

Peptide/Graphene Hybrid Assembly into Core/Shell Nanowires

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Graphene is an emerging carbon material consisting of planar monolayered hexagonal sp^2 hybridized carbons.^[1,2] Since its unexpected separation from natural graphite by micromechanical drawing,^[3] graphene has attracted tremendous research interest due to its excellent properties rivaling or even surpassing those of carbon nanotubes.^[4–6] In particular, graphene is considered an ideal two-dimensional reinforcing component for hybrids or composite materials, possessing an extremely large surface area,^[7] superior carrier transport,^[8] mechanical flexibility,^[9,10] and thermal/chemical stability,^[11–14] among a host of notable characteristics. To date, various synthetic methods have been developed for the mass-production of highly functional graphene.^[15–22] Among those, oxidative exfoliation of naturally abundant graphite and subsequent reduction may offer a highly efficient route to producing chemically functionalized graphene,^[7,20–25] which may play a key role in facilitating molecular organization into hybrid architectures.

Herein, we introduce a straightforward hybrid assembly of graphene and biomolecules into core/shell nanowires. Owing to the high specificity, diverse chemical and biological functionalities, and environmentally benign processing biomolecular self-assembly is considered a valuable pathway for nanofabrication.^[26–29] However, its poor electric properties and low thermal/chemical stability limit immediate application in functional devices.^[30–32] In this article, we focus on an aromatic peptide of diphenylalanine, which is known as the structural motif for the β -amyloid associated with Alzheimer's disease.^[27] This aromatic peptide has been found to self-assemble into highly stable nanoscale morphologies such as nanotubes,^[27,33,34] nanowires,^[34,35] and nanoribbons.^[36,37] Unlike usual biomolecular self-assembly, diphenylalanine assembly offers rapid formation of highly crystalline nanostructures with almost 100% conversion. We developed a facile and straightforward synthetic approach for producing diphenylalanine/graphene core/shell nanowires by single-step solution processing. The resultant hybrid nanowires were electroconductive and, as a simple

example of core/shell nanowire applications, they were further processed to create a hollow graphene-shell network, which could be employed as a supercapacitor electrode with remarkable performance.

We prepared an aqueous graphene oxide dispersion following a modified Hummers method.^[38,39] The following chemical reduction with hydrazine led to aqueous dispersion of reduced graphene.^[22] A thorough investigation on the morphology, chemical composition, and physical properties revealed that the reduced monolayer graphene sheets decorated with chemical functionalities such as epoxide, hydroxyl, and carboxylic acid groups were dispersed in aqueous medium (Supporting Information, Fig. S1).^[7,20–25] As demonstrated in Figure 1a, peptide/graphene core/shell nanowires were immediately created, as soon as an organic peptide solution (100 mg mL^{-1} solution of diphenylalanine in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP)) was diluted in an aqueous graphene dispersion under mild mechanical shaking. Under optimal assembly conditions, almost all reduced graphene and diphenylalanine participated in the core/shell assembly, leaving a transparent aqueous solvent. The resultant black aggregates composed of peptide/graphene core/shell nanowires were restored by vacuum-filtration and thoroughly washed with deionized water (Fig. 1b and 1c). Figure 1d and 1e presents low- and high-magnification transmission electron microscopy (TEM) images of hollow graphene shells that remained after the calcination of peptide cores (400°C for 20 min). Thin hollow shells consisting of tens of layers of graphene stacking maintained their structural integrity. In this hollow-shell morphology, graphene is simply wrapped around the peptide-nanowire surface without penetrating into the peptide cores (Supporting Information, Fig. S2). The average graphene interlayer spacing measured by X-ray diffraction (XRD) was $\sim 3.50\text{ \AA}$, slightly larger than that of natural graphite ($3.36\text{ \AA}$; Supporting Information, Fig. S3). This discrepancy is due to the chemical functional groups remaining at the reduced graphene surface.^[40,41] Further thermal reduction at 750°C under a H_2 atmosphere led to a higher-intensity XRD peak with a peak maximum shift to 25.4° ($\sim 3.45\text{ \AA}$). We note that the XRD measurements for hybrid nanowires confirmed that the peptide cores exhibited crystalline peaks that were consistent with those of pure peptide nanowires without a graphene shell, while the graphene shells exhibited a typical graphene interlayer spacing peak. (Supporting Information, Fig. S4).

The intermolecular interaction governing this marvelous core/shell assembly has been investigated by varying the pH of the assembling solution. HFP solutions of diphenylalanine were diluted in aqueous graphene dispersions having various pH

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DOI: 10.1002/adma.200903221

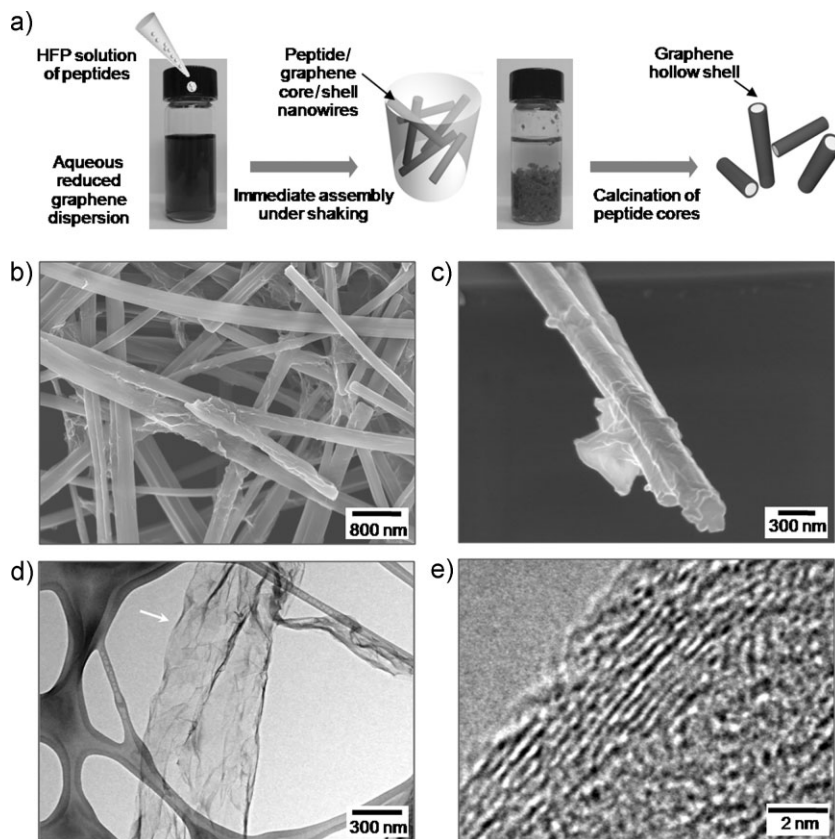


Figure 1. Peptide/graphene hybrid assembly into core/shell nanowires. a) Schematic illustration of a hybrid assembly. Peptide/graphene core/shell nanowires were assembled, as soon as a HFP solution of diphenylalanine was diluted in aqueous graphene dispersions under mechanical shaking. Calcination of the peptide core left a hollow graphene shell. b) Low- and c) high-magnification SEM images of core/shell nanowires. d) TEM image of the hollow graphene-shell structure. e) HRTEM image of a graphene shell.

values. Core/shell hybrid assembly occurred in the pH range of 3.7 ~ 5.4. In this pH range, dark aggregates consisting of core/shell nanowires were formed, as soon as the peptide solution was diluted in the graphene dispersion under mild mechanical shaking. Below pH 3.7, pure peptide did not assemble into nanowires and therefore hybrid assembly did not occur (Supporting Information, Fig. S5). The upper pH limit of 5.4 corresponds to the isoelectric point (pI) of diphenylalanine, where the net charge of diphenylalanine changes its sign.^[42] Figure 2b shows the variation of surface charges of peptide nanowires and graphene sheets as a function of pH, measured by the zeta potential. The surface charge of peptide nanowires turned from positive to negative at the pI. Graphene sheets were almost neutral at a highly acidic condition (below pH 3.7) but were negatively charged in the rest of the pH range, due to the dissociation of acid functional groups remaining at the reduced-graphene surface (typical assembling mixture prepared from neutral water showed a weak acidity (pH 5 ~ 6)).^[20,22] Taken together, peptide/graphene core/shell assembly occurred only when peptide nanowires (positively charged) and graphene sheets (negatively charged) are oppositely charged, suggesting that the molecular interaction triggering this peculiar core/shell assembly has an electrostatic origin (Fig. 2c).

Figure 3 shows the tunability of the graphene-shell thickness with pH variation. In the core/shell assembly pH range (3.7 ~ 5.4), as the pH increased, the positive charge at the peptide-nanowire surface monotonically decreased, while the negative charge at the graphene surface monotonically increased (Fig. 2b). As a consequence, the number of negatively charged graphene layers required to compensate the electrostatic interaction decreased. Figure 3A–C presents the TEM images of graphene shells assembled at various pH values. For pH 4.2, the average shell thickness was ~21 nm, corresponding to ~60 stacked graphene layers. The shell thicknesses for pH 5.0 and 5.5 were 13 nm and 9 nm, respectively, which correspond to significantly reduced stacking numbers of ~35 and ~30.

The electrical conductivity of an individual core/shell nanowire is directly measured by current versus applied voltage (*I*–*V*) measurements. Figure 4a shows a core/shell nanowire loaded across two gold electrodes, whose diameter and graphene-shell thickness were ~400 nm and ~10 nm, respectively. The *I*–*V* curves were measured at room temperature using a probe station and an HP parameter analyzer. As a reference, the electroconductivity of a peptide nanowire without a graphene shell was also measured. As shown in Figure 4b, the core/shell nanowires showed a significant electroconductivity, while pure peptide nanowires without graphene shell showed an insulating behavior. The *I*–*V* curve of the core/shell nanowire exhibited a linear Ohmic behavior, demonstrating that the outer reduced graphene shell was continuous over the entire nanowire length. The room-temperature resistance (*R*) measured from the *I*–*V* curve was approximately $2.4 \times 10^5 \Omega$. The electrical resistivity (ρ) defined by $\rho = R A/L$ was $\sim 1.9 \times 10^{-3} \Omega \text{m}$, where *L* and *A* correspond to the length and the cross-sectional area of the graphene shell, excluding the cross-sectional area of the peptide core.^[43] The electroconductivity did not fail up to a large voltage of 20 V, reflecting the high stability of the graphene-shell structure. Several repeated measurements verified the reproducibility of *I*–*V* measurement.

Thermal calcination (400 °C for 20 min) of peptide cores of highly entangled core/shell nanowires generated a hollow-graphene-shell network (Fig. 4c). The entangled hollow-shell morphology was preserved well under severe calcination, exposing a large surface area of the graphene shell. This self-sustaining morphology is significantly different from that of a planar graphene film deposited without peptides (Supporting Information, Fig. S6a). Owing to the high electroconductivity and chemical stability in electrolytes, graphene is an attractive material for current collectors.^[44–46] We fabricated supercapacitor electrodes by preparing entangled hollow graphene-shell networks on a FTO substrate. A planar graphene-sheet electrode was

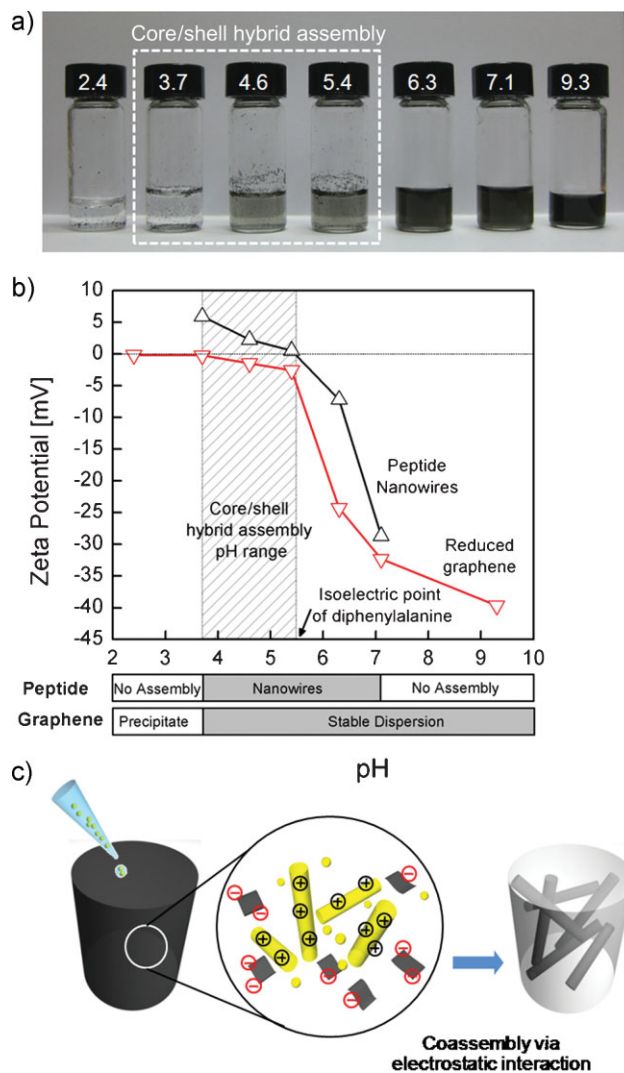


Figure 2. Intermolecular interaction of the peptide/graphene hybrid assembly. a) Photograph of a mixed graphene/peptide solution at various pH values. Core/shell assembly occurred in a pH range of 3.7 ~ 5.4. b) Zeta-potential measurements of surface charges of graphene sheets and peptide nanowires as a function of pH. Core/shell assembly occurred when graphene is negatively charged and peptides are positively charged. c) Schematic illustration of electrostatic-interaction-induced hybrid assembly.

also prepared by drop-casting aqueous graphene dispersion without peptides. The surface area of the graphene-shell network measured from the N_2 adsorption isotherm using the Brunauer–Emmett–Teller (BET) equation was $730\text{ m}^2\text{ g}^{-1}$, which is significantly higher than that of the planar graphene film ($610\text{ m}^2\text{ g}^{-1}$). The performance of the supercapacitor electrodes was analyzed using cyclic voltammetry (CV) at room temperature, employing a typical three-electrode configuration in a $0.1\text{ M H}_2\text{SO}_4$ electrolyte.

Figure 4d shows the CVs of the graphene supercapacitors, scanned at 50 mV sec^{-1} in a potential range of $0\sim 0.9\text{ V}$. The voltammograms exhibit nearly rectangular shape even at a high

scan rate of 100 mV sec^{-1} , indicating a high electric conductivity of the graphene electrode and its excellent contact to electrolyte (Supporting Information, Fig. S6b).^[45,47] A pair of broad redox peaks appeared at 0.34 and 0.24 V , versus a Ag/AgCl reference electrode, that were caused by the reversible oxidation and reduction of the functional groups at the reduced graphene surface.^[48,49] The specific capacitance was integrated according to the equation $C = I/(dV/dt \times m)$, where I is the current, m is the mass of graphene shells, C is the specific capacitance, and (dV/dt) is the potential scan rate. The specific capacitance of the device fabricated from a hollow-graphene-shell-network electrode reached 157 F g^{-1} . In contrast, the specific capacitance of the planar graphene-film device was 74 F g^{-1} . Such a high performance is attributed to the large surface area, good electrolyte accessibility, and high electro-conductivity of hollow-graphene-shell electrodes.

In summary, we have demonstrated a straightforward peptide-graphene hybrid assembly into core-shell nanowires. The electrostatic attraction between reduced graphene sheets and protonated peptides readily created core/shell hybrid nanowires through a simple solution mixing. The resultant core/shell nanowires exhibited electroconductivity through their continuous graphene shell. Further processing via thermal calcinations of peptide cores led to highly entangled networks of the hollow graphene shell, whose remarkable performance as a supercapacitor electrode has been demonstrated. Our facile and robust hybrid assembly principle that exploits the surface charges of reduced graphene can be further utilized to create various functional hybrid nanomaterials.

Experimental

Preparation of Graphene Sheets: Graphite oxide was prepared from natural graphite (Graphit Kropfmühl AG, MGR 25 998K) by a modified Hummers method [1,2]. Exfoliation into graphene oxide was achieved by sonication for 2 h in an aqueous solvent. The resulting aqueous graphene oxide dispersion was reduced with hydrazine following the procedure suggested by Li et al. [3], where a homogeneous graphene oxide solution ($0.03\text{ wt\%}$, 200 mL) was mixed with ammonia solution ($28\text{ wt\%}$ in water, Junsei Chemical, 1.2 mL) and hydrazine ($80\text{ wt\%}$ in water, Junsei Chemical, $600\text{ }\mu\text{L}$) and mechanically stirred at 100°C for 2 h. The dispersion was further centrifuged for 20 min at 15000 rpm (Hanil Supra 22K) to remove any flocculated aggregate. The finally obtained dispersion contained $\sim 0.01\text{ wt\%}$ of reduced graphene.

Preparation of Peptide/Graphene Core/Shell Nanowires: Diphenylalanine (Bachem, Switzerland) was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) to a concentration of 100 mg mL^{-1} . The peptide solution was diluted in an aqueous graphene dispersion to a predetermined concentration under mechanical shaking (Heidolph Vortex Shaker). Black aggregates composed of peptide/graphene core/shell nanowires were recovered by vacuum filtration (polyvinylidene fluoride membrane filter, 47 mm in diameter, $0.45\text{ }\mu\text{m}$ pore size; Millipore) and completely dried. The peptide cores were removed by calcination at 400°C for 20 min under air. The yield of the core/shell assembly measured from the weight difference between used reduced graphene and hollow graphene shells was $\sim 91\%$.

Characterization: The morphology of the monolayered graphene sheet was characterized in a tapping mode atomic force microscopy (AFM) instrument (Nanoman, Veeco). The sample for AFM imaging was prepared by drop-casting aqueous graphene dispersion on Si substrates and air-drying at room temperature. Fourier transform IR (FTIR; Bruker Optics, IFS66V/S & HYPERION 300 in transmittance mode) spectra of graphene sheets were obtained from KBr pellet samples. The number of scans was

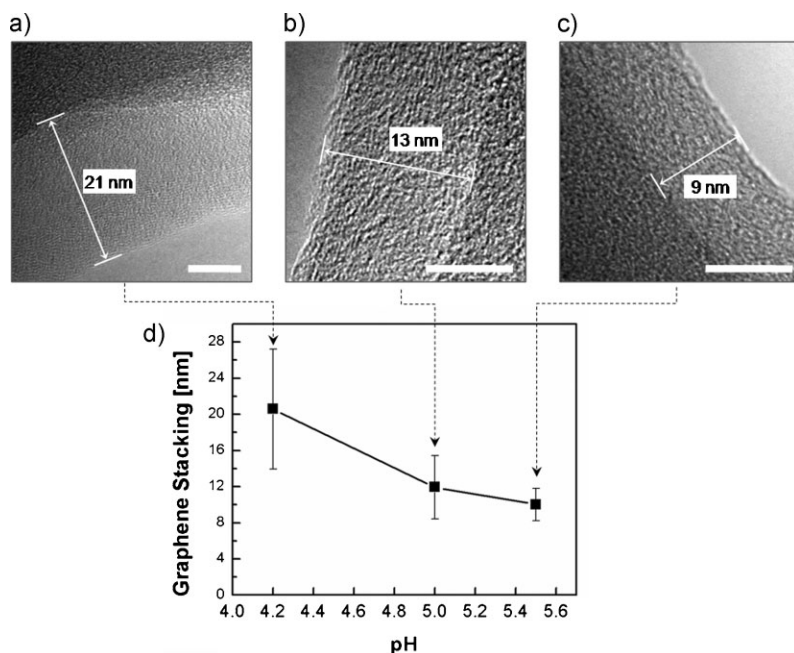


Figure 3. Variation of graphene shell thickness as a function of pH. TEM images of hybrid nanowires prepared at various pH values of 4.2 (a), 4.9 (b), and 5.5 (c). Scale bars are 8 μm . d) Thickness variation of graphene sheets plotted against pH.

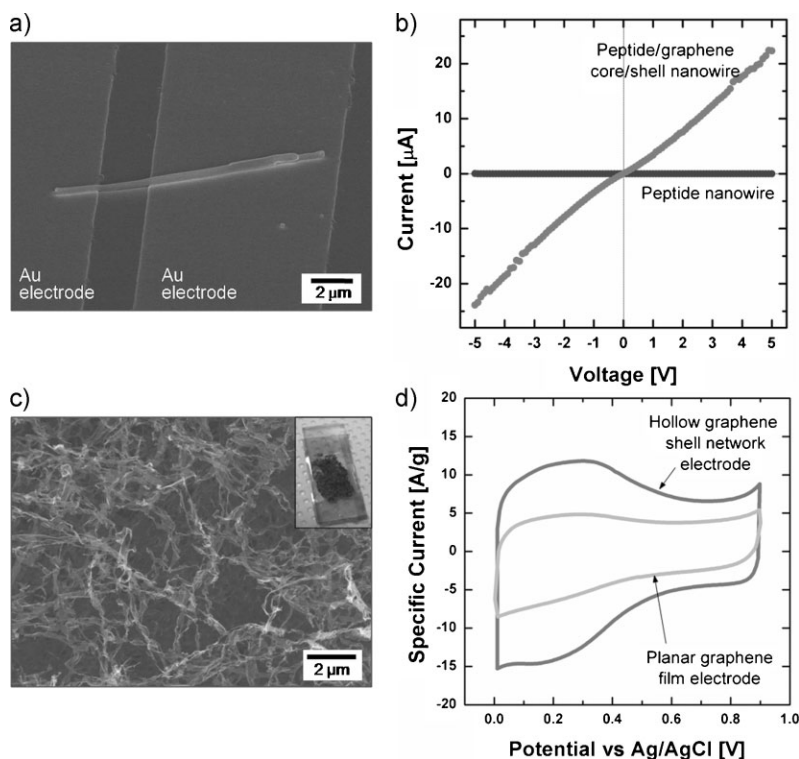


Figure 4. *I*-*V* characteristic of core/shell nanowires CV of graphene-based supercapacitors. a) SEM image of a graphene/peptide core/shell nanowire loaded across Au electrodes. b) *I*-*V* characteristics of a peptide/graphene hybrid nanowire and a peptide nanowire. c) SEM image of a hollow-graphene-shell network. The inset shows a supercapacitor electrode consisting of a hollow graphene network. d) CVs of graphene-based supercapacitors in a 0.1 M H_2SO_4 aqueous solution. Graphene-based electrodes show surface redox reactions.

68, and the scanning resolution was 2 cm^{-1} . The UV-vis spectroscopy of the aqueous graphene dispersion was obtained by a UV-vis-NIR (NIR = near infrared) scanning spectrophotometer (Shimadzu, UV-3101 PC). The conductivity of graphene films was measured with a 4-point-probe system (CMT-SR1000N, AIT). The graphene film was prepared by using vacuum filtration (polyvinylidene fluoride membrane filter, 47 mm in diameter, $0.45\text{ }\mu\text{m}$ pore size; Millipore). The morphologies of the core/shell nanowires and the graphene-shell network were characterized with a field-emission scanning electron microscopy (FESEM) instrument (Hitachi S-4800 SEM, Japan). The multilayered graphene-shell morphology was characterized by high-resolution TEM (HRTEM; Philips Tecnai F20). The BET surface area (S_{BET}) was analyzed by nitrogen adsorption (Quantachrome Instruments Autosorb-1). The sample was degassed at 200°C overnight prior to each measurement. The surface charges of the graphene dispersion and peptide nanowire dispersion were investigated by zeta-potential measurements (Photal Otsuka ELS-Z, Japan). Peptide molecules were diluted in an aqueous graphene dispersion with various pH values. The pH of the graphene dispersion was adjusted by adding ammonia solution or hydrochloric acid.

Measurement of Conductivity and Capacitance: Core/shell nanowires were deposited on a SiO_2 substrate, patterned with Au electrodes. The current versus voltage (*I*-*V*) curve of the nanowire was measured at room temperature using a probe station and an HP parameter analyzer. The supercapacitor electrodes were prepared by calcinating peptide/graphene core/shell nanowires on FTO substrates (400°C for 20 min under air). The FTO surface area uncovered by the graphene electrode (1 cm^2) was passivated with an insulating polyimide tape. The working electrode was clipped to a short copper wire. The reference electrode was $\text{Ag}|\text{AgCl}|3\text{ M NaCl}$. The auxiliary electrode was platinum wire. Three electrodes were immersed in 0.1 M H_2SO_4 electrolyte solution and the performance of the supercapacitor was analyzed using CV at room temperature (Solatron SI 1287).

Acknowledgements

This work was supported by the National Research Laboratory Program (R0A-2008-000-20057-0), the World Class University (WCU) program (R32-2008-000-10051-0), the Pioneer Research Center Program (2009-0093758), and the National Research Foundation (NRF 2008-0062204) funded by the Korean government. Supporting Information is available online from Wiley InterScience or from the author.

Received: September 19, 2009

Revised: November 22, 2009

Published online: March 29, 2010

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