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Damage-tolerance strategies for nacre tablets

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ABSTRACT

Nacre, a natural armor, exhibits prominent penetration resistance against predatory attacks. Unraveling its hierarchical toughening mechanisms and damage-tolerance design strategies may provide significant inspiration for the pursuit of high-performance artificial armors. In this work, relationships between the structure and mechanical performance of nacre were investigated. The results show that other than their brick-and-mortar structure, individual nacre tablets significantly contribute to the damage localization of nacre. Affected by intracrystalline organics, the tablets exhibit a unique fracture behavior. The synergistic action of the nanoscale deformation mechanisms increases the energy dissipation efficiency of the tablets and contributes to the preservation of the structural and functional integrity of the shell.

1. Introduction

Organisms have developed diverse strategies to synthesize biological composites that exhibit excellent mechanical properties (Bruet et al., 2008; Kamat et al., 2000; Killian et al., 2011; Li and Ortiz, 2014; Meyers et al., 2013, 2008, 2012; Tai et al., 2007; Weaver et al., 2012). One particularly intriguing material is nacre, which is found in mollusk shells. Nacre possesses a unique combination of remarkable strength and toughness and therefore offers outstanding protection against mechanical attacks (Barthelat and Espinosa, 2007; Barthelat et al., 2007; Currey, 1977; Gao et al., 2003; Jackson et al., 1988). Until recently, individual nacre tablets were not thought to contribute to the high toughness of nacre; instead, the toughness was attributed to the brick-and-mortar architecture and precisely designed organic-inorganic interfaces (Evans et al., 2001; Wang et al., 2012, 2001; Wang and Gupta, 2011) (Fig. 1a). However, recently, elaborate nanostructures within individual nacre tablets have been reported (Gries et al., 2009; Suzuki et al., 2011; Wang et al., 2015; Younis et al., 2012) (Fig. 1b), indicating that the nanoscale architecture may indeed contribute to the toughening mechanisms of nacre. In contrast to conventional single crystals, the nacre tablets contain randomly distributed defects that are visible in the bright-field transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images shown in Fig. 1c and d. An increased C/Ca ratio, as measured by energy dispersive X-ray spectroscopy (EDX) (Fig. 1e) and electron energy loss spectroscopy (ELLS), confirmed that these defects were intracrystalline organics (Gries et al., 2009; Suzuki et al., 2011; Wang et al., 2015; Younis et al., 2012). In addition, detailed high resolution transmission electron microscopy (HRTEM) investigations demonstrated that the crystal structure of the aragonite scaffold is homogeneous and continuous throughout the whole tablet and that the trapped intracrystalline organics do not affect the integrity of the scaffold (Wang et al., 2015).

Meanwhile as the structural study, the mechanical performance of individual nacre tablet was revealed (Bruet et al., 2005; Huang and Li, 2013; Huang et al., 2011; Katti et al., 2006; Li et al., 2006, 2004; Sumitomo et al., 2008). The impressions from nanoindentation tests showed characteristics of plastic deformation (Bruet et al., 2005; Li et al., 2004). Further investigations demonstrated that the toughness of the tablet originates from its sophisticated nanostructure (Huang and Li, 2013; Li et al., 2006). A recent study reported theoretical calculations that suggest the intracrystalline organics enhance the fracture resistance of nacre because they have lower elastic moduli than the aragonite scaffold; however, no experimental support was provided (Younis et al., 2012). These studies and calculations indicate that conventional toughing mechanisms at the brick-and-mortar level are insufficient to comprehensively explain nacre's damage tolerance. Thus, the nanoscale deformation mechanisms of the individual nacre tablets must be investigated.

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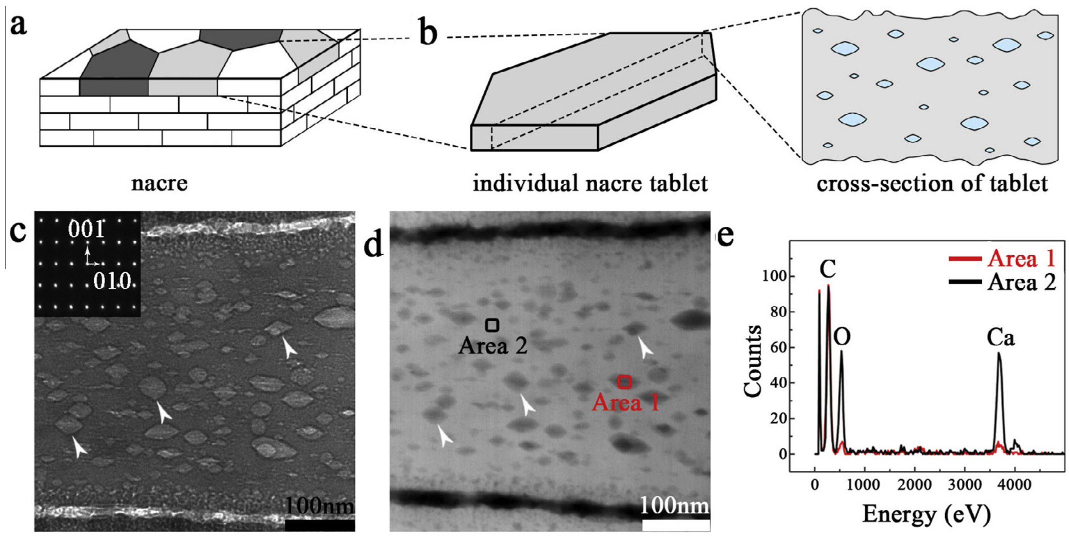

Fig. 1. Hierarchical architecture in nacre. (a) Schematic diagram of the brick-and-mortar architecture of nacre. (b) Schematic diagram of the nanostructure in an individual nacre tablet. (c) Bright-field TEM image and (d) HAADF-STEM image of a nacre tablet. The randomly distributed defects are indicated with arrow heads. (e) EDX spectra from the areas labeled in (a), showing the increased C/Ca ratio for the defect.

In this work, the origin of the damage localization in nacre (*Pinctada maxima*) at multiple scales is determined. Our results demonstrate that in addition to the brick-and-mortar architecture, the nanostructure of the individual tablets greatly affects the fracture behavior of nacre. These nanoscale deformation mechanisms lead to additional energy dissipation and promote the mechanical optimization of the shell.

2. Experimental section

2.1. Materials

Mature nacre materials from fresh *P. maxima* shells found in the South China Sea were chosen for the investigation. To minimize the detrimental effects from dehydration on the nanostructure and fracture behavior of the samples, the shells were cleaned and delivered in ice by airplane to the laboratory. The block nacre samples were cut from the nacreous layer of the shells with a water-cooled, low speed diamond saw.

2.2. Nanoindentation and FIB

The (002) plane of the block nacre samples and the geologic aragonite samples were successively ground with wet abrasive paper (up to 800 grit) and polished with a suspension of 20 nm aluminum oxide particles. Then, nanoindentation tests were performed on a Nano Indenter G200 (Agilent Technologies) using a spherical tip with a radius of 1 μm. The maximum load varied from 10 to 100 mN. A Dual Beam System (FEI Quanta 3D FEG) was used to cut samples from the indentations for TEM (Fig. S1 in the Supporting Information).

2.3. Microindentation and PIPS

Microindentations were performed using an HRD-150 Rockwell hardness tester at a load of 60 kg. The indented surfaces from two different samples were then bound together and 0.5 mm thick slices from the cross-sections of the indentations were cut. After mechanically grinding the sections to a thickness of 40 μm and polishing both sides, the sections were glued onto single-hole Cu microscopy grids. Ion milling was performed using a Precision Ion Polishing System (Gatan 695). Fig. S2 shows this sample preparation process.

2.4. SEM and TEM

Prior to SEM and TEM observations, all of the samples were sputter-coated with a thin film of Pt. SEM micrographs were acquired using a HITACHI S-4800 field emission scanning electron microscopy at an accelerating voltage of 5 kV. TEM micrographs were acquired using a Tecnai G^2 F20 field emission transmission electron microscope at an accelerating voltage of 200 kV.

3. Results

The fracture behavior of nacre in comparison to geologic aragonite was investigated via instrumented nanoindentation. A spherical diamond tip with a radius of 1 μm was used to avoid extrinsic anisotropic mechanical responses. Fig. 2 shows the residual nanoindentations from five different loads (10, 30, 50, 80, and 100 mN). The geologic aragonite exhibits good fracture resistance at 10 mN (Fig. 2a). However, as the load increases, radial cracks appear (50 mN) and cause catastrophic fracture (100 mN). In contrast, nacre has a more uniform and localized fracture behavior (Fig. 2b). To quantitatively analyze the indentations, two parameters were employed: R_0, the radius of the residual indentation crater that was directly in contact with the tip during the test and R_1, the radius of the entire fracture pattern determined by fitting it with the smallest possible circle (Li and Ortiz, 2014). Ten indentations were measured for each load and the R_1/R_0 values are presented in the histogram in Fig. 3. It is interesting to note that R_1/R_0 and the standard deviation increase as the indentation load increases for geologic aragonite, but these values are relatively constant for nacre. The results indicate that the damaged area of the geologic aragonite increases with the load, whereas nacre is able to confine the fracture within an optimal range at different loading conditions.

How does nacre achieve damage localization? To determine the underlying deformation mechanisms of the nacre, cross-sectional TEM samples of the indentations were prepared using a focused ion beam (FIB). Fig. 4a shows the damaged region around the indentation site. The tablets located more than 1 μm away from