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Synthesis and toughening behavior of bio-inspired nanocrystalline TiO_2/polyelectrolyte nanolayered composites

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ABSTRACT

Bio-inspired (nanocrystalline TiO_2/polyelectrolyte (PE))$_4$ nanolayered composites were synthesized by the layer-by-layer self-assembly and chemical bath deposition methods. The results show that the thicknesses of the TiO_2 and PE layers in the as-synthesized are 41.3 nm and 9.6 nm, respectively, and the grain size of the TiO_2 layer is about 5 nm. For the type I cracking, the fracture toughness (K_{IC} = 1.18 ± 0.67 MPa m$^{1/2}$) of 41.3 nm TiO_2/9.6 nm PE composite is larger than that of the bulk TiO_2. For the type II cracking, the crack deflection occurred in the composite. This toughening behavior was attributed to the low interfacial fracture energy and the large ratio of the crack deflection length to the crack penetration length. Our finding demonstrates that the crack deflection is an effective way to toughen the bio-inspired nanocrystalline TiO_2/PE nanolayered composites.

1. Introduction

Although the strength of materials can be effectively enhanced by reducing the microstructure scale down to the nanometer regime, the ductility of the materials always becomes degraded [1,2]. The basic reason is that monotonic length scales of the microstructures in the material may not well modulate the contradiction between the high strength and the low ductility. It is well recognized that the better synergy between high strength and good fracture toughness (damage tolerance) of nacre originates from the unique nanoscale layered structure, namely "brick to mortar" structure, which consists of soft organic biopolymer and hard inorganic materials [3,4]. The excellent resistance to brittle fracture of the layered biological materials is mainly attributed to some toughening mechanisms, such as crack deflection and bridging, etc. [5]. Moreover, the energy absorption of the materials due to the crack deflection, a toughening behavior, is primarily influenced by the crack path after the initial crack deflection occurs [6]. These inspire one to design and synthesize a material with layered structures, and think about whether the crack deflection will occur in the material [7].

In this paper, we present an investigation on synthesis of bio-inspired nanolayered composites (NLCs), which consist of organic polyelectrolyte (PE) layers prepared by the layer-by-layer (LBL) self-assembly method [8] and inorganic nanocrystalline TiO_2 layers by the chemical bath deposition (CBD) method [9,10]. The microstructure, strength, fracture toughness and toughening behavior of the NLCs were examined carefully, and the toughening mechanism was discussed.

2. Experimental

2.1. Preparation

A negative charged hydrophilic Si–OH layer was formed on the surface of the Si(0 0 1) substrate (dimensions: 4 × 5 mm^2) after the substrate was ultrasonically cleaned in acetone and immersed into Piranha solution [11] at 60 °C for 20 min. Then, the negatively-charged Si substrate was alternately immersed into three different solutions of PE, poly(ethyleneimine) (PEI, 70,000 g/mol, Aldrich), poly(sodium4-styrenesulfonate) (PSS, 70,000 g/mol, Aldrich) and poly(allylamine hydrochloride) (PAH, 60,000 g/mol, Aldrich) in the sequence of (PEI/PSS)(PAH/PSS)$_2$ [8,9]. The PE solutions were PEI (1.25 g/dm^3) in pure water, PSS (4 g/dm^3) in 0.5 M $MnCl_2$ and PAH (2 g/dm^3) in 1 M NaCl, respectively, and the pH of the solutions was adjusted by adding 1 M HCl to a value of 9 for PEI, and a value of 3.5 in the case of PSS and PAH. Each immersion in the respective polymer solutions was conducted at room temperature for 15 min. The thickness of the organic PE layers was controlled by the number of dipping cycles into PAH/PSS solutions, while two

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dipping cycles were carried out in the present work. The deposition of inorganic TiO_2 layers onto the PE surface was carried out in a 10 mM aqueous solution of titanium peroxo complex (TiO_2^{2+}) in the presence of 65 mM HCl by the CBD procedure [9]. The deposition time and temperature were 3 h and 60 °C, respectively. The TiO_2/PE NLCs with four bilayered-periods ($(PE/TiO_2)_4$) were prepared finally.

2.2. Characterization

Surface morphology of the NLCs was characterized by a scanning electron microscope (SEM, LEO Supra35). Microstructures of the NLC on the cross-section were observed by a transmission electron microscopy (TEM, Tecnai G2 F20) with high resolution capability. Hardness (H) and elastic modulus (E) of the NLCs were obtained by a nanoindenter (Hysitron TI 900) with a Berkovich tip (tip radius ~50 nm) at a constant loading rate of 20 μN/s at room temperature. Furthermore, fracture toughness (K_{IC}) of the $(TiO_2/PE)_4$ NLCs was determined by the microindentation testing method proposed by Xia et al. [12]. In this measurement, microindentation loading was applied to the NLC sample with partially coating of the $(TiO_2/PE)_4$ NLC on the substrate. The indentation on the uncoated portion of the substrate generated radial cracks from the indent corners, which propagated either into or away from the coated region. Thus, K_{IC} of the NLCs can be calculated by a comparison of the lengths between the indentation-induced radial cracks into and away from the coated region [12].

3. Results and discussion

The technique to synthesize PE layers is based on the electrostatic attraction between oppositely charged polyions, PEI, PSS and PAH, layer by layer [8]. It is found that the thickness and the surface quality of the TiO_2/PE NLCs are strongly influenced by the cycles of PAH/PSS (see Fig. S1 in Supplementary material) and the deposition time of TiO_2 (see Fig. S2 in Supplementary material). Therefore, we selected 3 h as the deposition time of TiO_2 and 2 cycles of PAH/PSS for PE to obtain the NLCs with the better quality. Fig. 1(a) shows that the surface of the $(TiO_2/PE)_4$ NLC is quite smooth and compact. A local region scratched by a needle reveals a typical multilayered-structure with four layers, as indicated by arrows in Fig. 1(b). These characterizations indicate that the TiO_2/PE NLCs with four bilayered-periods ($(TiO_2/PE)_4$) were prepared successfully by the above experimental process.

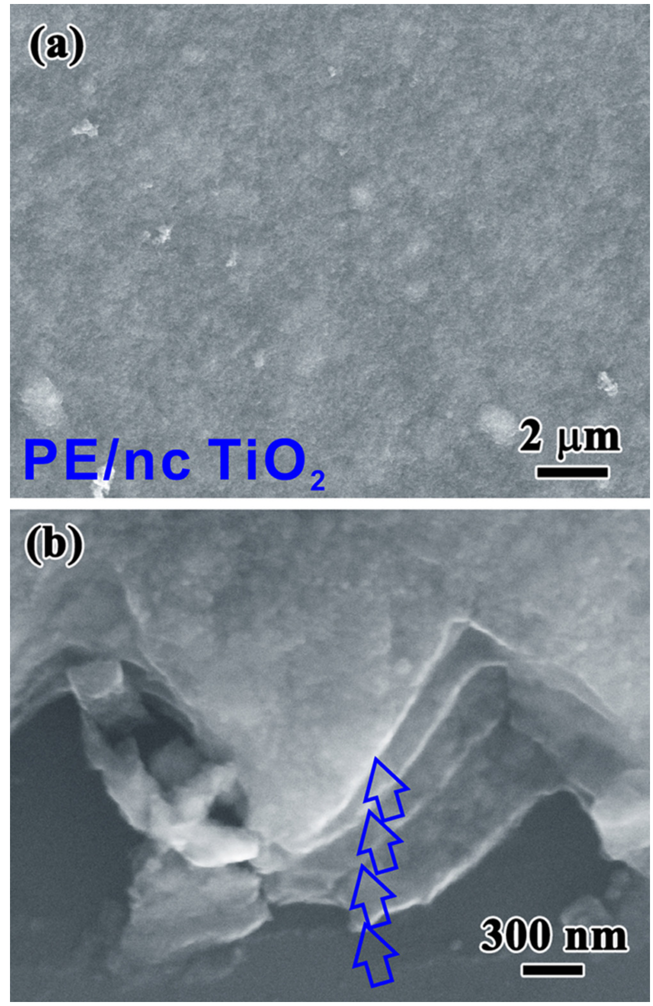

Fig. 1. SEM images of $(TiO_2/PE)_4$ nanolayered composite, (a) surface morphology and (b) layered structure.

A TEM cross-sectional micrograph (Fig. 2(a)) shows that the PE (bright region) and the TiO_2 (dark region) layers have average thicknesses of 9.6 nm and 41.3 nm, respectively, indicating that the total thickness of the NLC is about 200 nm. A close examination (Fig. 2(b)) reveals that the constituent layers are somewhat wavy. The mineral bridge-like morphology characterized by

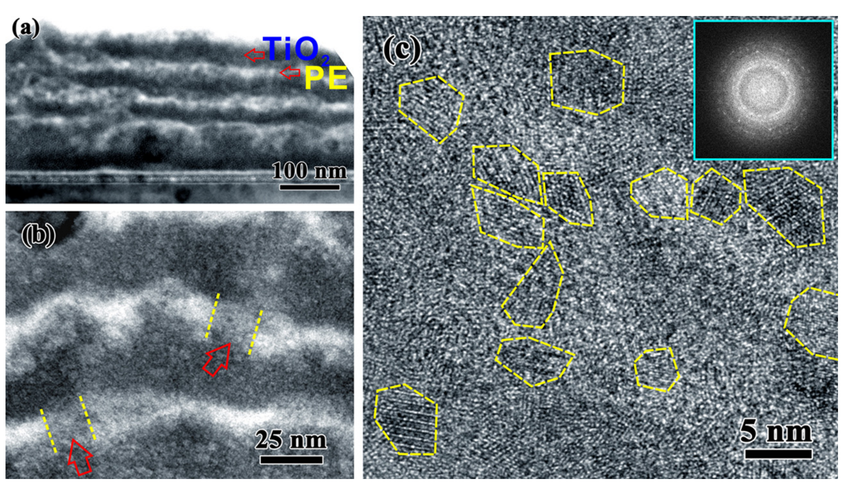

Fig. 2. TEM cross-sectional views of $(TiO_2/PE)_4$ nanolayered composite (a) at low magnification and (b) at high magnification. (c) HRTEM image of inorganic TiO_2 layer, showing the existence of nanocrystallines.