Mussel-Inspired Surface Functionalization of Graphene Oxide

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Statement of Purpose: Graphene-based materials have gained a great deal of attention on the areas of catalysts, composites, (bio)sensors, and transparent electrodes because of various extraordinary properties.[1] Methods for surface modification and reduction of graphene oxide (GO) have been revealed crucial,[2] but previous methods have some limitations for wider applications; surface modification is occurred under harsh reaction conditions such as organic solvents, and strong reductant like hydrazine is used. These have been abstacles for GO to be utilized in biomaterial applications. Herein, we introduce a facile, aqueous method for surface modification of GO. Norepinephrine, a catecholamine molecule inspired by the amino acid composition of adhesive pads of marine mussels, was used to functionalize GO surfaces. Under aqueous mild conditions, functionalization and reduction of GO were achieved by single one-pot procedure, and biodegradable polymers were synthesized on the surface of functionalized GOs.

Methods: *Materials* Graphite (sigma), norepinephrine (97%, sigma), trizma base (99%, sigma), trizma HCl (99%, sigma), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$,95% aldrich), ε-caprolactone (ε-CL, TCI), and anhydrous toluene (aldrich) were used as received.

Poly(norepinephrine) (PN) coating on the surface of GO. GO was prepared by modified Hummers method.[3] Poly(norepinephrine) coating was performed by mixing the GO solution (0.1 mg/mL) with buffer solution (2 mg of norepinephrine per mL of 10 mM Tris, pH 8.5) at room temperature. After 1-h functionalization, the sample was collected by a membrane filter, and subsequently washed by deionized water for several times.

Polymerization of ε-caprolactone on the surface of functionalized GO PN-coated GO was placed in a reaction vessel and dried under vacuum at 55 ^{o}C for 24 hrs. After drying, the PN-coated GO was treated with $Sn(Oct)_2$ (5 μL) in 5 mL of anhydrous toluene for 1 hr at 55 ^{o}C. The monomer, ε-CL (0.5 mL), was then slowly added by syringe and the mixture was heated at 55 ^{o}C for 24 hrs. The PCL-coated GO was separated and washed with toluene.

Results: Recently, a material-independent surface coating method inspired by adhesion mechanisms of mussels was investigated by Lee et al.[4,5] Dopamine and norepinephrine that contains catechol and amine are considered small molecule mimics of Mefp-5(*Mytilus edulis* foot protein-5) secreted by mussels, and the oxidative polymerization of them resulted in material-independent surface modifications. The surface of GO was modified as described in the methods (above). After 1-hr surface functionalization, GO solution exhibited visible changes in color, which is due to a coupled redox reaction of catechol oxidation and GO reduction (Fig 1a). PN coating on the surface of GO was characterized by UV-vis spectroscopy, showing a characteristic catechol peak at 280 nm, whereas the UV-vis spectrum of untreated GO showed no peaks at 280 nm.

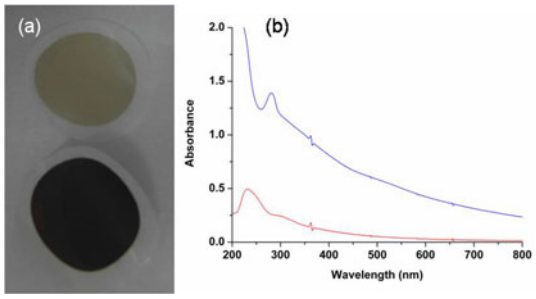

Figure 1. (a) Photographs of GO collected by membrane filter before (upper) and after (lower) poly(norepinephrine) coating. (b) UV-vis spectra of GO before (red) and after (blue) poly(norepinephrine) coating.

Surface functionalization by PN introduced alkyl hydroxyl groups, which can be used as a surface initiator for ring-opening polymerization (ROP). ROP on the PN-coated GO was investigated using ε-CL monomer in the presence of tin alkoxide catalyst. After 24-h polymerization, the resultants were characterized by scanning electron microscopy (SEM). In the SEM images of GO before and after ROP, we observed significant changes in morphology and roughness. There were sub-micrometer sized protrusions on the surface of GO which were produced during polymerization. It is known that small protrusions are produced when polymerization is occurred, and the presence of the protrusions indicates successful polymerization.

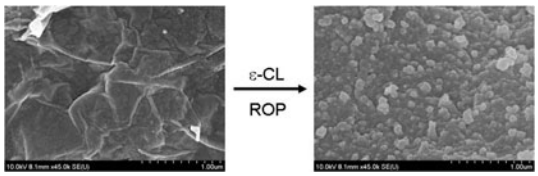

Figure 2. SEM images of (a) before and (b) after ring-opening polymerization.

Conclusions: We developed a facile approach for surface functionalization of GO using poly(norepinepheinr). The poly(norepinephrine)-coated GO serves as a platform for surface-initiated synthesis of a biodegradable polymer and at the same time reduction of GO.

References:

1. Geim AK. Nat. Mater. 2007; 6:183-191.
2. Park S, Ruoff RS. Nat. Nanotech. 2009;4:217-224.
3. Park S et al. Chem. Mater. 2008;20:6592-6594.
4. Lee et al. Science. 2007;318:426-430.
5. Kang et al. J. Am. Chem. Soc. 2009;131:13224-13225.