Fish-scale bio-inspired multifunctional ZnO nanostructures

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Abstract
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Keywords
fish, scale, bio, inspired, multifunctional, zno, nanostructures

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Fish-scale bio-inspired multifunctional ZnO nanostructures

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Scales provide optical disguise, low water drag and mechanical protection to fish, enabling them to survive catastrophic environmental disasters, predators and microorganisms. The unique structures and stacking sequences of fish scales inspired the fabrication of artificial nanostructures with salient optical, interfacial and mechanical properties. Herein, we describe fish-scale bio-inspired multifunctional ZnO nanostructures that have similar morphology and structure to the cycloid scales of the Asian Arowana. These nanostructured coatings feature tunable light refraction and reflection, modulated surface wettability and damage-tolerant mechanical properties. The salient properties of these multifunctional nanostructures are promising for applications in (i) optical coatings, sensing or lens arrays for use in reflective displays, packing, advertising and solar energy harvesting; (ii) self-cleaning surfaces, including anti-smudge, anti-fouling and anti-fogging, and self-sterilizing surfaces; and (iii) mechanical/chemical barrier coatings. This study provides a low-cost and large-scale production method for the facile fabrication of these bio-inspired nanostructures and provides new insights for the development of novel functional materials for use in ‘smart’ structures and applications.

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INTRODUCTION

In the past decade, techniques have been rapidly developed to produce ‘smart’ multifunctional nanomaterials by applying lessons learned from nature, materials termed ‘bio-inspired nanostructures’.1,2 This approach has naturally led to the development of bio-inspired multifunctional nanomaterials for use in various applications. For example, several researchers have described lotus-leaf-inspired self-cleaning surfaces, plant- and insect-inspired anisotropic superhydrophobic surfaces, fly-eye-inspired anti-fogging coatings, insect-inspired antireflection coatings, rose-petal- and gecko-foot-inspired highly adhesive surfaces, cactus-inspired fog-collecting surfaces and butterfly-wing-inspired optical materials.1-9 These materials are based on the fact that biological species have optimal structures that have been honed through millions of years of evolution and that exhibit amazing characteristics and swift stimulus-responsive capabilities, which provide inspiration to researchers for the design of multifunctional materials.

Fish have existed for ~500 Myr and have survived several catastrophic mass extinction events during global environmental disasters.10 Most fish have hard scales on their skin for protection. It has been suggested that the dermal armor of ancient fish served as a protection from predators and mechanical damage, and maximized survivability.11 Generally, fish scales serve three major functions: (i) providing mechanical protection from external mechanical disturbances and from invasion by bacteria and other microorganisms; (ii) providing low drag mobility in water to improve maneuverability and speed; and (iii) providing camouflage protection via light reflection and refraction to escape predators.10 The unique structures and functionalities of fish scales have attracted great interest, and some progress has been made in understanding their crystalline growth, morphologies, small length scale effects and fundamental properties. One of the most famous cases arising from this greater knowledge is a shark-skin-inspired swimsuit that has boosted swimming speed through its ability to reduce drag.12 An excellent bio-inspired surface that features underwater superoleophobicity has been fabricated by replicating shark pacooid and cycloid scales.13 Ortiz et al. have studied the mechanical properties of individual dermal armor plates and scales, and have further proposed design principles for bio-inspired
human body armor. Even though several reports have described studies of fish scales and their replica surfaces, no relevant reports can be found describing the facile synthesis of fish-scale bio-inspired inorganic nanostructures that can mimic their multiscale structures and multiple functions. The development of fish-scale bio-inspired inorganic nanostructures in this study will consequently greatly extend the use of bio-inspired materials to applications including micro-mechanical devices, heavy-duty machines (as protective coatings against mechanical damage and chemical corrosion), optical devices (as optical elements), photovoltaics and low-drag or low-friction surfaces in gaseous, liquid and solid media.

Herein, we describe the design of fish-scale bio-inspired multifunctional ZnO nanostructures that have similar surface structures to the cycloid scales of the Asian Arowana. The Asian Arowana (Scleropages), a member of Osteoglossidae and of the earliest fish to appear (~340 Myr ago during the Carboniferous period) continues to exist today. Figure 1a illustrates an Asian Arowana fish, which are usually ~ 60 cm in length and covered with large cycloid scales, each of which is generally longer than 2 cm. An enlarged image of the scales is shown in Figure 1b. In this study, bio-inspired ZnO nanostructures in the form of isolated microspheres (Figures 1c and d) and large-scale coatings (Figure 2), both of which have surfaces with a similar stacking...
sequence to that of the fish scales, were synthesized via a facile hydrothermal process. ZnO is a typical inorganic metal oxide that is easily fabricated into a variety of morphologies to meet different functional requirements. Both the structure and the surface composition of the fish scales are reportedly crucial for providing low drag mobility to improve the maneuverability and speed of fish in water. Therefore, appropriate surface modifications were also carried out on the bio-inspired nanostructured coatings. To explore the multifunctional applications of these unique bio-inspired nanostructures, their optical properties, surface wettability modulation (to superhydrophilicity or superhydrophobicity) and mechanical properties were studied. For the bio-inspired materials, the nanoscale properties are expected to be more interesting than those on the millimeter scale. On the basis of this consideration, we controlled the bio-inspired ZnO crystals at a nanometer scale in this study.

**EXPERIMENTAL PROCEDURES**

**Synthesis**

To prepare reaction solutions for the synthesis of the bio-inspired nanostructures, polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO20–PPO70–PEO20, Pluronic P123) surfactant and precisely controlled H2O and ethylene glycol (EG) co-surfactant were added to 3 ml ethanol to form a surfactant solution. Then, ZnAc2·2H2O was added to the surfactant solution, which was then stirred for ~10 min. Next, hexamethylenetetramine was added, and stirring was maintained for another 10 min to allow dissolution of all the crystals. After further stirring for ~3 h, a transparent solution was obtained. The transparent precursor solution was statically aged for 4 days. Then, the well-aged reaction solutions were transferred into an autoclave and heated at 100–150 °C for 5–15 h.

The fish-scale bio-inspired isolated microspheres were synthesized from the aged solution, which contained 0.8 g ZnAc2·2H2O, 0.5 g hexamethylenetetramine, 0.42 g H2O and 12 ml EG, and was then solvothermally heated at 110 °C for 15 h. To grow the bio-inspired nanostructured coatings, clean glass substrates with different ZnO nanoseed densities were placed into the aged reaction solutions and then solvothermally treated at 90–150 °C. Before the growth of the nanostructured coatings, a thin layer of PFOTES molecules was carefully pre-deposited on the substrates. The seed solution used for low-density seed deposition was 20 ml of an ethanol solution containing 0.02 g ZnAc2·2H2O. Seed deposition was carried out by spin coating the well-stirred seed solution onto the substrates at 2,000 r.p.m. for 30 s; this procedure was repeated 1–5 times at intervals of 15 min, depending on the case. After seed coating, the substrates were heated at 400 °C for 1 h. The seed solution used for high-density seed deposition was 20 ml of an ethanol solution containing 0.05 g ZnAc2·2H2O. After repeated spin coating (2–5 times), the substrates were heated at 300 °C for 1 h. Coatings with parallel scale-like nanostructures were grown on low-seed-density substrates from a solution containing 1 g H2O and 12 ml EG at 130 °C for 5 h, whereas coatings with parallel scale-like nanostructures mixed with some tilted scales were obtained with the low-density seed precoated substrates from a reaction solution containing 0.42 g H2O and 6 ml EG at 150 °C for 5 h. The coatings with tilted scale-like nanostructures were grown on high seed density substrates from the solution containing 0.42 g H2O and 12 ml EG at 150 °C for 5 h. In some cases, a shorter reaction time proved helpful to grow the nanostructures with lower growth stress.

**Surface modification**

Surface modification via perfluorinated silane molecules (IH1H, 2H2H-perfluoroctyltriethoxysilane, PFOTES) was performed with a room-temperature vacuum deposition approach. In detail, one drop of PFOTES liquid was placed beside the bio-inspired coatings; then, low vacuum (~250 Pa) was applied to the system. After allowing deposition for 24 h, a thin layer of PFOTES molecules deposited on the surface bio-inspired nanostructured coatings.

**Characterization**

The preferred orientations of the as-prepared bio-inspired nanostructured coatings were evaluated using a powder X-ray diffractometer (MMA, GBC Scientific Equipment LLC, Hampshire, IL, USA) operating under Cu Kα radiation. The morphology of the samples was observed with a scanning electron microscope (JSM-7500F, JEOI, Tokyo, Japan). High-resolution transmission electron microscope observations were carried out using a JEM-2011 F instrument (JEOL) operated at 200 kV. Nanoindentation testing was carried out with an Ultra-Micro Indentation System (UMIS-2000, CSIRO, Sydney, NSW, Australia), and a Berkovich tip with a radius of 200 nm was used to test the hardness and to determine Young’s modulus. Incremental loading and unloading tests were performed under load control, and the maximum load was...
RESULTS AND DISCUSSION

Synthesis of the bio-inspired nanostructures

Figures 1c and d show the microstructure of the fish-scale bio-inspired isolated ZnO microspheres that were synthesized at 110 °C for 15 h from the 4-day-aged reaction solution. The obtained bio-inspired microspheres were ~ 2 μm in diameter, and the surfaces were fully covered with fish-scale-like nanostructures, which exhibited a similar stacking sequence to that of natural fish scales, except that the size of the bio-inspired scales was in the range 200–500 nm; that is, much smaller than real fish scales. The synthesis of these highly ordered stacked fish-scale bio-inspired microspheres was unfortunately very sensitive to preparation parameters, such as the amount of precursors and surfactants added and, particularly, the aging time. Figure 1e presents high-resolution transmission electron microscopy image of one fish-scale-like nanostructure. The figure shows that the exposed basal planes of the scales are precisely the (001) planes of wurtzite ZnO. These well-sequenced, fish-scale-like, nanostructure-covered microspheres would be of great interest for their potential in applications involving micro-/nano-fluidity.

Compared with using isolated bio-inspired microspheres, it would be much more attractive if we could prepare fish-scale-like nanostructures on certain substrates as coatings to obtain low-friction/low-drag surfaces, anti-corrosion coatings, superhydrophobic or superhydrophilic surfaces and so on. Fish swiftly responds to the external stimulations by changing the orientation of their scales. To study the effect of fish-scale orientation, the bio-inspired coatings with fish-scale-like nanostructures were synthesized with different scale orientations on glass substrates, mainly by controlling the seed density and surfactants added and, particularly, the aging time. Figure 2a presents the growth of the bio-inspired coating with parallel scale-like nanosheets on a glass substrate that was precoated with a layer of low-density seeds that were crystallized at 400 °C. The fish-scale-like nanostructures on the coating have exposed basal planes; ZnO (002) orientations of the coating should appear mainly green under incident light at 20° and 40°, and is expected to appear orange at 30° and 60°. The bio-inspired coatings with tilted scales (Figure 3c) presented much stronger refraction and color variation, but exhibited much weaker reflections compared with the coatings with parallel scales. The bio-inspired coatings with tilted scales showed predominant yellow colors under white incident light, owing to the refraction caused by the tilted scale-like nanostructures, which work as prism arrays to refract and disperse light. The reflection spectra also revealed that the color of the coatings varied with the incident angle. On the basis of reflection spectra, the coating should appear mainly green under incident light at 20° and 40–50°, and is expected to appear orange at 30° and 60°. The bio-inspired coatings with tilted scales (Figure 3c) presented much stronger refraction and color variation, but exhibited much weaker reflections compared with the coatings with parallel scales. The bio-inspired coatings with tilted scales showed predominantly green colors at 20° and 30° but predominantly red colors at 50°. Unlike the bio-inspired coatings with parallel scales, in which yellow colors were dominant under white light, the coating with tilted scales presented clear rainbow-like strips. The results indicate that the flat exposed basal planes of the parallel scales function as mirror arrays, whereas the tilted scales act more like prism arrays.
The formation of colorful strips on the bio-inspired coatings might result from domains where the tilted scale-like crystals face in different directions. The rainbow-like, shimmering iridescence that resulted from the specific hierarchically ordered nanostructures in the fish-scale bio-inspired nanostructures is not only of great scientific interest but also might prove useful in a wide range of applications related to reflective displays, packaging, advertising and solar energy harvesting. The fish-scale bio-inspired nanostructured coatings provide a new way to design thin films or coatings with tunable optical properties for use in modern optoelectronic devices.

Surface properties of the bio-inspired nanostructures

As an interface between the inner organs and the water environment, fish scales have a key role in protecting fish from contamination by oil pollution and exhibit self-cleaning and anti-fouling properties. It was reported that natural fish scales provide underwater superoleophobicity. In this study, we found that the fish-scale bio-inspired nanostructured coatings with tailored scale orientations exhibited tunable wettability in response to surface modification. Figure 4a presents our concept for tuning the surface wettability of the fish-scale bio-inspired nanostructures by depositing perfluorinated silane (PFOTES) molecules or P123 molecules, respectively. When we applied perfluorinated silane to the ZnO surface, the silane head group formed a covalent bond by dehydration between the –CH2CH3 group in the head of the silane and an –OH group on the surface of the ZnO; in addition, the perfluorinated backbone provides a low surface energy that resists adsorption of water and enhances the hydrophobicity of the surface. Conversely, when P123 tails were exposed, hydrocarbon groups that are very reactive to water adsorbed free water molecules, resulting in a superhydrophilic surface.

Figures 4b–d presents the wettability of the bio-inspired coatings with different scale orientations before and after surface modification. As shown in Figure 4b, the pristine bio-inspired coating with parallel scales was hydrophobic with a contact angle of 89°. After modifying the coating with P123, the coating wettability was altered from hydrophobic to superhydrophilic with a contact angle of almost 0°. When a few layers of PFOTES molecules were deposited, the bio-inspired nanostructured coating exhibited hydrophobicity with a contact angle of 118°. The pristine surface of the coating with slightly tilting scales had a contact angle of 110° when tested for wettability. The silane-treated surface almost became superhydrophobic, showing a contact angle of 142°, whereas the P123-coated surface became superhydrophilic (Figure 4c). The bio-inspired coatings with tilted scales presented much more interesting behavior in response to water. As shown in Figure 4d, the contact angle of the pristine coating was ~125°. The angle was almost 0° for the P123-decorated surface, and the surface presented excellent superhydrophobicity with a contact angle of 162° after a PFOTES layer was deposited. The deviations of the measured contact angles were <3°. Interestingly, the contact angle of the pristine bio-inspired coatings increased with the degree of tilting of the scale-like nanostructures. This increase in contact angle is attributed to the increased surface roughness. Micro-grooves between the tilted scales can trap air inside, resulting in the liquid droplet adopting a Cassie–Baxter state.

To determine the superhydrophobic properties of the materials, it is necessary to determine not only the apparent water contact angle but also the dynamic contact angle (the sliding angle or tilting angle at which the water droplet rolls off an inclined surface). Figure 4e–g presents the sliding behavior of water droplets from PFOTES-modified bio-inspired nanostructured coatings when their substrates were tilted at 3–4°. The bio-inspired coatings with parallel scales showed a high
degree of adhesion, as shown in Figure 4e, and water droplets adhered to the tilted bio-inspired coating surface and did not slip off. This suggests that the water droplet on the bio-inspired coating with parallel, flat scale nanostructures almost obeys the Young–Dupre equation. Even though the bio-inspired coatings with mixing parallel-tilted scales appeared superhydrophobic to the water droplet, high adhesion was observed, as shown in Figure 4f, which shows that the water droplet adhered onto the tilted bio-inspired coating surface and did not slip off, indicating that the surface roughness was insufficient to reach a Cassie–Baxter state. The PFOTES-modified surface of the bio-inspired coating with tilted scales presented not only a high contact angle but also low energy toward a moving water droplet, or a low tilting angle (Figure 4g). It is surprising that water droplets rolled off within 0.1 s from the planes with a tilting angle of 3°. The high water contact angle and the low sliding angle of the bio-inspired coating with tilted scales indicate that the water droplets follow the Cassie–Baxter equation and do not penetrate into the grooves. High contact angles and low sliding angles are responsible for the self-cleaning properties observed in some natural species, such as cicada wings, and lotus and peanut leaves.

On the basis of the static wettability and sliding-off tests, it was concluded that both the wettability and the adhesion behavior of the fish-scale bio-inspired coatings can be tailored by changing the orientation of the scales or by modulating the surface functional groups. In particular, the PFOTES-modified bio-inspired coatings with tilted scales exhibited low surface energy and suitable surface roughness that prevented the adhesion of even tiny water droplets, thus demonstrating that the fish-scale bio-inspired nanostructures are promising superhydrophilic/superhydrophobic materials that might be useful for their anti-icing, anti-fogging, anti-corrosion, anti-bacterial and self-cleaning properties.
Mechanical properties of the bio-inspired nanostructures

One of the most important functions of natural fish scales is to provide sufficient mechanical protection for the inner soft organs. The fish-scale bio-inspired inorganic nanostructures are also expected to provide significant mechanical tolerance that meets the requirements for multifunctional applications. The mechanical properties of the fish-scale bio-inspired nanostructured coatings were examined via nanoindentation testing. Figure 5 shows the nanoindentation behavior of the fish-scale bio-inspired nanostructured coatings with different preferred scale orientations. Figures 5a–c display typical load–displacement curves of the fish-scale bio-inspired nanostructured coatings with parallel scales (coating with the (002) preferred orientation), with slightly tilted scales (coating with the (002) preferred orientation but mixing with small portion of tilted nanostructures) and with tilted scales (coating with the (101) preferred orientation), respectively. The loading–unloading curves obtained for the bio-inspired coatings are also presented in Supplementary Figure S5. Clearly, the differences in the preferred orientation of the scale-like nanostructures resulted in entirely different mechanical responses of the bio-inspired coatings. The bio-inspired coatings with parallel and flat scales (Figure 5a and Supplementary Figure S5(a)) and the coatings with slightly tilted scales (Figure 5b and Supplementary Figure S5(b)) allowed much deeper displacement compared with the 200 nm maximum that was obtained for the coating with tilted scales (Figure 5c and Supplementary Figure S5(c)), and the clear residual depths observed after unloading confirmed the plastic nature of both nanostructures.

The variations of the hardness ($H$) and elastic modulus ($E$) of the bio-inspired coatings as functions of the maximum displacement are plotted in Figures 5d–f. By analyzing the variations in the hardness and the elastic modulus of the coatings with parallel scales and slightly tilted scales, it was found that the values of $H$ and $E$ both decreased exponentially and reached a plateau when the displacement was $>500$ nm, indicating that the indenter had reached the softer inner layers. The large loading–unloading loops in Figures 5a and b and Supplementary Figure S5(a–b) indicate low plastic deformation resistance along the direction perpendicular to the exposed planes (the [001] direction). In other words, the parallel scales with plentiful...
thin edges are softer and more favorable for plastic deformation during the indentation process, which results in low values of $H$ ($H_{\text{mean}} = 0.70 \pm 1.17 \text{ GPa}$) and $E$ ($E_{\text{mean}} = 7.44 \pm 9.36 \text{ GPa}$) of the parallel scale coatings (Figure 5d) and slightly higher values of $H$ ($H_{\text{mean}} = 2.83 \pm 3.21 \text{ GPa}$) and $E$ ($E_{\text{mean}} = 32.28 \pm 27.54 \text{ GPa}$) for the coatings with slightly tilted scales (Figure 5e). When the indentation direction was mostly perpendicular to the [101] planes (as shown in Figure 5f), the tilted scales exhibited much higher values of hardness ($H_{\text{mean}} = 3.55 \pm 1.62 \text{ GPa}$) and elastic modulus ($E_{\text{mean}} = 40.86 \pm 13.50 \text{ GPa}$). Moreover, the values obtained on the tilted coatings did not sharply decrease with increasing displacement, and the scales were much more resistant to mechanical deformation. The higher hardness of the bio-inspired coatings with tilted scales can be attributed to their stacking mode; in this mode, the scales are packed against each other very closely, and insufficient space is present to allow deformation and cracking of the scale-like nanostructures. The measured hardness and elastic modulus of the bio-inspired coatings with tilted scales coincide well with reported data on nanostructured ZnO thin films, which are indicated by the dashed lines in Figure 5.36–39 Many pop-in events can be found in the curves describing the indentation of the bio-inspired thin films with tilted scales (Figure 5c). The tilted scales were much harder and tougher than the parallel scales, indicating that the mechanical properties of the hierarchically ordered nanostructures depend not only on the crystal structure of the material but also on the stacking mode.

On the basis of the nanoindendation results, it is concluded that the fish-scale bio-inspired nanostructures, especially those with parallel scales, possess the capability to dissipate the energy of mechanical damage and present damage-tolerant features; thus, the nanostructures can protect the inner weak substrates from catastrophic failure. The damage tolerance of the coatings can be further confirmed by the energy dissipated during mechanical deformation (Figures 5g–i), that is, the area enclosed by the loading-unloading curves. The amount of mechanical energy dissipation can provide a quantitative evaluation of the damage energy absorbed during mechanical damage and can indicate the capacity of the materials to prevent catastrophic failure resulting from mechanical impact.11,10 The bio-inspired coatings with parallel scales presented much larger mechanical loops than the reference ZnO nanocrystalline thin film and the bio-inspired coatings with tilted scales. As shown in Figures 5g–i, the bio-inspired coating with parallel scales and the coating with slightly tilted scales exhibited significant energy dissipation, on the order of hundreds of pJ, and reached average values of 163.86 ± 161.99 and 103.67 ± 151.09 pJ, respectively. Nevertheless, the mean energy dissipation for the bio-inspired coatings with tilted scales was only 22.5 ± 6.1 pJ. The values obtained for the coating with tilted scales are quite close to the energy dissipation of the reference ZnO nanocrystalline thin films that lacked a preferred orientation, as shown by the dashed lines in the figures (−25 pJ).36–37 Obviously, the mechanical properties of the fish-scale bio-inspired nanostructures are strongly correlated with the scale-stacking mode, and bio-inspired nanostructured coatings with tailored mechanical properties can be designed to meet the requirements of various application environments.

CONCLUSION

In summary, inspired by multifunctional fish scales with swift stimulus-responsive abilities, we developed inorganic nanostructured isolated particles and nanostructured coatings with surface morphologies that mimic those of natural fish scales via a facile self-assembly approach. The fish-scale bio-inspired nanostructured coatings feature tunable light refraction and reflection, tunable surface wettability and damage-tolerant mechanical properties. The salient properties of the fish-scale bio-inspired multifunctional nanostructures hold promise for use in the following applications: (i) optical coatings, sensing or lens arrays in reflective displays, packaging, advertising and solar energy harvesting; (ii) self-cleaning surfaces, including anti-smudge, anti-fouling and anti-fogging, and self-sterilizing surfaces; and (iii) mechanically/chemically protective coatings. Moreover, the facile self-assembly method allows the low-cost and large-scale fabrication of these bio-inspired nanostructures. Therefore, we believe that the fish-scale-inspired nanostructured microspheres and coatings represent a new platform for developing novel functional materials for use in ‘smart’ structures and other applications.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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