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# Synthesis and characterization of nacre-inspired zirconia/polyimide multilayer coatings by a hybrid sputtering and pulsed laser deposition technique

Hsi-Ming Yang [a], Yu-Chen Chan [a], Tsung-Hao Hsu [a], Hsian-Wei Chen [a], Jyh-Wei Lee [b], Jenq-Gong Duh [a], Po-Yu Chen [a,*]

[a] Department of Materials Science and Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Rd., Hsinchu 30013, Taiwan
[b] Department of Materials Engineering, Ming Chi University of Technology, 84 Gungjuan Rd., Taishan Dist., New Taipei City 24301, Taiwan

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ABSTRACT

Abalone nacre is a natural ceramic-based composite consisting of 95 wt.% stacked $CaCO_3$ tiles and 5 wt.% organic layers organized into a unique multilayer structure, which leads to exceptional fracture toughness. Multi-scale toughening mechanisms such as crack deflection at the organic/inorganic interfaces, viscoelastic organic glue, nano-asperities and interconnected mineral bridges between tiles, collaborate synergistically to prevent deformation and failure. Inspired from abalone nacre, multilayer coatings of zirconia and polyimide layers were synthesized by a hybrid PVD system combining sputtering and pulsed laser deposition. By introducing thin polyimide interlayers between zirconia layers, the fracture toughness of multilayer coatings (5.2 $MPa \cdot m^{1/2}$) was significantly enhanced, approaching six times higher than that of zirconia monolayer (1.0 $MPa \cdot m^{1/2}$). The thickness ratio of zirconia and polyimide was kept 10:1 while thickness and number of interfaces were altered to investigate the effect of organic/inorganic interfaces on the mechanical properties of the coatings. Results showed that multilayer structure could enhance the fracture toughness of coatings. Fracture toughness significantly increased with increasing number of interfaces yet the hardness slightly decreased. SEM observation verified that the major toughening mechanism of bio-inspired multilayer coatings was crack deflection at organic/inorganic interfaces, which prevented crack from direct propagation. With certain critical interfacial roughness, fracture toughness of multilayer can be further improved, similar to the function of nano-asperities in abalone nacre. Bio-inspired organic/inorganic multilayers could improve the toughness of intrinsically brittle ceramic or glass coatings and extend their applications in protection, wear and corrosion resistance, optical and biomedical fields.



## 1. Introduction

In nature, protection and predation have long been competing among various species through evolution. For an effective armor design, both hardness and toughness should be taken into account, since it is crucial to be able to dissipate energy without failure of the armor, which would expose the underlying body. Natural armors often possess high toughness and can prevent catastrophic damage and recovery themselves by self-healing capability. Various types of protective armors have been adopted by different creatures, such as mollusk shells, arthropod exoskeletons, fish scales, turtle shell, armadillo and alligator osteoderms, to survive from the predators' claws and teeth [1–3]. Abalone nacre is the most classic example and has been extensively studied [4–7]. Abalone nacre is an inorganic and organic multilayer composite consisting of 95 wt.% $CaCO_3$ (aragonite) tiles and 5 wt.% biopolymer layers (chitin and protein), organized into a characteristic hierarchical structure, as shown in Fig. 1(a). Abalone nacre is built by 500-nm-thick aragonite tiles separated by thin biopolymer layers (~50 nm) and the surface of tiles consists of nano-sized asperities and mineral bridges. The work of fracture of abalone nacre is 3000 times over that of its mineral constituents. The exceptional mechanical properties of abalone nacre are the results of multi-scale toughening mechanisms [4–7]. At sub-millimeter level, crack is deflected by organic mesolayer. At micrometer level, sliding of aragonite tiles creates a tortuous crack path. At nanometer level, three inter-tile toughening mechanisms operate synergistically at the organic/inorganic interfaces: (i) nano-asperities resist tiles from sliding, (ii) organic layers act as viscoelastic glue, and (iii) mineral bridges connect adjacent tiles, as shown in Fig. 1(b). The mechanical performance of thin films can be enhanced by multilayer and nano-composite approaches [8–14]. However, as the development of inorganic multilayer and nano-composite thin films gradually approaches the limit, abalone nacre-like organic/inorganic multilayer structures were fabricated using synthetic materials

* Corresponding author.
*E-mail address:* poyuchen@mx.nthu.edu.tw (P.-Y. Chen).

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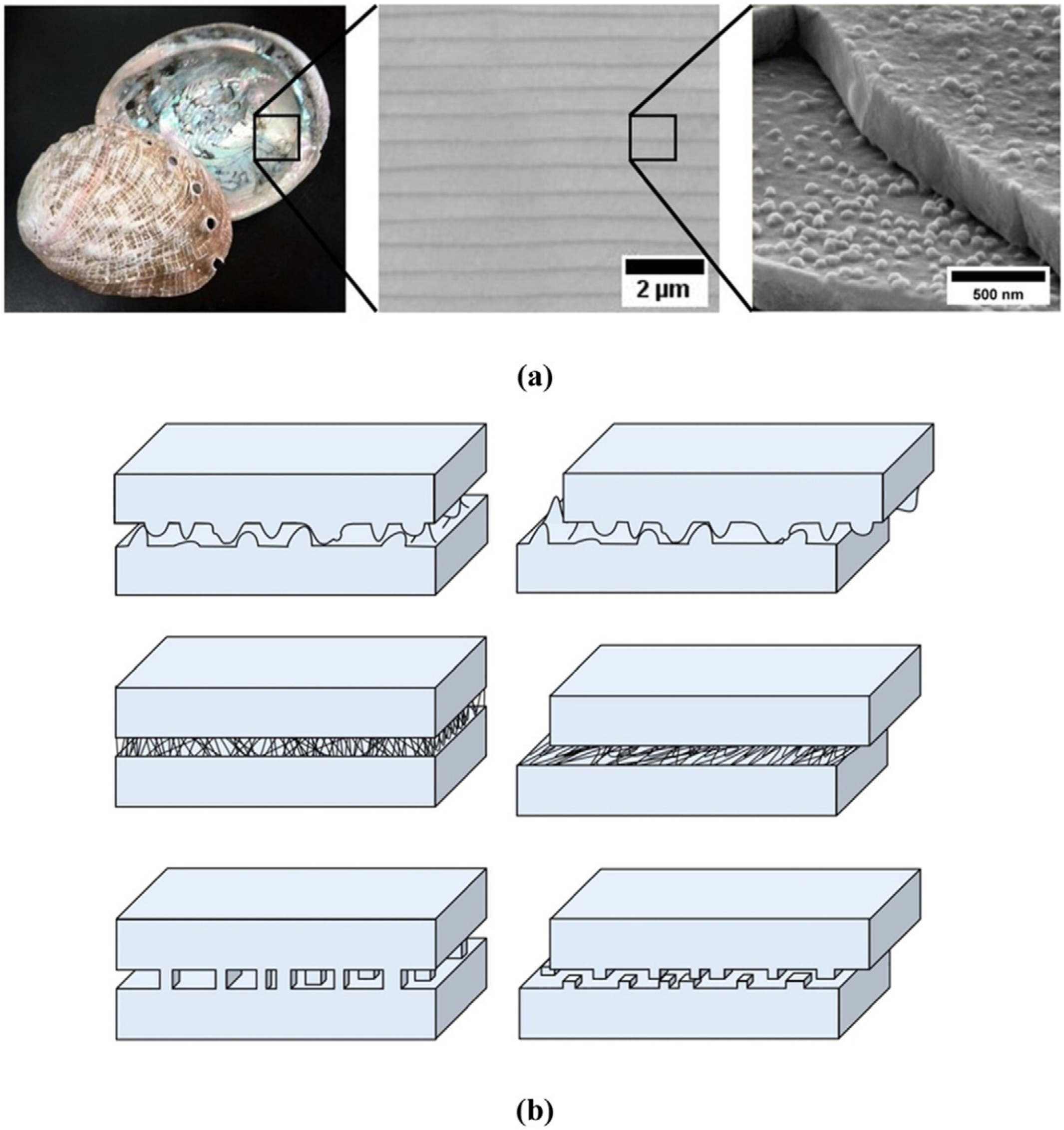


**Fig. 1.** (a) Hierarchical structure of abalone nacre (from left to right): abalone shell and inner nacre, multilayer microstructure of $CaCO_3$ tiles (~500 nm) and organic layers (~50 nm), nano-sized mineral asperities and bridges between adjacent tiles. (b) Toughening mechanisms between tiles include asperities, organic layer acting as viscoelastic glue and inter-connected mineral bridges.

[15–17]. Tang et al. [15] applied electrical potential to sequentially deposit clay platelets (0.9 nm in thickness) with polymers and fabricated a 5 μm film with 200 alternate layers yet the composite is more of a platelet-reinforced polymer, rather than ceramic-based nacre and the scale is too small. Chen et al. [16] further synthesized clay/polyimide multilayer films by a centrifugal deposition process with thickness up to 200 μm yet the organic fraction in the composite was 20 wt.%, higher than that in nacre (5 wt.%). Burghard et al. [17] combined the chemical bath deposition (CBD) of $TiO_2$ with layer-by-layer assembly of polyelectrolytes (PE) to synthesize hierarchically-structured organic/inorganic multilayer films which exhibit a significant enhancement in fracture toughness compared to $TiO_2$ monolayer films. $TiO_2$/PE multilayer films with thickness ratios of 20:1, 10:1, and 5:1 were synthesized and evaluated and results showed that the one with $TiO_2$/PE ratio of 10:1, like the aragonite tiles and bio-polymers in nacre, possesses the optimal mechanical performance due to the toughening mechanisms at the interfaces, such as inter-connected inorganic bridges and asperities. In this study, abalone nacre-inspired multilayer composite coatings of zirconia and polyimide are synthesized by a hybrid PVD system combining sputtering and pulsed laser deposition (PLD) in a single chamber. The periodic thickness, micro-/nano-structure and interfacial morphology of bio-inspired multilayer coatings can be precisely controlled by tuning the deposition parameters and the fracture toughness can be enhanced and optimized, opening out an unexplored territory and fulfilling promising potential applications in protective coatings, decorative and optical coatings, flexible electronic devices and biomedical fields.

## 2. Experimental procedure

### *2.1. Thin film deposition by the hybrid PVD system*

The hybrid physical vapor deposition system (hybrid PVD system) including sputtering and pulse laser deposition (PLD) was designed and integrated in the same vacuum chamber. Two coating systems can be operated within one vacuum chamber sequentially without breaking the vacuum. Fig. 2 showed the schematic diagram of the hybrid PVD system and the operation procedure under (a) sputtering mode and (b) PLD mode, respectively. The substrate holder was set to