transfer behavior of high-quality graphene as recently reported by Banks *et al.*,<sup>6</sup> the response times of graphene-based electrochromic systems were compared with those of the commercial indium tin oxide (ITO) electrode.

A transparent and high-quality graphene film with 1 cm<sup>2</sup> area was prepared by a CVD method based on the literature method.<sup>5</sup> Raman spectroscopy showed that the prepared materials mainly consisted of single-layered graphene, which matches well with a reported result (Fig. 1c and S1 in ESI†).<sup>5</sup> The aqueous precursor solution containing 5.0 mM  $\text{FeCl}_3$ , 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ , 0.10 M KCl and 0.10 M HCl was prepared and then PB nanoparticles were electrodeposited on the graphene film with 0.9 cm<sup>2</sup> area through cyclic voltammetry. Fig. 1a shows the scanning electron microscopy (SEM) image of the PB nanoparticles on graphene that were prepared by 40 scans between +0.30 and +0.80 V with a scan rate of 100 mV s<sup>-1</sup> (Fig. 1d). As shown in the photograph in Fig. 1e, the transparent graphene film was coated with blue-colored materials. The average size of the PB particles was measured as  $45 \pm 6$  nm (Fig. 1b). The UV-visible absorption spectroscopy showed the maximum absorption peak at 720 nm (Fig. 1e).

The amount of loaded PB nanoparticles was controlled to prepare seven materials by changing the scan-cycle number from 10 (**P-10**) to 20 (**P-20**), 30 (**P-30**), 40 (**P-40**), 60 (**P-60**), 80 (**P-80**) and 100 (**P-100**). The absorbance in UV-vis absorption spectroscopy gradually increased with increasing scan-cycle numbers (Fig. 2a). SEM analysis revealed that the size of the PB nanoparticles and the thickness of the materials increased gradually (Fig. 2b and S4 and S5 in the ESI†).

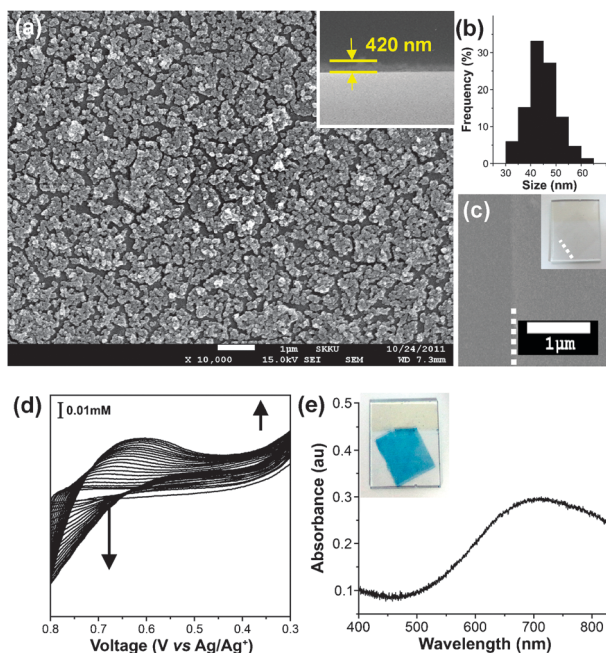
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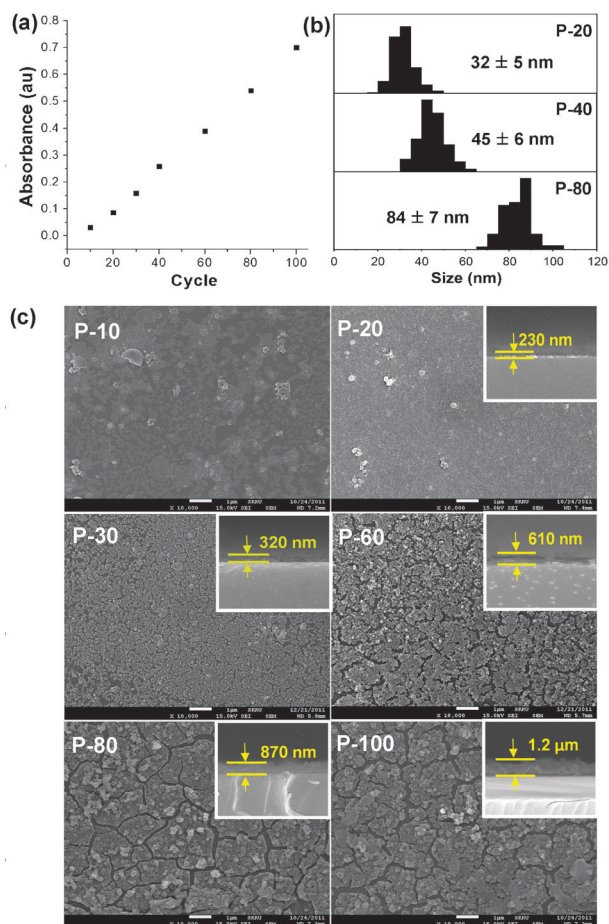


**Fig. 1** (a) SEM image, (b) size distribution diagram of PB nanoparticles (**P-40**, 420 nm thickness) on graphene, (c) SEM image and photograph of graphene on glass, (d) cyclic voltammograms of electrodeposition process and (e) UV-vis absorption spectroscopy and photograph of **P-40**.

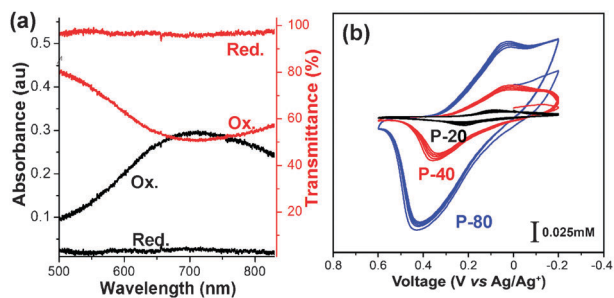
The electrochromic performance of the PB nanoparticles on graphene was studied in aqueous 0.10 M KCl electrolyte solution by cyclic voltammetry, chronoamperometry and UV-vis absorption spectroscopy. The cyclic voltammetry of the PB nanoparticles on graphene showed the reversible reduction peaks at +0.15 V (vs. Ag/Ag<sup>+</sup>) with color change from blue to colorless (Fig. 3). Depending on the amount of materials, the difference between the oxidative wave and the reductive wave increased, indicating the slower electron transfer in the thicker materials.

As described in the introduction part, the response time is a very important factor in practical applications of electrochromic systems. The response time was defined as the time required to reach 90% of the maximum absorbance change. Usually, inorganic polymeric materials showed a relatively slow response time due to the low conductivity and the resultant slow electron transfer. The response times of PB materials in the literature were reported in range of 5–10 s and were dependent on the structure and thickness of the PB films.<sup>12</sup> To improve the response time, organic polymer electrolyte–PB composites were fabricated.<sup>13</sup> In the present work, we studied the response time of the PB nanoparticles on graphene using chronoamperometry by applying  $-0.30$  V (for bleaching) and  $+0.60$  V (for coloring). Fig. 4 and Table 1 summarize the results.

As the thickness (Fig. 2 and S4 in the ESI<sup>†</sup>) and intensity change of the PB on graphene increased, the response times gradually increased (Table 1). The observed response times revealed that the re-coloring process is generally faster than the bleaching one. From **P-60** through **P-80** to **P-100**, the response times sharply increased from 13.4 through 25.3 to 38.0 s (in the bleaching process). According to the SEM studies, the PB films on graphene in **P-10**, **P-20**, **P-30** and **P-40** had a



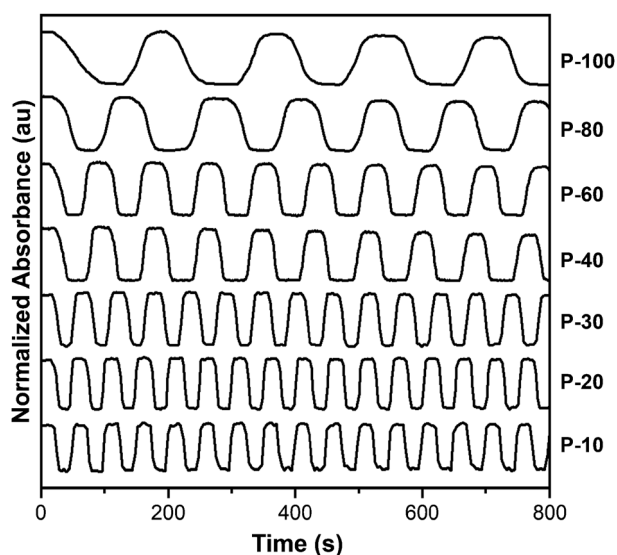
**Fig. 2** (a) Absorbance at 720 nm depending on scan-cycle number, (b) size distribution and (c) SEM images of PB nanoparticles on graphene.



**Fig. 3** (a) Electrochromic properties of **P-40** and (b) representative cyclic voltammograms of **P-20**, **P-40** and **P-80**.

space among the materials which allowed the electrolyte to penetrate through the films. In comparison, **P-60**, **P-80** and **P-100** showed the relatively compact characteristic of materials and a deficient space between the PB materials. Thus, the sharp increase of the response times in **P-60**, **P-80** and **P-100** was attributed to the compact structure and thick thickness of film.

The response times of the PB nanoparticles on graphene were compared with those on the commercial ITO electrode. Because the electron transfer in graphene was considered to occur mainly through a peripheral edge,<sup>14</sup> a high quality graphene with a large basal and low edge plane showed a slow electron transfer.<sup>6</sup> The CVD method using a copper



**Fig. 4** Absorbance changes at 720 nm of PB nanoparticles on graphene with  $-0.30$  V and  $+0.60$  V (vs.  $\text{Ag}/\text{Ag}^+$ ) respectively. The transmittance changes of P-10, P-20, P-30, P-40, P-60, P-80, and P-100 at 720 nm were 7%, 18%, 31%, 50%, 59%, 71% and 80% respectively.

**Table 1** Response times of PB nanoparticles on graphene<sup>a</sup>

Materials	Observed response times/s		Intensity change $\Delta T$ (%)
	Bleaching <sup>b</sup>	Coloring <sup>c</sup>	
P-10	4.2 (2.8)	3.3 (2.4)	7
P-20	7.5 (4.1)	5.8 (3.3)	18
P-30	8.9 (4.3)	6.1 (3.8)	31
P-40	9.7 (4.7)	7.2 (4.0)	50
P-60	13.4 (6.7)	8.9 (6.1)	59
P-80	25.3 (12.2)	17.1 (10.9)	71
P-100	38.0 (19.4)	28.6 (18.6)	80

<sup>a</sup> The absorbance changes at 720 nm were measured using 0.10 M KCl as the electrolyte solution. The values in parentheses correspond to the response times for PB materials with the same intensity changes on the commercial ITO electrode (refer to the ESI). <sup>b</sup>  $-0.30$  V (vs.  $\text{Ag}/\text{Ag}^+$ ) was applied. <sup>c</sup>  $+0.60$  V (vs.  $\text{Ag}/\text{Ag}^+$ ) was applied.

catalyst was known to produce a high quality graphene with single or a few layers. The PB materials on the commercial ITO electrode with nearly the same UV-vis absorbance at 720 nm were systematically prepared by controlling the cycles of cyclic voltammetry in electrodeposition (Fig. S2 and S3 in the ESI<sup>†</sup>). As summarized in Table 1, the response times of the PB materials on graphene are about half as fast as those on the ITO electrode. As mentioned above, although the response times were quite dependent on the materials themselves, the properties of electrode materials are also critical in this study and therefore are considered in practical applications. The results suggest that PB materials on transparent graphene film are a promising candidate system for smart (flexible) window devices.

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