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Biosynthesis of cathodoluminescent zinc oxide replicas using butterfly (*Papilio paris*) wing scales as templates

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ABSTRACT

Papilio paris butterflies have an iridescent blue color patch on their hind wings which is visible over a wide viewing angle. Optical and scanning electron microscopy observations of scales from the wings show that the blue color scales have very different microstructure to the matt black ones which also populate the wings. Scanning electron micrographs of the blue scales show that their surfaces comprise a regular two-dimensional array of concavities. By contrast the matt black scales have fine, sponge-like structure, between the ridges and the cross ribs in the scales. Using both types of scale as bio-templates, we obtain zinc oxide (ZnO) replicas of the microstructures of the original scales. Room temperature (T=300 K) cathodoluminescence spectra of these ZnO replicas have also been studied. Both spectra show a similar sharp near-band-edge emission, but have different green emission, which we associate with the different microstructures of the ZnO replicas.

1. Introduction

Template-directed synthesis is an ideal approach to replication, for the fabrication of inorganic materials with predetermined structural properties. There are a number of biological species that have been used as templates for the formation of such ordered inorganic structures, amongst these are bacteria [1] and fungal colonies [2], wood cells [3], diatoms [4], echinod skeletal plates [5], pollen grains [6], eggshell membranes [7], human and dog's hair [8], and silk and spider silk [9].

Recently, the use of butterfly wing scales as templates has attracted attention. Cook [10] and co-workers undertook pioneering studies of the synthesis of "silicified" peacock butterfly wings, which is a beautifully iridescent 2D-photonic bandgap material. In their work, silicate minerals were deposited in the inner spaces of the wing scales with a further coating (100–150 nm thick) being deposited on the surfaces by chemical vapor deposition. Silver et al. [11] fabricated nano-structured phosphorescent materials using butterfly wings as templates. Li et al. [12] created ordered lead lanthanum zirconate titanate structures with micrometer and submicrometer periods using dipping or impressing sol–gel process. These processes do not replicate the wing scales, in fact they are really just negative casts. Zhang et al. [13] suggested that they had fabricated a three dimensional photonic crystal structure using *Mopho menelaus* wing scales as templates. By using zinc nitrate water-free ethanol or water-ethanol solution as precursor, we fabricated ZnO microtubes and ZnO replicas using wing scales as templates in our previous work [14,15]. Rather than depositing the precursor on the surface of the scale, zinc ions penetrate into the smallest gaps within the scale, causing the ridges and micro-ribs themselves to be mineralized *in situ*. Based on electron microscopy analysis, the method we used would appear to give better wing scale replicas than either the sol–gel process or the nano-particle infiltration method mentioned above.

ZnO is a particularly attractive material for luminescent nanoparticle applications due to its wide band gap (3.37 eV), large exciton binding energy (60 meV), resistance to high energy irradiation, stability to intense ultra-violet illumination and low toxicity. Various ZnO nanostructures with different morphologies have been fabricated, such as nanotubes [16], nanowires [17], nanorods [18], nanoribbons/belts [19], and tetrapods [20]. For potential device applications and further improvements in ZnO nanostructures, the characterization of the optical properties of individual nanostructures is of some significance. In this present study we undertook cathodoluminescence (CL) imaging and spectroscopy for this purpose, the aim being to evaluate the relationship between the microstructure of the ZnO replicas and their CL properties. All the samples were synthesized in the same manner.

2. Experimental

The butterfly wings we chose as our bio-template are from *Papilio paris* Linnaeus (subfamily *Papilionidae* of the family *Nymphalidae*), which were kindly supplied by Shanghai Natural Wild-insect Kingdom Co., Ltd. Analytic grade reagents HCl, NaOH, $Zn(NO_3)_2$ and alcohol were purchased from the Shanghai Chemical Company. In this work, we adopted the same approach used before [15] to produce ZnO replicas from biological templates.

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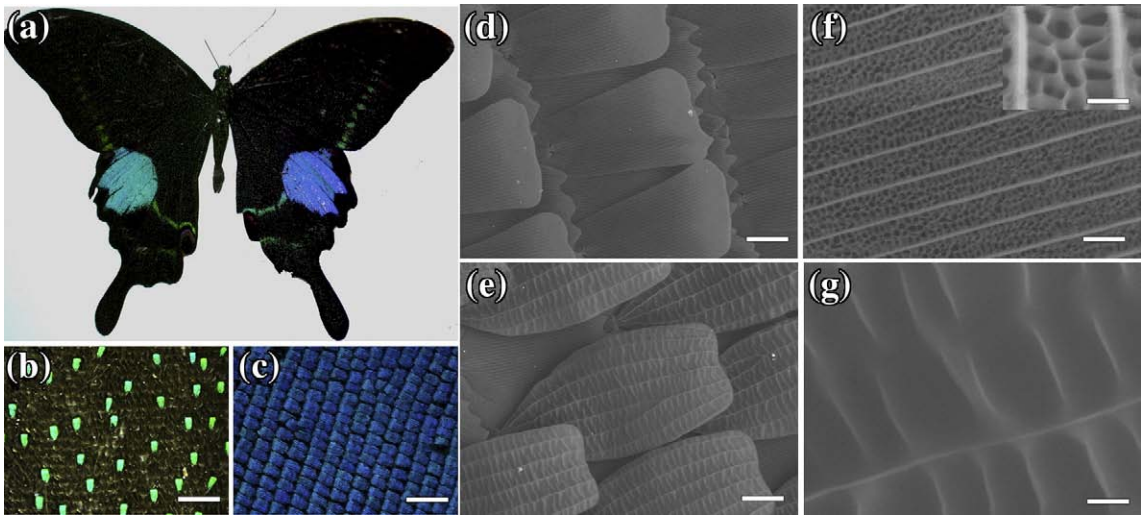

Fig. 1. Photograph and FESEM images of *Papilio paris* wing scales. (a) Photograph of *Papilio paris*, the right wing's photograph is taken at different angles; (b) and (c) Digital microscope images of the matt black regions and the metallic patch on the hind wings, respectively. (d)–(g) Low vacuum scanning electron micrograph (LVSEM) images of black scales and blue ones. The inset image shows the high magnification of Fig. 1(f). Scale bars (b) and (c) 200 um; (d) and (e) 50 μm; (f) and (g) 5 μm; inset 1 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A digital microscope (Keyence VHX 100) was used to observe the morphologies of the original butterfly wing scales at low magnification and a scanning electron microscope (Jeol JSM-6380LV) was used to observe the morphologies at high magnification. Transmission electron microscope investigations were conducted on a JEOL JEM-100CX and CL measurements were performed in a scanning electron microscope (FEI

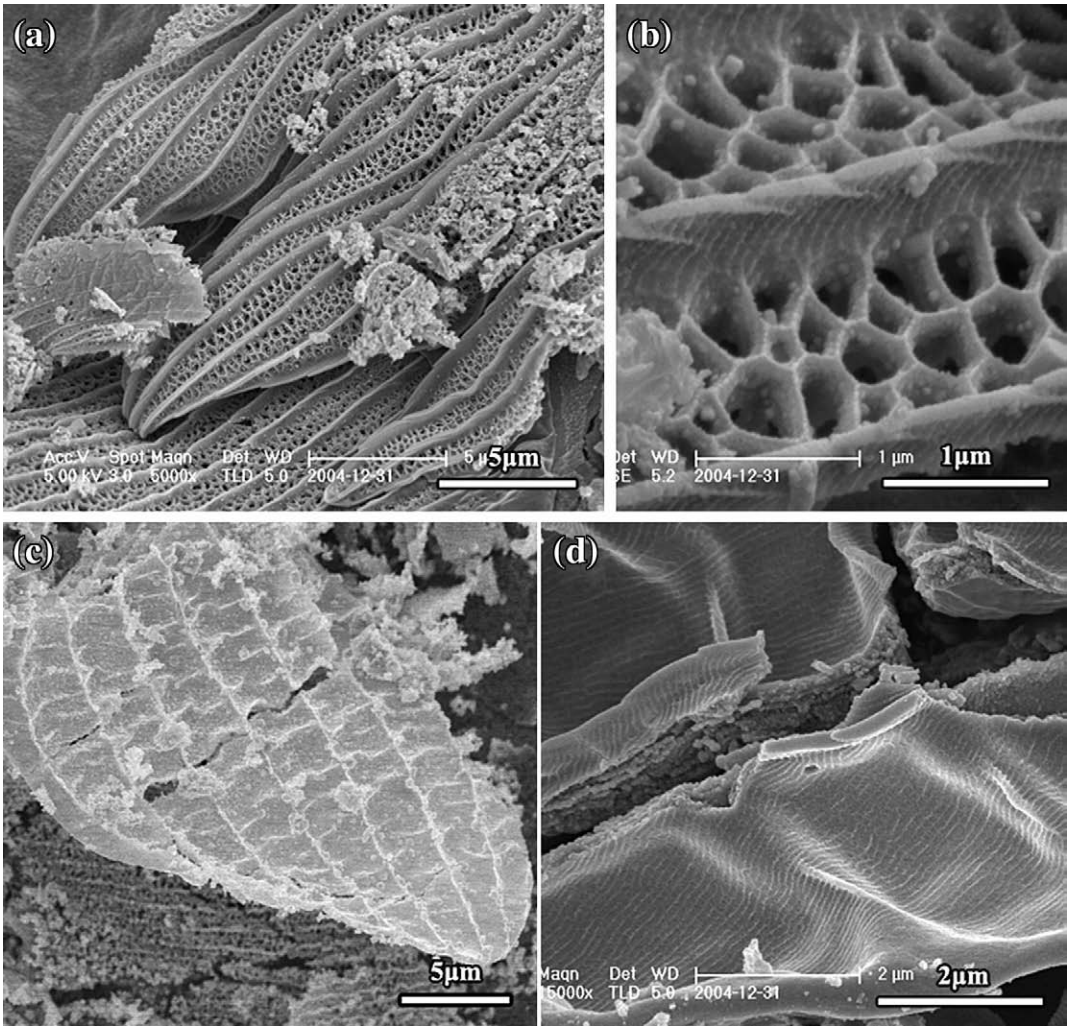

Fig. 2. FESEM images of BAR and BUR. (a) Low magnification image of the BAR; (b)High magnification image of the BAR; (c) Low magnification image of the BUR; (d) High magnification image of the BUR.