Original Paper

Dispersion of Graphene in an Aqueous Solution with Poly(sodium 4-styrenesulfonate) Monitored by Capillary Electrophoresis

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Abstract

Graphene was dispersed in an aqueous solution with poly(sodium 4-styrenesulfonate) as a dispersant. The charge of the graphene came to be apparently negative by the adsorption of poly(4-styrenesulfonate) ion (PSS). Two kinds of PSS were examined: the average molecular masses of 70,000 and 1,000,000 (PSS 70,000 and PSS 1,000,000, respectively). Capillary electrophoresis was used to evaluate the dispersion of the apparently anionic graphene in an aqueous solution. A broad signal corresponding to the dispersed graphene was detected in the electropherograms. The effective electrophoretic mobility of the dispersed graphene was somewhat larger at higher concentrations of PSS 70,000, suggesting that the adsorbed amount of PSS 70,000 increased. Even when the separation buffer did not contain PSS, the broad signal of the anionic graphene was still detected. The peak height and/or the peak area, as well as the effective electrophoretic mobility of the graphene decreased little at the reduced applied voltages, *i.e.*, at longer separation/detection time. Therefore, the adsorption of PSS is irreversible or the desorption of PSS from the graphene surface is very slow. Accordingly, the dispersed graphene with PSS would be separated from the matrix PSS by the electrophoretic separation.

Keywords: Graphene; Dispersion; Capillary electrophoresis; Poly(sodium 4-styrenesulfonate)

1. Introduction

Graphene is two-dimensional carbon material, and its mechanical and electrical properties are in the center of the attention [1]. Dispersion of graphene in solution is essential to form structural arrangement of graphene. Capillary electrophoresis is useful to evaluate the dispersion of graphene in aqueous solution [2-4]. It is reported that low concentration of salt or the buffer components is effective to disperse graphene in an aqueous solution [2]. We have previously reported that a surfactant of sodium dodecylbenzenesulfonate (SDBS) is effective to disperse graphene in an aqueous solution [4]. Shot signals corresponding to the graphene aggregates were suppressed, while a broad signal was detected reflecting a wide variety of graphene [4]. Addition of neutral polymer, such as polyethylene glycol, poly(vinyl alcohol), or polyvinylpyrrolidone, can substitute the DBS adsorbed on the graphene surface during the electrophoretic migration [5]. In this study, anionic polyelectrolyte of poly(sodium 4-styrenesulfonate) was examined as a dispersion matrix for graphene. Poly(4-styrenesulfonate) (PSS) has been used for the dispersion of carbon nanotubes [6]. Exfoliation of graphene from neutral graphite and its suspension in aqueous solution was examined with small ionic molecules possessing aromatic moiety and PSS through the UV-vis spectrophotometry and zeta potential measurements [7].

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PSS was also utilized to suppress the aggregation of graphene sheets on the reduction from graphene oxide with ascorbic acid [8]. UV-spectrophotometry was used for the monitoring of the dispersion. Conjugated polyelectrolyte of PPE-SO$_3^-$ [9], cationic vinylimidazole-based polymer [10], cationic phenosafranin [11], and bovine serum albumin [12] were also examined for the dispersion of graphene in aqueous media.

PSS possesses both hydrophobic aromatic moiety of polystyrene skeleton and hydrophilic sulfonate moiety, and it would be helpful to disperse graphene in an aqueous solution by the adsorption through the hydrophobic π-π interaction and by the electrostatic repulsion between the sulfonate moieties. The polymer chain would also be helpful on strong adsorption to the graphene surface. In this study, capillary electrophoresis (CE) was used to evaluate the dispersion of graphene in an aqueous solution. An anionic signal with broad width was detected by CE corresponding to the dispersed graphene. The adsorption of graphene was also monitored through the effective electrophoretic mobility. The CE involves electrophoretic separation, excess PSS in the dispersed graphene solution is separated from the graphene-PSS complex. The dispersed graphene was still anionic under the CE separation. Therefore, the adsorption of PSS is considered to be irreversible, or the desorption of PSS from the graphene surface to be very slow.

2. Experimental
2.1. Chemicals

Graphene Nanoplatelets was purchased from XG Sciences (xGnP, grade C, 750 m^2 g^{-1}, Lansing, MI, USA). Dispersion reagents of poly(sodium 4-styrenesulfonate) were from Sigma-Aldrich (St. Louis, MI, USA), with the average molecular masses of ~70,000 and ~1,000,000 (PSS 70,000 and PSS 1,000,000, respectively). Sodium ethylbenzenesulfonate (Tokyo Chemical Industry, Tokyo, Japan) was also examined for comparison. Sodium tetraborate decahydrate (borax) was used as a buffer component of the separation buffer; it was from Wako Pure Chemical (Osaka, Japan). Water used was purified by Milli-Q Gradient A10 (Merck Millipore Japan, Tokyo, Japan). Unless otherwise stated, all other reagents were of guaranteed reagent grade and used without further purification.

2.2. Apparatus

An Agilent Technologies (Waldbronn, Germany) ^{3D}CE capillary electrophoresis system was used, equipped with a photodiode array detector. A fused-silica capillary purchased from GL Sciences (Tokyo, Japan) was cut to a required length, and it was used as a separation capillary after a detection window was made by burning a small portion of the polyimide coating. The capillary was held in a capillary cassette cartridge. The dimensions of the capillary were 64.5 cm in total length, 56 cm in the effective length from the injection point to the detection point, 50 μm inner diameter, and 375 μm outer diameter. An Elma-Hans Schmidbauer Transsonic T310 was used for the ultrasonic radiation (35 kHz, 45 W, Singen, Germany).

2.3. Procedure

An aliquot amount of graphene powder (typically 0.03 g) was taken in a 10 mL volumetric flask, and an appropriate volume of 1 %(w/v) PSS solution was poured into the flask. Then, ultrasonic vibration was irradiated to the flask in a water tank for 5 min to disperse graphene in the PSS solution. The graphene solution was diluted to a final volume with the purified water, and the solution was stood for at least 12 h to precipitate the insoluble carbon substances. The supernatant solution was used for the CE analysis.

Separation buffers were prepared with 5 mM borax (pH ≈ 9.2) and an appropriate amount of PSS. Sample solutions were prepared as described above; 1~2%(v/v) ethanol was added in the sample solution to monitor the electroosmotic flow (EOF). After the separation buffer was filled in both anodic and cathodic reservoir vials, as well as into a capillary, the sample solution was injected into the capillary hydrodynamically by applying pressure at 50 mbar to the inlet vial for 5 s placed at the anodic end. A DC voltage of 10~25 kV was then applied to the capillary for the electrophoresis. Graphene was photometrically detected at 420 nm, while the electroosmotic flow was monitored at 200 nm. The capillary was thermostat at 25 ℃ through the measurement. An Agilent ChemStation software (Ver. B.04.02) was used for recording and analyzing the electropherograms.

3. Results and discussions
3.1. Dispersion of graphene in an aqueous solution with PSS

It has been reported that a surfactant of sodium dodecylbenzenesulfonate (SDBS) is a good dispersing agent for graphene in an aqueous solution [4]. Aromatic moiety of DBS$^-$ was attributed to its interaction with the 2-dimensional graphene surface, and the anionic charge of DBS$^-$ on the graphene surface prevented the staking between the graphene planes by the electrostatic repulsion [4]. Although SDBS is a good dispersant for graphene, a considerable concentration of the surfactant was necessary as much as 20 mmol dm^{-3} and the surfactant coexists in the graphene solution. Thus, anionic polyelectrolyte of PSS was examined as an alternative dispersant. Although PSS was previously examined as a dispersant of graphene, measurement of UV-vis absorptiometry was used and it was

difficult to distinguish between the dispersion and the suspension of graphene [6]. Therefore in this study, the dispersion of graphene was examined with the electropherograms in CE. When the graphene is dispersed in the aqueous solution with any dispersant, a broad peak would be detected with the dispersed graphene, as well as irreproducible shot signals with the aggregated graphene [4, 5].

Preparation of the graphene-dispersed solution was firstly examined with PSS as a dispersant. Ultrasonic radiation is generally necessary on the dispersion of the graphene in an aqueous solution, although longer radiation would break the graphene particles into further small pieces [2]. The radiation time was thus set at as short as 5 min. The ultrasonic radiation was examined at two different steps on the preparation of the graphene solution. One was the radiation to the graphene solution before diluting to the final volume, and the other was the radiation after diluting to the final volume. In the former case, graphene would be dispersed in a relatively high concentration of PSS solution; the volume was about 1/10 to the final volume, and all the solutes were at higher concentrations than at the final volume. The results on CE electropherograms are shown in Fig. 1. For the diluted solution, the radiation did not work well on the dispersion of graphene, as shown in the electropherogram (a); broad-peak was not clearly detected. On the other hand, a broad-peak was distinctly detected in the electropherogram (b) with the graphene dispersed solution, when ultrasonic was irradiated before diluting to the final volume. Irradiation to the high concentrations of the solutes was effective for the dispersion of graphene in the PSS solution. Generally, the dissolution/dispersion rate is fast at higher concentrations of
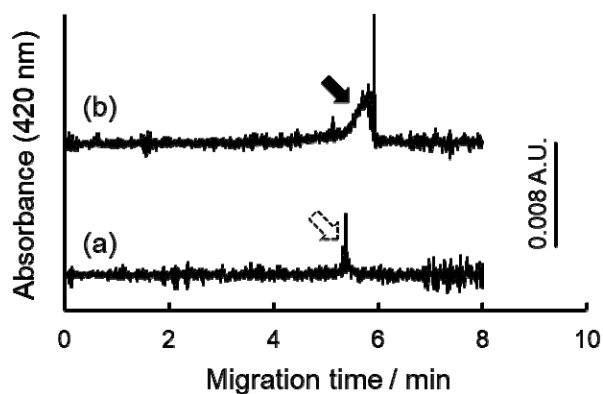
the solute and/or the dispersant. On the preparation of the graphene-PSS dispersed solution, high concentration of PSS at the final volume would promote the dispersion of graphene. However, the higher concentration of PSS may increase the viscosity of the solutions. Thus, the latter format, ultrasonic radiation before dilution to the final volume, is favorable for the dispersion study.

When 4-ethylbenzenesulfonic acid sodium salt (EBS), a monomer unit of PSS, was examined as a dispersant of graphene at the concentration of 0.05 %(w/v) ($\approx 2.4 \times 10^{-3}$ mol dm^{-3}), the supernatant of the graphene-dispersed solution was clear. Thus, graphene is less soluble in the EBS solution. Polymer structure of PSS would induce the multipoint interaction with the graphene surface, and the multipoint interaction promotes the dispersion of graphene.

3.2. Effect of the concentration of PSS

Graphene can be dispersed in the PSS solution by ultrasonic radiation, and the concentration of PSS was examined at its concentration range between 0.01 %(w/v) and 0.1 %(w/v). The concentrations of PSS were set at the same both in the sample solution and in the separation buffer. The results on electropherograms are shown in Fig. 2. A broad peak is detected with each electropherogram, suggesting that the graphene is dispersed in the PSS solution. The migration of the dispersed graphene, a broad peak, is slower than the EOF (indicated as "S" in Fig. 2),

Fig. 1. Electropherograms of graphene on the preparation of the dispersed graphene solutions. (a) Ultrasonic irradiation after diluting to the final volume. (b) Ultrasonic irradiation before diluting to the final volume.
Separation buffer: 5 mM borax (pH 9.2) + 0.05 %(w/v) PSS 70,000. Sample solution: 2 mg/mL graphene + 0.05 %(w/v) PSS 70,000. CE conditions: applied voltage of 25 kV, detection wavelength at 420 nm, sample injection under 50 mbar pressure for 5 s, capillary temperature at 25 °C.
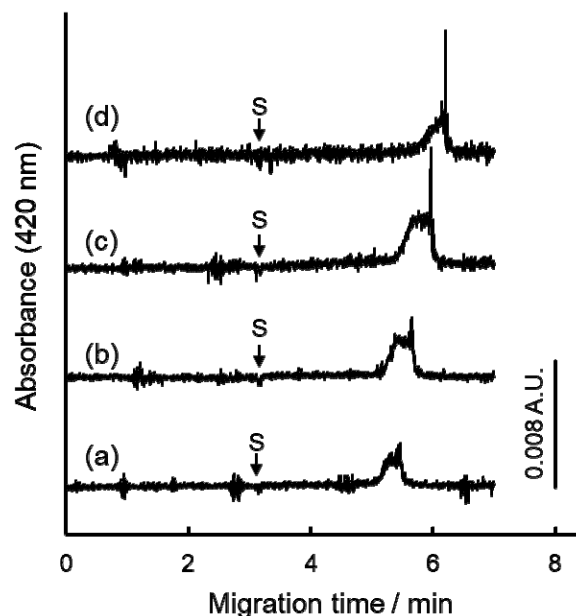

Fig. 2. Typical electropherograms of graphene with different concentrations of PSS 70,000. Concentrations of PSS (%(w/v)): (a), 0.01; (b), 0.02; (c), 0.05; and (d), 0.1. S: solvent (EOF).
Separation buffer: 5 mM borax (pH 9.2) + PSS 70,000. Sample solution: 3 mg/mL graphene + PSS 70,000. CE conditions: applied voltage of 25 kV, detection wavelength at 420 nm, sample injection under 50 mbar pressure for 5 s, capillary temperature at 25 °C.

and the graphene is apparently anionic. The anionic charge is introduced to graphene by the adsorption of PSS on it.

The concentration range of the dispersant, PSS, is much lower than SDBS (~20 mmol dm^{-3}, 0.7 %(w/v)) [4] or nonionic polymers (1~6 %(w/v)) [5]. Therefore, PSS is adsorbed on the graphene surface more strongly than DBS^{-} surfactant.

It can be noted from the electropherograms in Fig. 2 that the migration time of the broad peak took longer at higher concentrations of PSS. The result suggests that graphene is apparently more anionic. It is also noted from Fig. 2 that the migration time of EOF is almost identical in the PSS concentration range examined. Therefore, the viscosity of the separation buffer is not changed so much. The effective electrophoretic mobility of graphene (μ_{eff}) was calculated in an ordinary manner using the migration times of the graphene and the EOF. The result is shown in Fig. 3. The effective electrophoretic mobility of graphene gradually increased with increasing concentrations of PSS 70,000. The increase in μ_{eff} suggests that the increased net charge of the graphene; PSS 70,000 would be adsorbed more densely on the graphene surface at its higher concentrations. In the case of PSS 1,000,000, the absolute value of μ_{eff} is larger than in the case of PSS 70,000, and the increase in μ_{eff} is slight. The effective electrophoretic mobility of PSS 70,000 and PSS 1,000,000 were measured by CE, and the μ_{eff} values were -4.40×10^{-4} cm^2 V^{-1} s^{-1} and -4.54×10^{-4} cm^2 V^{-1} s^{-1}, respectively. Therefore, the effective electrophoretic mobility of the graphene-PSS complex at 0.1%(w/v) PSS are about 80% and 92% against the free PSS for PSS 70,000 and PSS 1,000,000, respectively. The result also suggests the dense adsorption

of PSS 1,000,000. From the comparison of the μ_{eff} values of graphene-PSS complexes, the mass fraction of graphene in the graphene-PSS complex is larger with PSS 70,000 than with PSS 1,000,000. The result also ascertain the adsorption properties of PSS. Since PSS 1,000,000 is much longer molecule, a small portion of PSS 1,000,000 would adsorbed on the graphene surface, and most portion of PSS 1,000,000 would be free in the separation buffer.

3.3. Dispersion ability of graphene with PSS

Different amounts of graphene were dispersed in a PSS solution to examine the dispersion ability of PSS. Peak area of the broad peak in the electropherograms was examined with different concentrations of graphene in the prepared sample solution. The electropherograms are shown in Fig. 4, and the peak area is plotted against the concentration of graphene as in Fig. 5. Although the concentration of graphene indicated is based on the taken amount of graphene powder, it is not the actual concentration of graphene in the PSS solution. Graphene is complicated carbon material, and a considerable amount of the graphene/graphite is precipitated in the prepared graphene solution. However, peak area of the dispersed graphene linearly increased with its amount up to 4 mg/mL (Fig. 5). The linear calibration range suggested that the graphene component in the powder would be well dispersed in the PSS solution in this concentration range.

It is also noted from Fig. 4 that the migration time of graphene as well as its effective electrophoretic mobility,
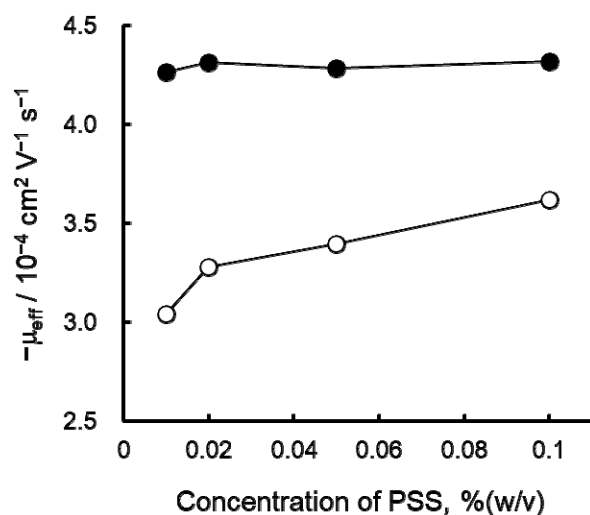

Fig. 3. Changes in the effective electrophoretic mobility of the dispersed graphene with increasing concentrations of PSS. The conditions are the same as in Fig. 2. PSS: ○, PSS 70,000; ●, PSS 1,000,000.
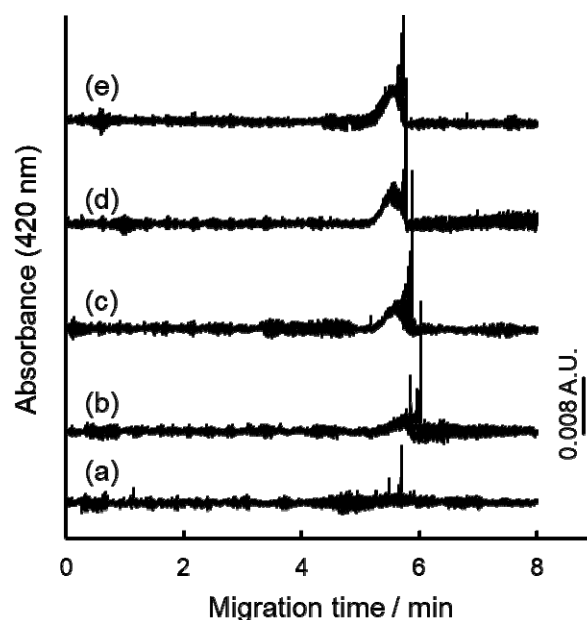

Fig. 4. Electropherograms for different concentrations of graphene. Concentrations of graphene (mg/mL): (a), 1; (b), 2; (c), 3; (d) 4; and (e), 5. The conditions are the same as in Fig. 2, except the concentration of graphene. PSS concentration: 0.05 %(w/v).
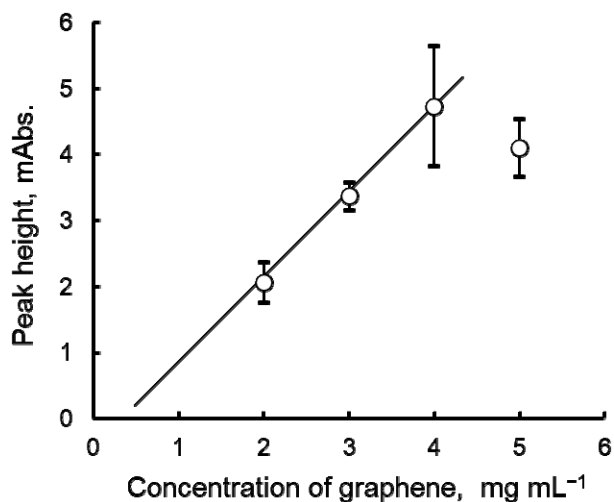
Fig. 5. Relationship between introduced Graphene concentration and peak height in CE. Concentrations of PSS: 0.05 %(w/v). The conditions are the same as in Fig. 4.

μ_{eff}, is almost identical over the graphene concentrations. Thus, the concentration of PSS 70,000 would be sufficient to be adsorbed on the graphene over this concentration range.

3.4. Irreversible adsorption of PSS to the graphene

The electrophoretic migration of the dispersed graphene was also examined with a separation buffer without PSS. When the separation buffer does not contain PSS, the dispersed graphene-PSS complex and excess PSS in the sample zone would be electrophoretically resolved, and the PSS adsorbed on the graphene would be desorbed from the graphene-PSS complex by the dissociation of the complex. The desorption rate is the related with the reaction time, and the reaction time can be controlled with the applied voltage. Lower separation voltage would take longer detection time of the dispersed graphene and the detection time corresponds to the reaction time of the dissociation. The results are shown in Fig. 6. As in Fig. 6B, the dispersed graphene as anionic complex is still detected in the absence of PSS 70,000 in the separation buffer, as well as in the case of Fig. 6A containing PSS 70,000 in the separation buffer. The peak height of the dispersed graphene is almost comparable between in the absence and the presence of PSS 70,000 in the separation buffer. The relative value of the peak height is in the range from 78% to 116%. Similarly, the peak area of the dispersed graphene divided by the migration time was as well; in the range from 99% to 115%.

The effective electrophoretic mobility was also compared; the result is shown in Fig. 7. In the presence of PSS in the separation buffer, the μ_{eff} value of the dispersed graphene is almost identical at different applied voltage. The result agrees with the definition of the effective electrophoretic mobility. When PSS was not contained in
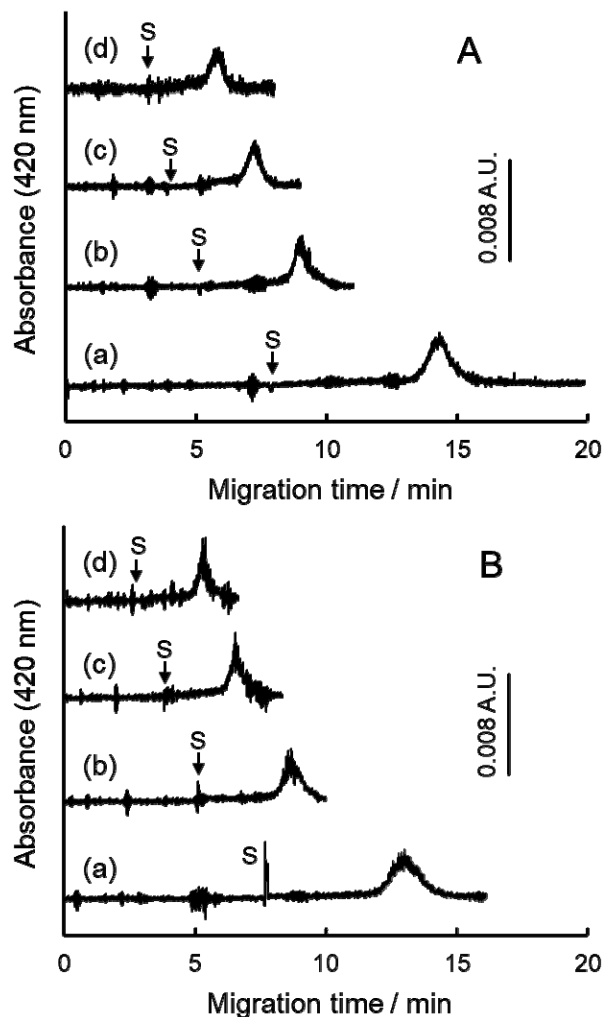

Fig. 6. Typical electropherograms of graphene in the presence and absence of PSS 70,000 in the separation buffer.
Separation buffer: A, 5 mM borax + 0.05 %(w/v) PSS 70,000; B, 5 mM borax. Sample solution: 3 mg/mL graphene + 0.05 %(w/v) PSS 70,000. CE conditions: detection wavelength at 420 nm, sample injection under 50 mbar pressure for 5 s, capillary temperature at 25 °C. Applied voltage: (a), 10 kV; (b), 15kV; (c), 20 kV; and (d), 25kV.

the separation buffer, the μ_{eff} value of graphene is slightly decreased but close to the one in the presence of PSS in the separation buffer. Additionally, the decrease in the μ_{eff} values is not extended at the lower voltage or the longer separation time. Anionic properties of the graphene-PSS complex remained even in the absence of PSS in the separation buffer. Therefore, the desorption rate of PSS from the graphene surface would be very slow, or the adsorption of PSS would be irreversible. As PSS is a long-chain polymer, a large number of benzene moieties in PSS interacts with the graphene surface, and the multipoint interactions would suppress the desorption of PSS.

Regarding that the graphene-PSS complex in the sample solution is resolved from the excess PSS by CE, the graphene-PSS complex would be separated from the matrix
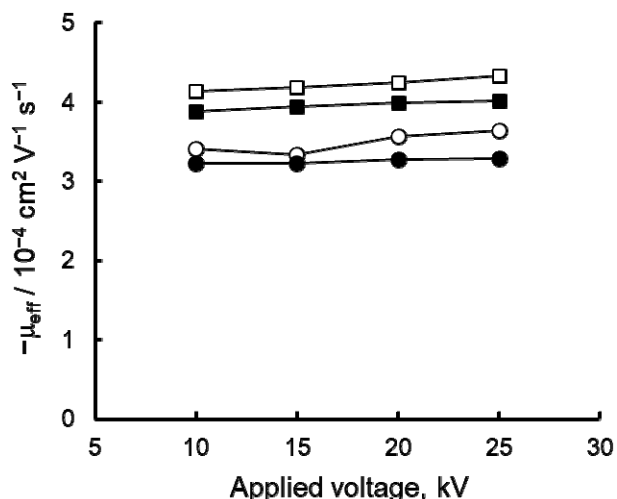
Fig. 7. Effective electrophoretic mobility of graphene in the presence and absence of PSS in the separation buffer.
The concentration of PSS 70,000 in the separation buffer: ○, 0.05 %(w/v); ●, none.
The concentration of PSS 1,000,000 in the separation buffer: □, 0.05 %(w/v); ■, none.

PSS by the electrophoretic separation. The electrophoretic separation technique would be utilized for the isolation of anionic graphene-PSS complex.

4. Conclusion

In this study, monitoring of dispersed graphene in an aqueous solution is demonstrated by a CE analysis. Poly(4-styrenesulfonate) ion worked as a dispersant of graphene, and the dispersed graphene was detected as a broad signal according to its wide variety of the shape and size. Apparently anionic graphene was detected even in the absence of PSS in the separation buffer, and the adsorption of PSS is found to be irreversible or the desorption of PSS is very slow. Since the graphene-PSS complex and free PSS are resolved by CE, the electrophoretic separation would be utilized for the isolation of anionic graphene-PSS complex.

Acknowledgements

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