Electronic Supplementary Information

In-situ polymerization of a novel surfactant on graphene surface for the stable graphene dispersion in water

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Experimental

Materials

Graphene powder was provided by Sekisui Chemical Co., Ltd. (Tokyo, Japan). *N,N*-Dimethylformamide (DMF) was purchased from Watanabe Chemical Industries, Ltd. (Hiroshima, Japan). Tetradecylamine, hexadecylamine, octadecylamine and divinylbenzene were purchased from Tokyo Chemical Industry (Tokyo, Japan). Ammonium peroxodisulfate was purchased from Nacalai Tesque (Kyoto, Japan). 2-Chloroethyl acrylate and α-cyano-4-hydroxycinnamic acid were purchased from Sigma (St. Louis, MO). Other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

The water used was high-quality deionized water (Milli-Q water, >15 MΩ cm^{-1}), produced using a Milli-Q Advantage A100 system equipped with an Elix UV 3 system (Millipore, Molsheim, France).

Synthesis of non-polymerizable surfactants (C*n*-2EG$_3$)

n-Alkylamine (20 mmol) and potassium carbonate (48 mmol) were dissolved in DMF (45 mL) by stirring in a round bottom flask at 80 °C. Triethylene glycol 2-bromoethyl methyl ether (40 mmol) was dissolved in DMF (25 mL). The solution was transferred to the reaction flask under nitrogen followed by refluxing the reaction mixture for 24 h at 80 °C. The reaction mixture was filtered and evaporated. The resulting brown oil was dissolved in ethyl acetate (30 mL), washed with 0.1 M HCl (1×30 mL) and water (2×30 mL), dried with magnesium sulfate, filtered and evaporated. ^{1}H NMR (300 MHz) spectra were recorded in a $CDCl_3$ solution on a Varian Gemini 300 spectrometer. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for 1H) as internal standard. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MS) was performed on ultrafleXtreme-KB mass spectrometer (Bruker Daltonics). α-Cyano-4-hydroxycinnamic acid was used as the matrix unless otherwise noted.

C14-2EG$_3$ was collected as a clear brown oil (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.76–3.44 (m, 28H, -*CH_2*-O-*CH_2*-), 3.38 (s, 6H, -O-CH_3), 2.70 (t, *J*=6.9 Hz, 4H, -CH_2-N-*$(CH_2)_2$*-), 2.48 (t, J=7.7 Hz, 2H, -*CH_2*-N-$(CH_2)_2$-), 1.36–1.13 (m, 24H, -$C_{12}H_{24}$-), 0.88 (t, J=6.6 Hz, 3H, -$C_{12}H_{24}$-*CH_3*). MALDI-TOF/MS ($[M+H]^+$ calcd for $C_{32}H_{67}NO_8$, m/z = 594.5; found, 593.2).

C16-2EG$_3$ was collected as a clear brown oil (63% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.73–3.43 (m, 28H, -*CH_2*-O-*CH_2*-), 3.36 (s, 6H, -O-CH_3), 2.68 (t, *J*=6.0 Hz, 4H, -CH_2-N-*$(CH_2)_2$*-), 2.47 (t, J=7.4 Hz, 2H, -*CH_2*-N-$(CH_2)_2$-), 1.31–1.11 (m, 28H, -$C_{14}H_{28}$-), 0.86 (t, J=5.5 Hz, 3H, -$C_{14}H_{28}$-

CH$_3$). MALDI-TOF/MS ([M+H]$^+$ calcd for $C_{34}H_{72}NO_8$, m/z = 622.5; found, 624.5).

C18-2EG$_3$ was collected as a clear brown oil (59% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.75–3.45 (m, 28H, -*CH*$_2$-O-*CH*$_2$-), 3.38 (s, 6H, -O-CH$_3$), 2.70 (t, *J*=5.5 Hz, 4H, -CH$_2$-N-*(CH$_2$)$_2$*-), 2.48 (t, J=7.1 Hz, 2H, -*CH*$_2$-N-(CH$_2$)$_2$-), 1.34–1.12 (m, 32H, -C$_{16}$H$_{32}$-), 0.88 (t, J=6.3 Hz, 3H, -C$_{16}$H$_{32}$-*CH*$_3$). MALDI-TOF/MS ([M+H]$^+$ calcd for $C_{36}H_{76}NO_8$, m/z = 650.5; found, 652.1).

Synthesis of 2-iodoethyl acrylate

Sodium iodide (119 mmol) was dissolved in acetone (70 mL). 2-Chloroethyl acrylate (70 mmol) was added to the solution. The solution was stirred at 40 °C for 98 h. Diethyl ether (140 mL) was added to the reaction mixture. The solution was filtrated, washed with water (2×80 mL), dried with magnesium sulfate, filtered and evaporated. The product was collected as a clear oil (31% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.60–6.35 (m, 1H, C*H*H=CH-), 6.21–6.08 (m, 1H, CHH=C*H*-), 5.94–5.85 (m, 1H, CH*H*=CH-), 4.41 (t, *J*=7.4 Hz, 2H, -COO-CH$_2$-), 3.33 (t, *J*=6.9 Hz, 2H, -COO-CH$_2$-*CH*$_2$-).

Synthesis of polymerizable surfactants (C*n*-ac-2EG$_3$)

Non-polymerizable surfactant (C*n*-2EG$_3$, 10 mmol), hydroquinone (0.5 mmol) and potassium carbonate (14 mmol) were dissolved in acetonitrile (10 mL). 2-Iodoethyl acrylate (40 mmol) was dissolved in acetonitrile (30 mL). The solution was transferred to the reaction flask under nitrogen

followed by refluxing the reaction mixture for 24 h at 70 °C. The reaction mixture was filtered and evaporated. The crude product was then dissolved in ethyl acetate (30 mL), cooled in a refrigerator overnight, filtrated and evaporated. The residue was washed with *n*-hexane (2×60 mL).

C14-ac-2EG$_3$ was collected as clear reddish brown oil (28% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.56–6.37 (m, 1H, -OCO-CH=C*H*H), 6.25–6.09 (m, 1H, -OCO-C*H*=CHH), 5.99–5.79 (m, 1H, -OCO-CH=CH*H*), 4.31 (t, *J*=4.9 Hz, 2H, -CH_2-OCO-), 4.09–4.00 (m, 2H, -N-*CH_2*-CH_2-OCO-), 4.00–3.93 (m, 2H, -N-*CH_2*-CH_2-O-), 3.92–3.83 (m, 2H, -$C_{14}H_{28}$-*CH_2*-O-), 3.76–3.48 (m, 28H, -*CH_2*-O-*CH_2*-), 3.41–3.35 (s, 3H, -O-CH_3), 1.37–1.11 (s, 24H, CH_3-*$C_{12}H_{24}$*-), 0.88 (t, *J*=5.8 Hz, 3H, *CH_3*-$C_{12}H_{24}$-). MALDI-TOF/MS ($[M+H]^+$ calcd for $C_{37}H_{75}NO_{10}$, m/z = 693.5; found, 694.4).

C_{16}-ac-2EG$_3$ was collected as a clear reddish brown oil (20% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.54–6.39 (m, 1H, -OCO-CH=C*H*H), 6.24–6.04 (m, 1H, -OCO-C*H*=CHH), 5.98–5.81 (m, 1H, -OCO-CH=CH*H*-), 4.31 (t, *J*=5.2 Hz, 2H, -CH_2-OCO-), 4.06–3.98 (m, 2H, -N-*CH_2*-CH_2-OCO-), 3.97–3.91 (m, 2H, -N-*CH_2*-CH_2-O-), 3.91–3.83 (m, 2H, -$C_{16}H_{32}$-*CH_2*-O-), 3.73–3.48 (m, 28H, -*CH_2*-O-*CH_2*-), 3.40–3.34 (s, 3H, -O-CH_3), 1.35–1.08 (s, 28H, CH_3-*$C_{14}H_{28}$*-), 0.87 (t, J=6.9 Hz, 3H, *CH_3*-$C_{14}H_{28}$-). MALDI-TOF/MS ($[M+H]^+$ calcd for $C_{39}H_{79}NO_{10}$, m/z = 721.6; found, 722.8).

C18-ac-2EG$_3$ was collected as a clear reddish brown oil (22% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.50–6.36 (m, 1H, -OCO-CH=C*H*H), 6.20–6.01 (m, 1H, -OCO-C*H*=CHH), 5.95–5.77 (m, 1H, -OCO-CH=CH*H*-), 4.28 (t, *J*=4.7 Hz, 2H, -CH_2-OCO-), 4.04–3.95 (m, 2H, -N-*CH_2*-CH_2-OCO-), 3.95–3.88 (m, 2H, -N-*CH_2*-CH_2-O-), 3.88–3.80 (m, 2H, -$C_{16}H_{32}$-*CH_2*-O-), 3.73–3.43 (m, 28H, -*CH_2*-

O-*CH*$_2$-), 3.39–3.30 (s, 3H, -O-CH$_3$), 1.30–1.10 (s, 32H, CH$_3$-*C*$_{16}$*H*$_{32}$-), 0.85 (t, J=6.3 Hz, 3H, *CH*$_3$-C$_{16}$H$_{32}$-). MALDI-TOF/MS ([M+H]$^+$ calcd for $C_{41}H_{83}NO_{10}$, m/z =749.6; found, 751.5).

Preparation of graphene aqueous dispersion using surfactants

Surfactants (100 mg) were dissolved in water (7 mL), mixed with graphene powder (1 mg), and sonicated (Ultrasonic cleaner VS-D100, 31 kHz, As One Corporation, Osaka) for 30 min at room temperature. To separate undispersed and stacked graphene, the suspension was left overnight and centrifuged (CF15RX, Hitachi Koki Co., Ltd., Tokyo) at 5000×g for 5 min. The supernatant was then used as the graphene aqueous dispersion in the following experiments.

In situ polymerization of a polymerizable surfactant on the surface of graphene

N,N-Methylenebisacrylamide (MBAA, 6.7 μmol) or divinylbenzene (DVB, 6.7 μmol), as a crosslinker, was added to the aqueous dispersion of graphene (4 mL) in a Schlenk flask. Ammonium peroxodisulfate (6.67 μmol) and *N,N,N',N'*-tetramethylethylenediamine (6.67 μmol), as an initiator, was added to the mixture to start the in-situ polymerization of the surfactant (C18-ac-2EG$_3$) on the graphene surface. The solution was stirred under nitrogen at room temperature for 24 h to prepare polymerized-surfactant/graphene (p-C18-ac-2EG$_3$/graphene).

Washing procedure for polymerized-surfactant/graphene

The polymerized-surfactant/graphene was washed as follows to remove non-immobilized surfactants. After the in-situ polymerization of C18-ac-2EG_3 on the graphene surface, the supernatant (500 μL) of the aqueous dispersion was freeze-dried. The resultant dry powder of the polymerized-surfactant/graphene was added to 500 μL $CHCl_3$, followed by ultrasonication for 10 min. The mixture was left overnight and centrifuged at 5000×g for 5 min. The supernatant was removed and the residual solvent was evaporated to prepare the washed p-C18-ac-2EG_3/graphene. Water (500 μL) was added to the residue. The mixture was left overnight and centrifuged at 5000×g for 5 min. The supernatant was collected as the redispersion of washed polymerized-surfactant/graphene.

Characterization of the graphene dispersion

UV-Vis absorption spectra of the graphene dispersions were recorded using a double-beam spectrophotometer (JASCO, V-770). The spectra were measured in the 400–900 nm wavelength range. The concentration of graphene in the dispersions was estimated from the absorbance at 660 nm by using the extinction coefficient of graphene (α=1390 mL mg^{-1} m^{-1}).[1]

TEM images were obtained using JEOL 2100F transmission electron microscope operated at 200 kV. A drop of a graphene dispersion was placed on a copper grid covered with elastic carbon films manufactured by Okenshoji Co., Ltd. (Tokyo) and dried under vacuum at room temperature.

Thermogravimetric curves were recorded using TG/DTA analyzer (DTG-60, Shimadzu, Kyoto). Prior to the measurements, the washed p-C18-ac-2EG_3/graphene was placed under vacuum overnight

to evaporate the solvent. Thermogravimetric measurements were performed in an air atmosphere with a heating rate of 10 °C/min using Pt crucibles.

XRD was performed using an X-ray diffractometer (RINT-2000, Rigaku, Tokyo) at 40 kV employing Cu−Kα radiation 2°/min.

Evaluation of electrical properties

The aqueous dispersion of surfactant/graphene was filtrated through filter paper 8 mm in diameter and 4 μm in pore size (Kiriyama Grass Co., Ltd., Tokyo). The surfactant/graphene composite on the filter paper was dried at 100 °C for 5 min. Electrical resistance measurements were performed using a four-point-probe ohmmeter (LorestaAX MCP-T370, TFP-prove, Mitsubishi Chemical Analytec Co., Ltd., Chigasaki, Japan).

Reference

1. L. Guardia, M. J. Fernandez-Merino, J. I. Paredes, P. Solis-Fernandez, S. Villar-Rodil, A. Martinez-Alonso and J. M. D. Tascon, *Carbon*, 2011, **49**, 1653-1662.

Supplementary Figures

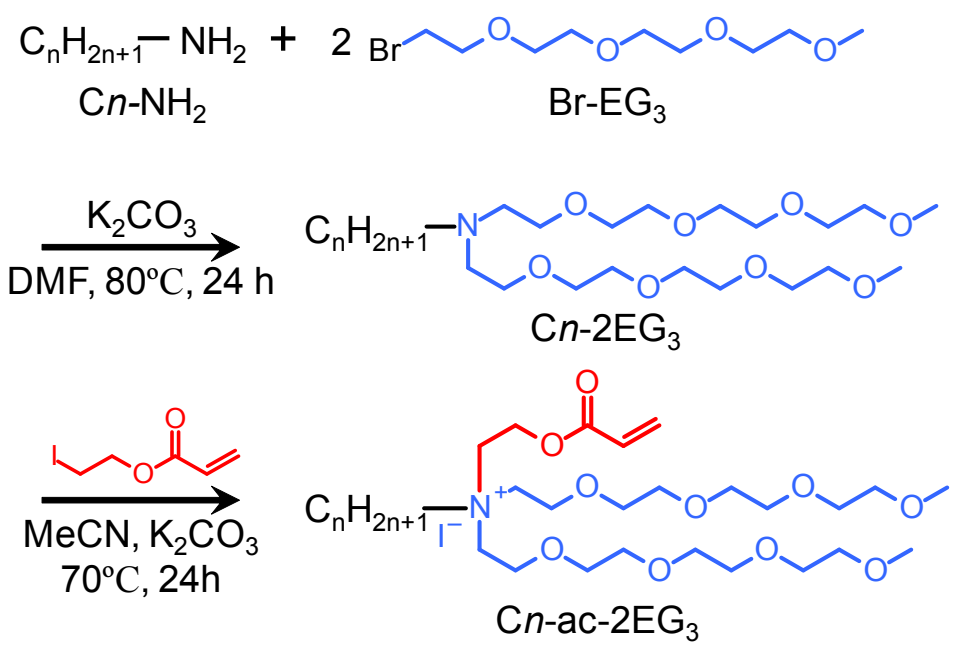

Figure S1. Synthesis of precursors (non-polymerizable surfactants) and polymerizable surfactants.

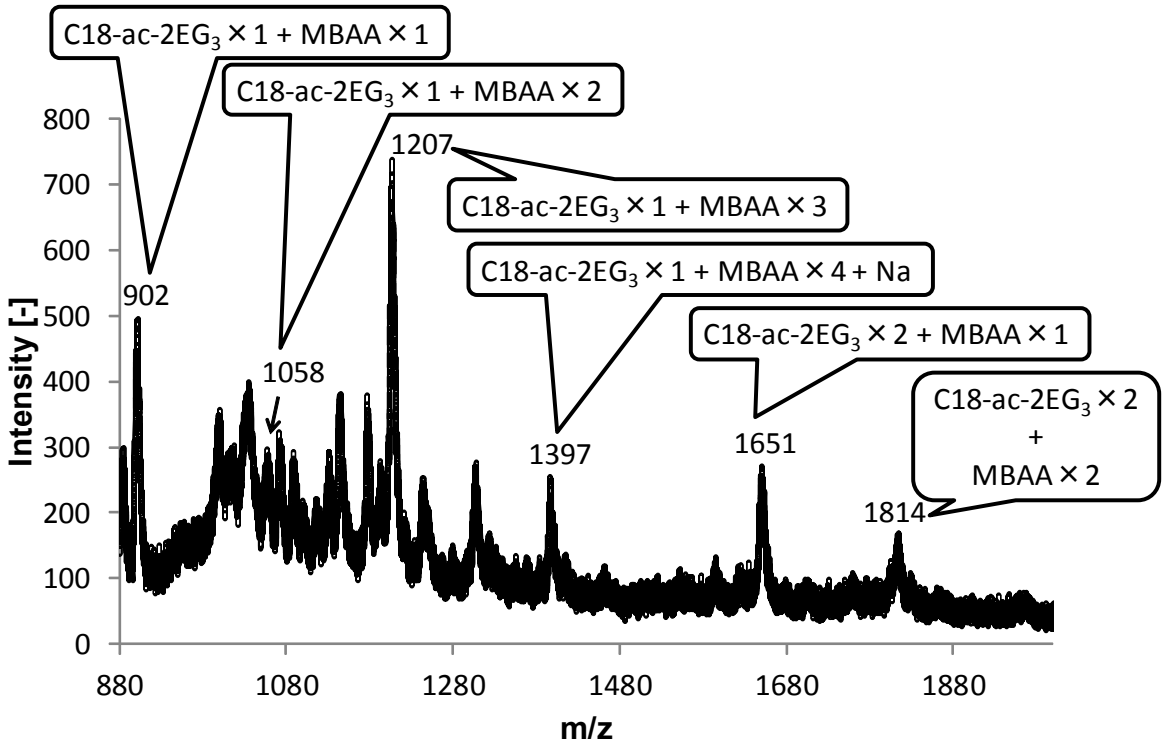

Figure S2. MALDI-TOF/MS spectrum of p-C18-ac-2EG$_3$ with MBAA. The sample was collected by washing p-C18-ac-2EG$_3$/graphene with dichloromethane. The polymerization was carried out in the presence of MBAA.

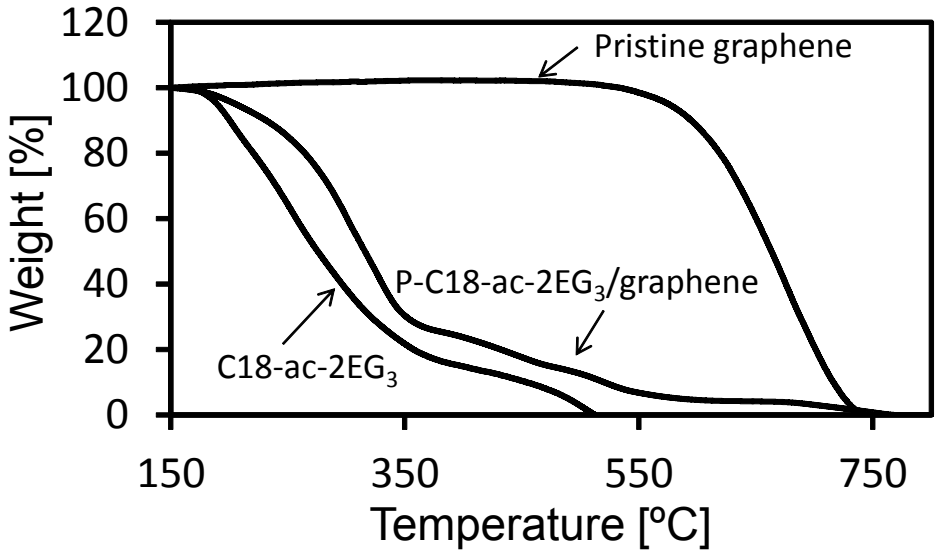

Figure S3. Thermogravimetric curves of pristine graphene, C18-ac-$2EG_3$ and p-C18-ac-$2EG_3$/graphene after washing with $CHCl_3$. The measurements were performed in an air atmosphere with a heating rate of 10 °C/min using Pt crucibles.

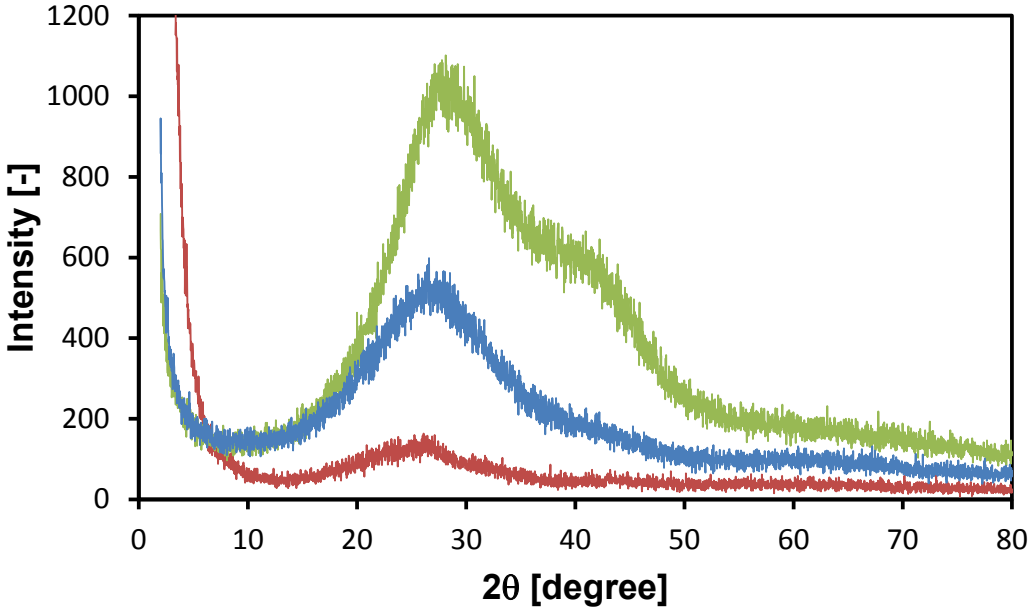

Figure S4. XRD patterns of pristine graphene (red), C18-ac-2EG$_3$/graphene (green) and p-C18-ac-2EG$_3$/graphene. The p-C18-ac-2EG$_3$/graphene was prepared with MBAA.

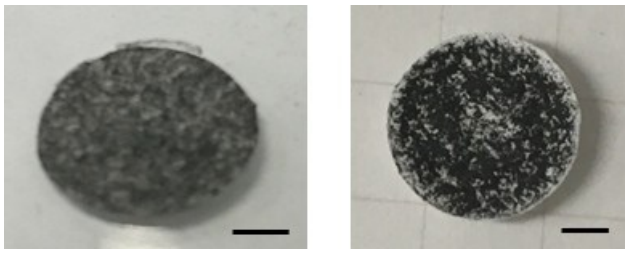

Figure S5. Photographs of the conductive surfactant/graphene composites formed on filter paper. (a) p-C18-ac-2EG$_3$/graphene with MBAA and (b) SDS/graphene. Scale bars represent 2 mm.