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Editor's Choice

Enwrapping Conjugated Polymer Microspheres with Graphene Oxide Nanosheets

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Water-dispersible conjugated polymer microspheres were obtained by enwrapping with graphene oxide (GO) nanosheets. Simply mixing the polymer microspheres and GO in water results in an exclusive formation of GO-wrapped microspheres. The photoluminescence (PL) spectra of the GO-wrapped single microsphere show whispering gallery modes, in which the PL lines are broadened in comparison with bare microspheres without GO. The broadening is attributed to scattering and reabsorption of the confined PL.

Keywords: Graphene oxide | Conjugated polymer | Microsphere

Nanocarbons such as graphene and carbon nanotubes (CNTs) are materials with promising electronic and mechanical properties, such as high flexibility, high stiffness, and light weight.[1] However, nanocarbons hardly disperse in a medium because of their poor solubility in both water and organic solvents, which makes it difficult to fabricate composites with other materials such as polymers.[2] Recently, conjugated polymers (CPs) were found to adsorb strongly on nanocarbons via π–π interaction.[3] As a result of the strong adsorption of CPs, the nanocarbon composites become highly dispersive in various organic solvents. On the other hand, graphene oxide (GO) has also received increasing attention due to its oxidizing, electron-accepting, and catalytic properties.[4] Due to charged substituents such as carboxy, epoxy, and hydroxy groups at the periphery of GO, composites of GO with nanocarbons and CPs are highly dispersive in water.[5]

In this letter, we show that self-assembled CP microspheres can be entirely wrapped with GO. As a result of being wrapped by GO, the microspheres become dispersible in water. The GO-wrapping of the microspheres is confirmed by electron microscopy and surface potential studies, and further evidenced by micro-photoluminescence (μ-PL) spectroscopy. The whispering gallery mode (WGM) PL lines from GO-wrapped CP microspheres are noticeably broadened, possibly because of light scattering and reabsorption by the GO layers at the surface of the microspheres.

The CP microspheres are prepared according to a reported procedure.[6] Thus, an alternating copolymer **1**, comprising 9,9-dioctylfluorene (F8) and 2,3,7,8-tetramethylbithiophene (Figure 1a, left),[7] was dissolved in $CHCl_3$ (2 mL, [**1**] = 1 mg mL^{-1}) and MeOH vapor was allowed to slowly diffuse into the solution. Microspheres were exclusively precipitated after being aged for 3 days at 25 °C. The GO nanosheets were

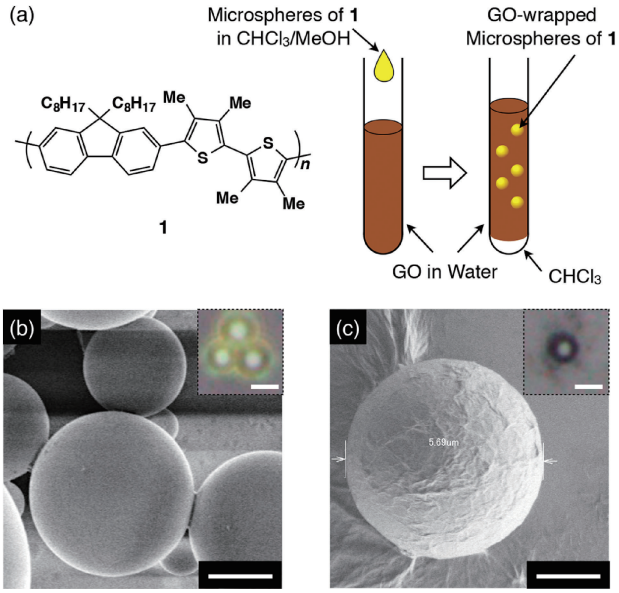

Figure 1. (a) Molecular structure of π-conjugated alternating copolymer **1** and schematic representation of the preparation of microspheres of **1** enwrapped by GO. (b, c) SEM micrographs of air-dried suspensions of the microspheres of **1** before (b) and after (c) addition into an aqueous solution of GO. Insets show optical micrographs of the corresponding microspheres. Scale bars: 2 μm.

prepared by a modified Hummers method from graphite powder (particle size; 45 μm, Wako Pure Chemical Industries).[8] Typically, 1.0 g of graphite powder and 0.8 g of $NaNO_3$ were added to concentrated H_2SO_4 (95%, 40 mL). Then, 4.5 g of $KMnO_4$ was slowly added to the solution at 0 °C. The mixture was stirred over 72 h at room temperature. The resultant solution was then purified by centrifugation several times. Finally, the resultant suspension was ultrasonicated for 10 h after addition of 300 mL of water to form a dark-brown aqueous solution of GO ([GO] = 3.3 mg mL^{-1}) with an average width of several hundreds of nanometers (Figure S1).[8]

When a 10 μL $CHCl_3$/MeOH suspension of microspheres of **1** was dropped into a diluted solution of GO (200 μL, [GO] = 5.5 μg mL^{-1}) and the mixture (**1**/GO = 10/1.1 w/w) was gently stirred and kept for a few minutes, the $CHCl_3$ phase was separated at the bottom of the water phase (Figure 1a, right). A color change of the $CHCl_3$ solution from yellow to colorless

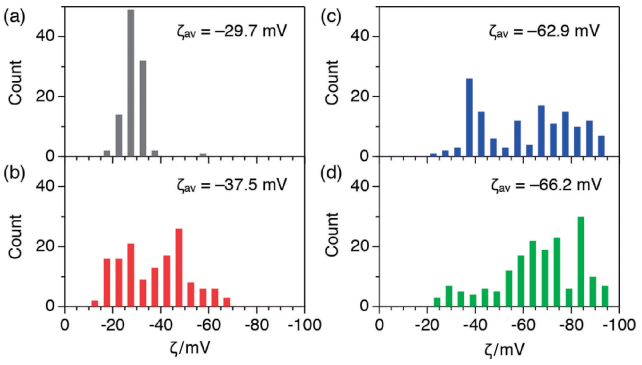

Figure 2. Histograms of the zeta potential of GO in water (a), GO-wrapped microspheres of **1** in water (b), microspheres of **1** in MeOH/water (1/1 v/v) (c), and microspheres of **1** in MeOH (d), measured by tracking each particle under applied voltages of 10 (a–c) and 30 V (d). The number of the counted particles: 100 (a), 142 (b), 150 (c), and 178 (d).

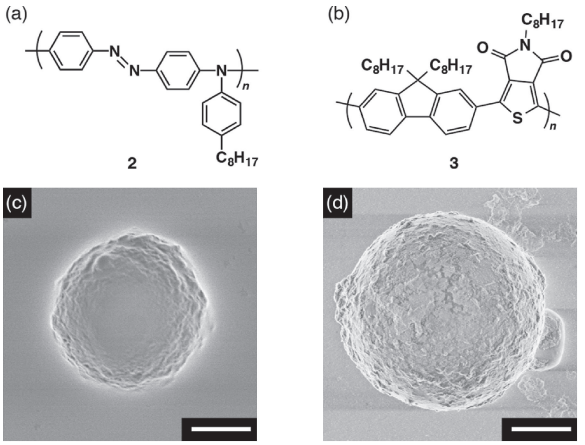

Figure 3. (a, b) Molecular structures of alternating copolymers **2** (a) and **3** (b). (c, d) SEM micrographs of air-dried suspension of the microspheres of **2** (c) and **3** (d) after addition into an aqueous solution of GO. Scale bars: 2 μm.

indicates that the microspheres of **1** have been transferred into the water phase. Scanning electron microscopy (SEM) observations of the air-dried solution show that the microspheres are found only in the water phase. Careful inspection of the resultant microspheres shows that their surface morphology is rough (Figure 1c) in comparison with those just after preparation in $CHCl_3$/MeOH (Figure 1b). Because the pristine microspheres of **1** hardly disperse in water, the resultant microspheres are likely enwrapped by the water-soluble GO. Indeed, the optical micrographs show that the color of the microsphere changed from yellow to dark brown by addition to the GO solution (Figures 1b and 1c, inset).

The zeta potential (ζ) of the microspheres of **1** before and after addition into the GO solution shows clear differences. The microspheres of **1** showed an average ζ value (ζ_{av}) of −62.9 mV in MeOH/water (1/1 v/v, Figure 2c) and −66.2 mV in MeOH only (Figure 2d). In contrast, after addition into the GO solution, the ζ_{av} of the microspheres shifted to −37.5 mV (Figure 2b), which is close to the ζ_{av} of GO in water (−29.7 mV) (Figure 2a). These results indicate that the surface of the microspheres of **1** is covered by GO.

We attempted the GO wrapping of microspheres composed of CPs **2** with *N*-(4-octylphenyl)iminoazobenzene repeating units (Figure 3a)[6c,9] and **3** with F8 and 5-octylthieno[3,4-*c*]pyrrole-4,6-dione (TPD) repeating units (Figure 3b).[6e,10] However, the microspheres were not well wrapped by the GO nanosheets, and the resultant microspheres became ill-shaped with the adsorption of agglomerated GO (Figures 3c and 3d). We suppose that the fluorene moiety is an important structural unit for well adsorbing to the π-electronic surface of GO.[3] Another factor is the donor–acceptor interaction between the polymer (donor) and GO (acceptor). For copolymer **3**, the TPD unit is highly electron deficient; hence, the donor–acceptor interaction between GO and **3** is weak in comparison with that between GO and **1**. As a result, GO nanosheets did not adsorb well on the surface of the microsphere of **3** but formed cluster-like domains.

To investigate the PL properties of a single microsphere of **1** enwrapped by GO, we conducted μ-PL measurements (experimental setup, see Supporting Information and Figure S2). As reported previously, a microsphere of **1** displayed WGM PL, in which sharp and periodic PL lines appear, superimposed on a broad PL originating from the intrinsic PL of **1** (Figure 4a).[6c] The periodic PL lines are characterized as transverse electric (TE) and magnetic (TM) modes, in which the electric field vectors of the confined PL are parallel and perpendicular to the polymer/air interface plane, respectively. In the present spectrum in Figure 4a, the TE mode was clearly observed, while the TM mode appeared very weak.[6c] Similarly, WGM PL lines were observed for GO-wrapped microspheres of **1** (Figures 4b–4e). As the diameter (d) of the microsphere increased, the interval of the WGM PL lines became narrow because of the increase in the optical path length of the circumference of the spheres. However, the PL lines became broadened compared to those of the pristine microsphere of **1** without GO. The Q-factors, defined as the wavelength divided by the full width at half-maximum of the PL, decreased by roughly a factor of 2 after wrapping with GO (Figure 4f). Scattering and reabsorption by the GO layers possibly caused a decrease in the efficiency of total internal reflection at the polymer/air interface. Because of the laminar structure of GO and the resulting anisotropic conductivity (in-plane vs. out-of-plane), we expect the TE modes to be more strongly damped by GO wrapping than the TM mode.

We identified the WGM indices (angular momentum, l) of each PL peak using the following equation,[11]

$$n\pi d = l\lambda \quad (1)$$

where n is the refractive index. From the λ^{-1} vs. l plots (Figures 4a–4e, inset), the indices of WGM peaks for microspheres with various diameters are identified. The n values for the GO-wrapped microspheres are evaluated to be ca. 1.8, which is slightly larger than that of the pristine microsphere of **1** (ca. 1.7).[6c] This result is reasonable, considering that the n value of GO is around 1.9 in the visible wavelength region, as evaluated by spectroscopic ellipsometry (Figure S3). For comparison, microspheres of **2** and **3**, covered by the clustering GO (Figures 3c and 3d), hardly showed WGM PL because of the strong scattering of PL at the surface, which disturbs the confinement of PL inside the sphere (Figure S4).

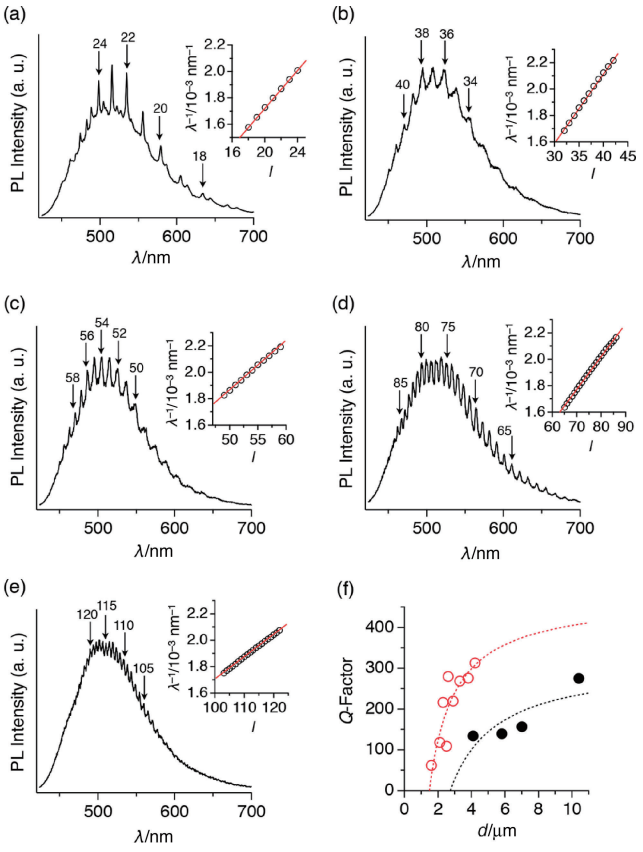

Figure 4. (a–e) PL spectrum of a single microsphere of **1** (a, $d = 2.6\,\mu m$) and GO-wrapped microspheres of **1** with d of 4.1 (b), 5.8 (c), 7.0 (d), and 10.4 μm (e). The numerical numbers in the graphs are the WGM indices (l), simulated from the plots of λ^{-1} versus l shown in the insets. The red lines in the inset graphs indicate the linear fittings. The n values are calculated from the slope of the linear fitting. (f) Plots of Q-factors versus d for the GO-wrapped microspheres of **1** (filled circles) and microspheres of **1** without GO (open circles, data from ref 6c). The broken curves indicate the exploration of the least-squares fit to the phenomenological equation; $Q = -703d^{-1} + 475$ for microspheres of **1** without GO (red) and $Q = -869d^{-1} + 319$ for GO-wrapped microspheres of **1** (black).

In summary, self-assembled microspheres composed of a π-conjugated alternating copolymer with fluorene-tetramethyl-bithiophene repeating units are successfully enwrapped by graphene oxide (GO) nanosheets. The donor–acceptor interaction between the electron-rich surface of the microsphere and electron-deficient GO is one possible attractive force for the formation of such an inclusion by GO. As a result of the wrapping, the resonant photoluminescence peaks from the microspheres become broadened with a noticeable decrease in the Q-factors of the resonators. Such water-soluble polymer microspheres will be usable for application in aqueous media such as biological systems.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.160504.

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