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Facile and controllable fabrication of multifunctional nanohybrid films composed of reduced graphene oxide and titanium dioxide through layer-by-layer assembly

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ABSTRACT

A facile fabrication strategy of multi-functional hybrid thin films of reduced graphene oxide (RGO) and TiO_2 was developed by using layer-by-layer (LBL) assembly of titanium(IV) bis(ammonium lactato)dihydroxide (TALH) and polyallylamine grafted reduced graphene oxide (PAA-RGO) as negatively and positively charged components. The fabrication process of hybrid films was thoroughly characterized by using UV–vis spectroscopic, ellipsometric and atomic force microscopic analysis. This fabrication strategy provided precisely-controlled thickness, surface roughness through 1–10 LBL assembly cycles. By thermal treatment, the PAA-RGO and TALH in the hybrid films were respectively converted into RGO and TiO_2 with the restoration of their electrical conductivity, UV-resistance and photo-catalytic self-cleaning properties.

1. Introduction

Graphene, single layered sp^2 carbon network, has attracted much attention because of its unique chemical, mechanical and electrical properties [1]. Graphene oxide (GO) is an oxidized form of graphene presenting various oxygen containing functional groups, dispersible in water, and convertible into reduced GO (RGO) by chemical and thermal reduction [2]. In addition, GO possesses unique properties distinguishable from graphene such as fluorescence, non-linear optical absorption and surface enhanced Raman scattering (SERS) [3]. Because of the chemically amenable surface and interesting properties, GO has been extensively harnessed as a building block to construct multifunctional nanohybrid structures with functional nanomaterials such as metal and semiconductors [4].

Especially, the hybridization of TiO_2, wide band-gap semiconductor, with GO derivatives has been extensively investigated for its important potential applications such as photocatalysis, photoelectrochemistry, dye-sensitized solar cell, UV protection and self-cleaning coating based on its electron-hole pair separation by UV absorption corresponding to its band gap energy [5–8]. The fabrication of RGO/TiO_2 nanohybrid structures relied on self-assembly, sol-gel processes and photochemical reactions, and the resulting structures have exhibited the significantly enhanced performance for the applications based on the electrical conductivity and electron acceptability of RGO, retarding the electron-hole pair recombination process on TiO_2 [9–12].

The advance in fabrication processes of RGO/TiO_2 nanohybrid structures is of the utmost importance to fully harnessing the unique and excellent properties of RGO and TiO_2 with synergistic effects. The fabrication strategy should be facile, controllable and reproducible for their successful applications. In this regard, the layer-by-layer (LBL) assembly technique is a promising strategy to precisely control the structure of nanohybrid materials by alternative deposition of individual building blocks [13]. This technique has been employed in the in-depth investigation of functional nanohybrid structures for various applications such as drug delivery, transparent electrodes, electrochemical devices, surface-enhanced Raman scattering and laser desorption/ionization mass spectrometry [14–18]. GO derivatives have been also employed for LBL assembly in combination with functional nanomaterials [19–21]. Recently, the fabrication of RGO/TiO_2 nanohybrid thin films was reported by repeated sol-gel reactions of titanium tetrabutoxide inside LBL assembled polydiallyldimethylammonium chloride (PDDA)/RGO

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films [22]. Although the nanohybrid films showed interesting multifunctionality including transparency, broadband photoresponse and self-cleaning, this strategy still requires multi-steps of LBL assembly of RGO and poly (diallyldimethylammonium chloride) (PDDA), repeated post-incorporation of TiO_2 precursor, and thermal calcination of the resulting hybrid films which could result in undesired side reactions and structural heterogeneity.

Herein, we demonstrated the simple and controllable fabrication of RGO/TiO_2 nanohybrid films by LBL assembly of polyallylamine-grafted RGO (PAA-RGO) and titanium(IV) bis(ammonium lactato)dihydroxide (TALH) that are precursors for RGO and TiO_2, respectively. Since TALH presented negative charges, it can be directly deposited by LBL process on the charged substrates with positively charged species and converted into TiO_2 by thermal treatment [23]. Therefore, the thickness and surface properties of PAA-RGO and TALH nanohybrid films were precisely controlled within 10 cycles of LBL assembly. The formation process and surface properties of $(PAA\text{-}RGO/TALH)_{1-10}$ nanohybrid films, where the subscript number is the number of LBL assembly cycles, were systematically characterized and the fabricated $(PAA\text{-}RGO/TALH)_{1-10}$ films were thermally treated to convert them into $(RGO/TiO_2)_{1-10}$ films presenting the interesting multifunctional properties such as UV resistance, self-cleaning, controllable electrical conductivity and transparency (Fig. 1). For the best of our knowledge, this is the first example of the direct LBL assembly of functionalized RGO sheets and TiO_2 precursor and thus the RGO/TiO_2 nanohybrid films were straightforwardly fabricated by the subsequent thermal treatment. This simple fabrication process enables to precise manipulation of the structures of resulting RGO/TiO_2 nanohybrid films with controllable and excellent multifunctionality including electrical conductivity, transparency, UV-resistance and self-cleaning.

2. Experimental section

2.1. Materials

Graphite (FP 99.95% pure) was purchased from Graphit Kropfmühl AG (Hauzenberg, Germany). Sodium nitrate, potassium hydroxide and hydrogen peroxide (30% in water) were purchased from Junsei (Japan). 3-glycidylpropyltrimethoxysilane (3-GPTMS), methylene blue (MB), poly(stryrene sulfonate) (PSS), potassium permanganate, anhydrous toluene and PAA (MW 15,000) were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Nitric acid and sulfuric acid were purchased from Samchun (Seoul, Korea). Ethanol was purchased from Merck (Darmstadt, Germany). TALH was purchased from Alfa aesar (Ward Hill, MA, USA). Si substrates (500 μm in thickness) and quartz substrates (500 μm in thickness) were purchased from STC (Japan) and i-Nexus (Stamford, USA), respectively. All chemicals were used as received.

2.2. Preparation of GO

3 g of graphite and 1 g of sodium nitrate were added in 46 mL of sulfuric acid and stirred in an ice-bath. Then, 6 g of potassium permanganate was slowly added to the mixture with stirring and the temperature of this reaction mixture was maintained below 20 °C. After finishing the addition, the temperature of the reaction mixture was raised to 35 °C and the mixture was stirred for 1 h. 40 mL of water was then added to the mixture, stirred for 30 min and 100 mL of water was added to the mixture in an ice-bath to prevent rapid boiling. Finally, 6 mL of hydrogen peroxide (30%) was gradually added to the mixture and upon addition, the color of the reaction mixture changed to bright yellow. The mixture was filtered with a filter paper (Number 3, Whatman) and washed with a plenty of water until the filtrate was neutralized. The filtered cake was dried under vacuum for 2 days. The prepared graphite oxide powder was analyzed by FT-IR spectroscopy with a KBr pellet method. The graphene oxide was prepared by sonicating the graphite oxide powder in water (1 mg/mL).

2.3. Synthesis of PAA-RGO sheets

GO was synthesized by Hummers and Offeman's method (for detailed experimental procedure, see supporting information) [24]. The synthesized GO was simultaneously reduced and functionalized with PAA by our previously reported method [25]. In detail, GO (10 mg) was dispersed in 50 mL of water containing 40 mg of PAA, and 50 mg of KOH by sonication for 1 h. The suspension was vigorously stirred at 70 °C for 24 h. After cooling to RT, the PAA-RGO was purified and collected by centrifugation at 8228 rcf for 30 min and re-suspended in water by sonication. The centrifugation and re-suspension processes were repeated three times.

2.4. 3-GPTMS functionalization of a substrate

The quartz and Si substrates were treated in Piranha solution for 10 min at 125 °C, washed with water and ethanol, and dried under a stream of nitrogen. The treated substrates were immersed in a 10 mM anhydrous toluene solution of 3-GPTMS for 30 min, washed with ethanol and water and dried under a stream of nitrogen.

2.5. Fabrication of $(RGO/TiO_2)_n$ films

The 3-GPTMS treated substrates were immersed in PAA-RGO suspension (1 mg/mL) for 30 min, washed with water and ethanol and dried under a stream of nitrogen. The PAA-RGO coated substrates were then immersed in 5% TALH solution for 30 min, washed with water and ethanol and dried under a stream of nitrogen. These processes were repeated up to 10 cycles. The fabricated $(PAA\text{-}RGO/TALH)_n$ thin

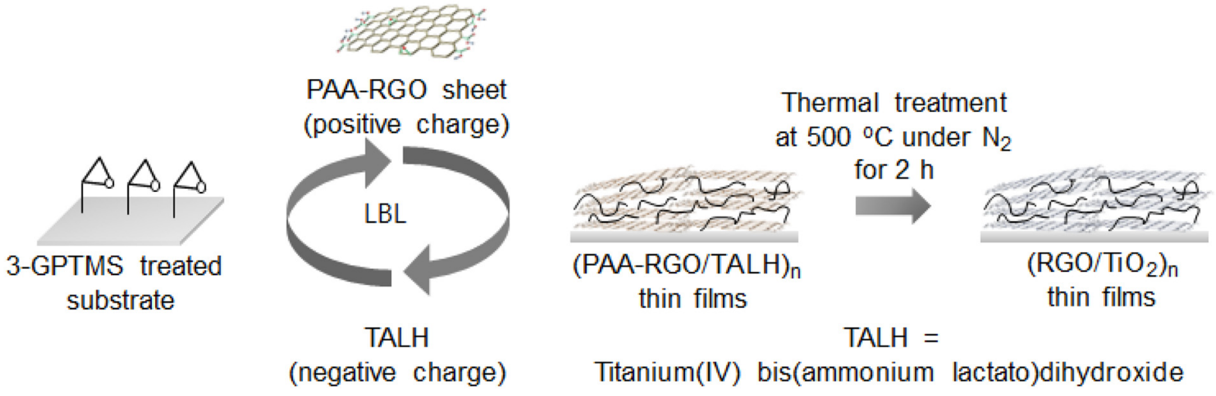

Fig. 1. Fabrication of $(PAA\text{-}RGO/TALH)_n$ thin films by using LBL assembly technique.