Investigation of manifestation of optical properties of butterfly wings with nanoscale zinc oxide incorporation

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Abstract In this work, microstructural and optical characteristics nanoparticles of wings of Tailed Jay (Graphium Agamemnon) butterfly were studied before and after treating it in a precursor solution of zinc acetate and ethanol. We speculate that the butterfly scales are infiltrated with ZnO nanoparticles owing to reduction of Zinc hydroxide under ambient condition. The ZnO butterfly scales so produced were characterised using optical microscopy, UV-Vis reflectance spectroscopy, and electron microscopy etc. From the reflectance spectra, we could see that after treating it in the solution, optical properties vary. We anticipate that this change may be due to the formation of ZnO nanoparticles as well as the loss in periodicity due to the chemical treatments, which could be assessed from the SEM micrographs.

1. Introduction
Nature provides ample number of biological systems which display beautiful patterns and colours. The study of the microstructures in these systems gives hints about fabricating artificial photonic structures [1]. These biological systems provide novel platforms and templates so as to accommodate interesting inorganic materials. There are several biomaterials, such as bacteria [2] and fungal colonies [3], wood cells [4], diatoms [5], echinoid skeletal plates [6], pollen grains [7], eggshell membranes [8], human and dog’s hair [9] and silk [10] which have been used for the biomimetic synthesis of a range of organized inorganic make ups that has potential in catalysis, magnetism, separation technology, electronics and photonics. Several research groups have worked on different novel methods to produce such inorganic materials using natural templates. In the recent years, butterfly wings as templates have gained enormous attention because of its complex yet extraordinary architecture. The wings of some of the butterflies contain natural photonic crystals which may be modified using semiconductor oxide nanoparticle incorporation. Gary Cook et al. have worked on the synthesis of silicify butterfly wings [11]. In his work, silicate minerals were deposited in the inner space of the wing scales and a heavy coating (100–150 nm thick) was produced on the surfaces by a chemical vapour deposition technique. Zhang et al. have worked on fabricating ZnO replica using butterfly wings and have claimed to fabricate three dimensional photonic crystals. But no prominent photonic properties are found to be observed [1, 12]. Zinc oxide is a wide band gap semiconductor oxide, which exhibits intense light emission features in the UV-Vis range of the spectra. There are also reports on the modification of the Photonic Band Gap (PBG) and the emission pattern of ZnO infiltrated PCs.
The present work highlights incorporation of ZnO nanoparticles in the forewing of Tailed Jay butterfly and subsequently, microstructural morphology and optical properties of the wings have been discussed.

2. Experimental: Materials And Methods

2.1. Material:
The material chosen for our work is a Tailed Jay butterfly (Graphium Agamemnon) of papilionidae family belonging to G.agamemnon species. The butterfly wing has black appearance with isolated green patterns distributed over it. We opted for the forewings of the butterfly, which measures typically of 4.3 mm and 2.3 mm in length and width respectively. The dimensions of the complete wing are approximately 8 mm and 5 mm in length and width respectively. The beautiful coloured bright patterns have motivated us to undertake this study. The digital image of the butterfly has been shown in Figure. 1.

2.2. Synthesis of ZnO incorporated butterfly wings:
The forewing of the butterfly is sectioned carefully for ZnO incorporation. Firstly, the wings were pretreated before growing ZnO particles on it [13]. The pretreatment process involves three steps: The wing slice was dipped in 5% HCl solution for 3 h. After washing carefully with deionised water, it was again dipped in a solution of 10% NaOH at 100°C for 4h. The wing slice was rinsed properly with deionised water before dipping it in a precursor solution prepared by dissolving zinc acetate [Zn(O2(C2H5))2.2H2O] in absolute ethanol in a closed vessel for 24 h. The wing was gently collected from the solution, washed with deionised water and dried in air, by placing the wing between two glass slides to keep the wing flat. The dried wings are then placed in an oven at 200°C for about 1 h. This would help growth of nanoparticles through reduction of zinc hydroxide available on the template.

3. Characterisation
The optical micrographs and digital images for the pure and ZnO grown forewings of the Tailed Jay butterfly are shown in Fig 1. The complex architecture of the butterfly wing was initially viewed through an inverted optical microscope (Leica DM IL LED) by employing a 20x objective. In this microscope, transmitted light is considered for optical imaging. The optical properties of the butterfly wings and ZnO grown wings are investigated through the UV-Vis-NIR spectrophotometer (2450 Shimadzu Co.) and an optical microscope. Further, scanning electron microscopy (SEM, JEOL, JSM 6390 LV) is employed for detailed microstructure analysis of the given specimen. Prior loading into
the SEM chamber, the surface of the specimen was subjected to a few nm Pt coating to avoid charging effect during imaging. The images are captured at different magnifications to reveal microstructural details along with the chitinous elements that make up the scale structures.

4. Results And Discussions

4.1. Imaging through optical microscopy
The digital image of the specimen is shown in figure 1 (a). Figure 1(b) depicts the optical micrograph of the green part of the butterfly wing. Figure 2 (c, d) presents the digital image and the optical image for the part of the wing which was dipped in the precursor solution. The properly arranged cover and ground scales are found to be disrupted and the periodicity is found to be lost due to chemical treatment.

4.2. Measurement through UV-Vis-NIR reflectance spectroscopy:
The optical properties of the pure butterfly wings and ZnO infiltrated butterfly wings are studied through UV-Vis spectroscopy. The reflectance spectra of the butterfly wings before and after ZnO inclusion are as shown in figure 2.

![Figure 2. Reflectance spectra for the pristine butterfly wings and after ZnO loading.](image)

The reflectance spectra of the untreated as well as ZnO loaded butterfly wings exhibit a small peak at ~ 485nm and a distinct peak at ~ 539 nm. The green coloured patterns distributed over the highly pigmented black surface corresponds to 539 nm peak and this may be as a result of the unique microstructure in the wing scales. After ZnO is grown over the wing surface, there is an alteration in the reflectance spectra with featureless characteristics and a linear rise towards the higher wavelength regime. This change can be attributed to the change in surface morphology due to ZnO loading as there is a strong probability that nanoparticle incorporation might fill in the spaces between cross ribs and ribs, leading to change in refractive index and hence in the optical properties [1]. Non observation of peaks can also be due to the loss of periodicity, as we observe from the OM image. We anticipated that ZnO nanoparticles would be decorated on the wing, but formation might not be perfect, as a result, leaving with Zn$^{2+}$ ions. Also, there is a probability that ZnO nanoparticles might have formed but some of the unreacted sites may be left with only Zn$^{2+}$ ions.

4.3. Microstructural analysis of surface structure:
The SEM micrographs for the untreated and ZnO loaded butterfly wings are shown in figure 3.
From the SEM micrographs, we see the presence of cover scales and ground scales distributed uniformly all over the wing surface. The ground scales lie directly above the wing lamina whereas the cover scales overlay these [14]. The length and width of the cover scales are 131.80 µm and 44 µm respectively. Further magnification reveals the presence of different components that make up the scales. The longitudinal ridges are distributed parallel all along the wing surface. The cross ribs are interconnected in such a manner so as to form a gyroid type structure and are cross linked to each other [15]. The approximate dimensions of the windows between the ribs and cross ribs are 568 nm and 409 nm in length and width; respectively. The width of the longitudinal ridges is approximately 340 nm. When the treated wing scales undergo heat treatment, the cover and ground scales are seen to be broken and changes are also observed in the dimensions of the scales and the scale components. The gyroid type structure takes more of honeycomb like structure after ZnO incorporation. The nanopores become quite clear and they shrink to approximately 509 nm and 314 nm in length and width respectively. Although precise chemical composition of the scales is not known, all insect cuticles primarily contain chitin layer and other protein groups like resilin or scleretin. Surface functional groups on the chitin layer such as hydroxyl and amino groups may act as centres and bring Zn\(^{2+}\) ions close through hydrogen bond formation [16]. Table below shows the change in scale parameters before and after ZnO loading and the calculated shrinkage factor.

4.4. Correlation between surface morphology and optical properties

The reflectance properties are closely related to the surface morphology of the incident material. As a result of ZnO incorporation on the wing surface, wing scales are found to be deformed, and the dimension of the scale components varies. This alteration will have a strong effect on the optical properties. The distinct green peak that is found in pure butterfly wings is found to disappear in the ZnO grown wings. The arrangements of the ridges, cross ribs on the cover scales of the wing are in

![Figure 3. SEM micrographs for the (a) pristine butterfly wings (b) ZnO loaded wings.](image-url)
such manners that form a multilayer structure, with the dimensions of the nanopores approximately of 568 nm, which may be attributed to the green colour of the wing. Previous studies have reported that the cover scales are mainly responsible for the reflected colour, whereas the ground scales contains the pigment melanin, where it absorbs almost all of the transmitted light [14], thus appearing black.

Table 1: Scale parameters calculated from SEM image.

| Scale parameter                      | Before ZnO loading (L1) µm | After ZnO loading (L2) µm | Shrinkage factor [1- (L2/L1)] % |
|--------------------------------------|-----------------------------|---------------------------|---------------------------------|
| Length of cover scale                | 131.78                      | 116                       | 11.9                            |
| Width of cover scale                 | 44                          | 63.8                      |                                 |
| Width of longitudinal ridge          | 0.34                        | 0.33                      | 2.9                             |
| Spacing between longitudinal ridges  | 1.5                         | 1.37                      | 8.66                            |
| Spacing between two cross ribs       | 0.636                       | 0.40                      | 37                              |

5. Conclusions
In this work, we made an attempt to understand the effect of ZnO incorporation on the wings of Tailed jay butterfly belonging to Papillionidae family and G. agamemnon species. The optical properties studied through UV-Vis reflectance spectroscopy for the pure as well as treated samples gave us an idea regarding the alteration in optical properties as a result of nanoparticle incorporation and also due to loss in periodicity. The scale components are found to shrink due to chemical and heat treatment, with different percentages, with a highest of 37% for the spacing between the cross ribs. This decrease in the dimension of the nanopores as a result of ZnO incorporation contributes to the change in the reflectance spectra. Thus, this study shows how structure and optical properties change as a result of nanoparticle inclusion.

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