

Supporting Information

Electrochemical Fabrication of Graphene Nanomesh via Colloidal Templating

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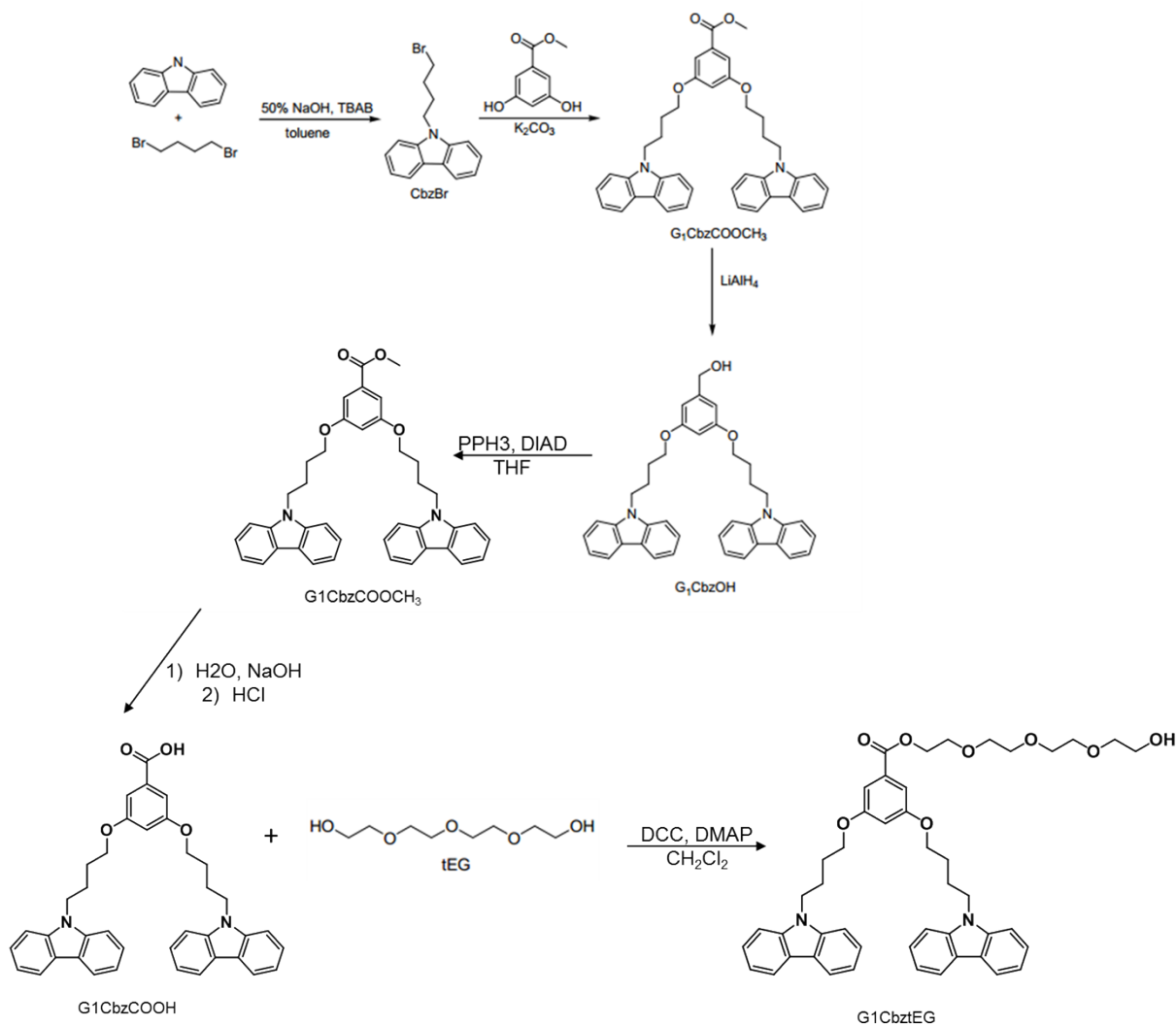
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Experimental Section

Synthesis



Synthesis of 9-(4-bromobutyl)-9H-carbazole [CbzBr]. The synthesis of CbzBr was done by combining carbazole (20.64 g, 0.1236 mol), 1,4-dibromobutane (132 mL, 1.095 mol), tetrabutylammonium bromide (4 g, 0.0124 mol), toluene (200 mL), and 50% NaOH (200 mL). The resulting mixture was stirred at 45 oC for 3 hrs and continuously stirred at room temperature

overnight. The clear, yellow organic layer was then washed with 100-mL portions H₂O followed by 100 mL brine solution. This was then dried over anhydrous Na₂SO₄. The solvent was removed via rotary evaporator and the excess 1,4-dibromobutane via vacuum distillation. After which, the resulting cream-like solid residue was slowly dissolved in small portions of CH₂Cl₂. The yellow-brown solution was recrystallized using ethanol. The resulting white solid residue was dried under vacuum overnight. ¹H NMR (δ ppm in CDCl₃): 8.12 (d, 2H), 7.22-7.48 (m, 6H), 4.36 (t, 2H), 3.3 (t, 2H), 1.95-2.07 (m, 4H).

Synthesis of methyl 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzyl alcohol [G1CbzOH]. The synthesis of compound G1CbzOH was carried out by first dissolving G1CbzCOOCH₃ (10.5 g, 0.01719 mol) in dry THF. Into a 3-necked flask flowed with nitrogen was placed 100 mL THF and this was cooled in an ice bath. Approximately 1 g LiAlH₄ was put into the flask and the G1CbzCOOCH₃ solution added dropwise through a dropping funnel. The resulting mixture was then stirred overnight. After which, the reaction was quenched by adding water until all LiAlH₄ was consumed. This was then acidified using concentrated HCl and extracted with dichloromethane. The organic layer was further washed with water for several times and then dried with Na₂SO₄. The dichloromethane was evaporated using a rotary evaporator and the desired white solid compound was further dried under vacuum. ¹H NMR (δ ppm in CDCl₃): 8.09 5 (d, 4H, J = 7.5), 7.47-7.18 (m, 12H), 6.43 (s, 2H), 6.27 (s, 1H), 4.57 (d, 2H, J = 5.7), 4.38 (t, 4H, J = 6.9), 3.90 (t, 4H, J = 5.9), 2.09-2.01 (m, 4H), 1.84-1.79 (m, 4H).

Synthesis of 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzoic acid [G1CbzCOOH]. G1CbzCOOCH₃ (2g, mol) was dissolved in THF. Ethanol (50 mL) was then added to the solution. To this was

added KOH (10 eq). This was then refluxed for 2 days. After which, the reaction mixture was cooled down and acidified to pH = 2-3. This was then extracted with dichloromethane and the solution washed with NaHCO₃. After drying with Na₂SO₄, the desired product was precipitated in hexane. ¹H NMR (δ ppm in CDCl₃): 8.09 (d, 4H, J = 7.8), 7.46-7.14 (m, 14H), 6.55 (s, 1H), 4.39 (t, 4H, J = 6.7), 3.93 (t, 4H, J = 6.0), 2.08-2.03 (m, 4H), 1.84-1.82 (m, 4H).

Synthesis of 2-(2-(2-(2-hydroxy)ethoxy)ethoxy)ethyl-3(4-(9H-carbazol-9-yl)butoxy)-5-(4-(9H-carbazol-9-yl)butoxy))benzoate [G1CBztEG]. In a one-necked flask were combined G1CBzCOOH (100 mg, 0.1676 mmol), tetraethylene glycol (97.53 mg, 0.5027 mmol), and 4-dimethylaminopyridine (2.909 mg, 0.0238 mmol). The mixture was dissolved in minimal amount of dichloromethane, bubbled with nitrogen, and placed in an ice bath. After which, a solution of dicyclohexylcarbodiimide (47.94 mg, 0.2327 mmol) in dichloromethane was added dropwise to the reaction mixture. This was then stirred vigorously for 30 mins, warmed to room temperature and stirred for 2 days. The solid by-product was filtered off and the filtrate was washed with water (5x) and brine solution (2x). The mixture was then subjected to column chromatography using 3% MeOH/CH₂Cl₂. The desired product was further purified by precipitating out other by-products with ethyl acetate. The supernatant was then concentrated and dried under vacuum. ¹H NMR (δ ppm in CDCl₃): 8.19 (d, 4H, J = 7.8), 7.56-7.49 (m, 8H), 7.35-7.29 (m, 4H), 7.24 (d, 2H, J = 2.4), 6.63 (t, 1H, J = 2.7), 4.55 (t, 2H, J = 4.8), 4.48 (t, 4H, J = 6.6), 4.03 (t, 4H, J = 6.0), 3.89 (t, 2H, J = 4.8), 3.78-3.61 (m, 12H), 2.22-2.12 (m, 4H), 1.97-1.88 (m, 4H). MALDI-TOF-MS for C₄₇H₅₂O₈N₂ m/z: calcd, 772.9364 [M⁺]; found, 772.7447.

Colloidal Templating. PS nanoparticle solution was prepared by mixing 500 nm PS latex microbeads (Polysciences, Inc) with 34.7 mM sodium n-dodecyl sulfate (Sigma Aldrich) in Milli-Q water (18.2 M Ω cm resistivity). The resulting solution was sonicated for at least 60 min prior to use ensuring that the PS particles are well-dispersed. The nanoparticles were deposited by a similar procedure reported earlier. For this experiment, CVD-grown graphene obtained from Graphene Supermarket was used as a substrate which was clipped vertically and was dipped into the PS nanoparticle solution. The substrate was then vertically withdrawn at a lift-up rate of 0.1-0.3 mm/s. The resulting film was dried by suspending it for few minutes followed by vacuum drying for 12 hrs. For the electropolymerization, 5 mM of G1CbztEG in acetonitrile (ACN) was prepared and mixed with tetrabutylammonium hexafluorophosphate (TBAH) such that the concentration of TBAH is 0.1M. This solution was electropolymerized onto previously PS nanoparticle-coated graphene by cyclic voltammetry (CV). The nickel substrate functioned as the working electrode, while Platinum (Pt) and Ag/AgCl wire as the counter and reference electrodes, respectively. Voltage was swept back and forth from 0 to 1.1 V for 10 cycles at a rate of 50 mV/s. The resulting film was washed with ACN and was dried under N₂ stream. Monomer-free scan was performed in 0.1M TBAH following the same condition. The PS spheres were etched by dipping the sample in THF for 20 min twice. The sample was dried in vacuum until used.

Electrochemical Oxidative Etching. The colloidally-templated sample was subjected to electrochemical oxidative etching. This was accomplished by a three-electrode system where the graphene deposited on nickel served as the working electrode while the Ag/AgCl saturated in 3M NaCl and platinum wire served as the reference and counter electrodes, respectively.

Electrochemical etching was done by applying a constant voltage of 3 V in 0.1 M NaCl electrolyte solution.

Lift off. In order to lift off the graphene or GNM fabricated on nickel substrate, the following steps were performed: A PMMA solution was spin-casted on top of the substrate to form a thin coating. This was then followed by a soft bake at 185 °C for 1 min. After which, the samples were then soaked into a 6:1 buffered oxide etchant solution (80 g NH₄F, 20 mL H₂O, 20 mL 49% HF) for 15 min to etch SiO₂. To etch the underlying nickel, the sample was then placed in 1M FeCl₃ solution until nickel is completely etched away. The PMMA/graphene or PMMA/GNM was then transferred onto water for rinsing. With a use of a tweezer, the thin film can be completely detached from the substrate. The now free-floating thin film was transferred on gold substrate. It was then soaked in acetone to dissolve the PMMA coating. The graphene and GNM transferred on gold were used for microscopic and spectroscopic studies.

Instrumentation. The SEM images were obtained on JEOL JSM 840A operating at an accelerator voltage of 5 kV. The electrodeposition experiments were performed in a conventional 3-electrode cell using Autolab PGSTAT 12 potentiostat (Brinkman Instruments) controlled by GPES software. The G1CbztEG was electrodeposited using cyclic voltammetry with Ag/AgCl as reference electrode, Pt wire as counter electrode and graphene on Nickel as the working electrode. AFM imaging was done under ambient conditions with a piezo scanner from Agilent Technologies. Commercially available tapping mode tips (TAP300, Silicon AFM Probes, Ted Pella, Inc.) were used as cantilevers with resonance frequencies in the range of 290-410 kHz. The scan rate was between 1-1.5 line/s.

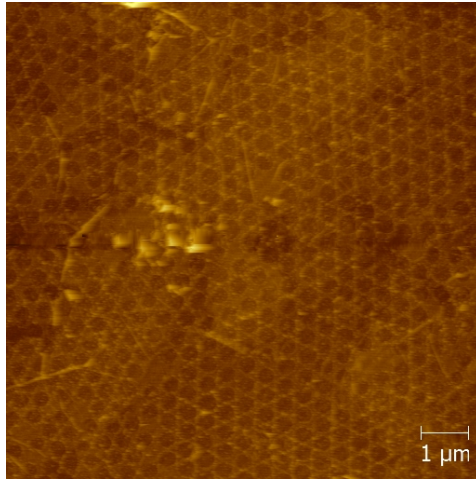


Figure S1. Large area AFM image of Graphene Nanomesh.