Materials Suitable for preparing Inorganic Nanocasts of butterflies and other insects

2015 J. Phys.: Conf. Ser. 619 012050

(http://iopscience.iop.org/1742-6596/619/1/012050)

Materials Suitable for preparing Inorganic Nanocasts of butterflies and other insects

J. Silver, G R Fern and T G Ireland

Centre for Phosphors and Display Materials, Wolfson Centre for Materials Processing, Brunel University, Kingston Lane, Uxbridge, Middlesex, UK

Jack.silver@brunel.ac.uk

Abstract. Replication of 3D-structures, in particular those that have a periodic modulation of a dielectric material at optical wavelengths and below have proven very difficult to fabricate. The majority of such replication techniques are complex or use moisture sensitive precursors requiring the use of for example a glove box. Here we demonstrate how an air stable supersaturated europium-doped yttrium nitrate phosphor precursor solution has the ability to easily impregnate a structure or produce a cast yielding faithful replicas composed of $Y_2O:Eu^{3+}$ after a final short annealing step. New replicas of Lepidoptera (moth) wing scales using field emission scanning electron microscopy, structures down to 10 nm have been imaged. Moreover as these replicas are made of phosphors, their luminescence in some cases may be modulated by the internal periodic modulation built into their structures. In this work we will discuss more recent results on the use of the phosphors for making nanocasts of moth wing scales and show a range of beautiful pictures to show what the method can achieve.

1. Introduction

The class of insects belonging to the order Lepidoptera is a large, varied range of butterflies and moths containing at present approximately 175,000 known species, with upward estimates including unclassified species numbering 250,000 (more than any other type of insects except beetles). Various estimates have put a figure of approximately seven percent of all life forms for the members of this order. There are around 15,000 butterfly species, the rest of the order are moths, (the number of species increases as new species are discovered) [1,2]. The inexact nature of the science of taxonomy in conjunction with the introduction of various new techniques such as DNA sequencing [3,4], microbiology [5] and larval morphology [6] has resulted in reclassification of the relationships between species.

Butterflies and moths have different wings than those of other insects [7]. They are formed from a transparent double epithelial chitin membrane which is crisscrossed with tubular veins which nourish and hold their structure in place, in addition to transporting insect blood (haemolymph), functioning as part of the insect's respiratory system and providing ducts for their nervous system [8-11]. The wings have a covering of overlapping scales attached by a single stem on both their upper and lower sides. The size of butterfly and moth wing scales differ from species to species, and individual scales are approximately 50 to 100 μm in width by 150 to 200 μm in length. There are a small number of butterflies that have areas of their wing that are not covered by scales such as *Danais tytia*, *Greta-oto (glasswinged butterfly)* and *Graphium ridleyanus*. There is a great diversity in wing scale form yet they all share a common structure. The upper layer of a wing scale consists of longitudinal ridges

connected by transverse crossribs creating an open rectangular netlike structure. These openings may contain various structures or hollow air spaces depending on the butterfly species. Columnar pillars called trabeculae occur within the upper and lower layers of the scale. Lattices of microribs and ridge-lamellae, in these structures are found along the longitudinal ridges, in these structures the iridescent colours of the Lepidoptera are created by preferential reflection/diffraction of certain wavelengths of light [12].

The soft interior of Lepidoptera members are supported by a hard exoskeleton of chitin and a matrix of fats and proteins, chitin is found in the wing scales of these insects in the form of fibrils approximately three nanometers in diameter [13]. The chitin fibrils within the Lepidopteran wing scales are composed of molecular chains crosslinked together by hydrogen bonding endowing the material with exceptional toughness [14]. The Lepidoptera wing usually has two types of scale; (a) cover scales that contain the structural colour (iridescent blues, greens and metallic lustres) and pattern elements of their individual design and (b) ground scales that are generally pigmentary forming the background of the wing scales (producing black, brown, red and yellow colouring) [9]. Lepidopteran wing scales in common with other macrochaetes are grown from specialised epidermal hair producing cells (trichogen) that have a socket enclosed in a tormogen cell [15]. The pedicel of each individual scale is attached to these sockets. These wings have been evolved by many species to suit their many survival strategies and pre-reproductive approaches.

The majority of butterfly wings display vibrant, highly saturated colours (produced at the sub-micrometer level by the intrinsic structure of these wing scales) which are used as communication signals for attraction, repulsion, or camouflage [9]. Some butterfly species such as *Morphidae* and *Papillo* have developed exceptionally striking iridescent colours (within the blue to green spectral colour range); this phenomenon has attracted extensive studies resulting in both an accurate classification and a deep understanding of the colour generation by the hierarchical micro-structuring of the wing scales. Whereas *Lycenid* butterlies produce iridescent colours from photonic bandgap (PBG) crystal-like structures situated in lower part of the wing scale [16,17], other species exhibit varying shades of black, brown or a range of spectral colours (in some cases going beyond the visible into the ultraviolet), as well as displaying optical polarization effects. The different effects of structural colour and colour as perceived from pigments and dyes are obvious in butterfly and some moth wings. Structural colours are vibrant and do not fade over time, in contrast to many pigments and dyes which fade at rates that depend on their colour fastness. This is because the structural colour of such wings arises from light interference that is caused by its periodic structure, in contrast to the colour of a pigment or dye molecule that is due to the selective absorption of light.

The thrust of our work was to explore the feasibility of producing casts of nanostructures that had known photonic properties using inorganic metal oxides and find ways to eventually mass fabricate these three-dimensional PBG structures. As introduced above Lepidoptera wing scales and hairs are highly structured natural photonic materials and were chosen herein and previously [18-21] as templates to fabricate replica structures out of phosphor materials. A Y_2O_3:Eu^{3+} precursor solution was used previously to prepare Lepidopteran wing scale [18-22] and hair replicas successfully and further studies will be presented in this work. There are two reasons for the choice of yttrium oxide as a lattice for these structures: (a) it has been synthesised into a range of structures; and (b) it is an important technological material.

Herein we report biomorphic mineralisation replication studies on a moth wing scale template replicas using optical, field emission gun scanning electron microscopy (FEGSEM).

Materials and Methods

2.1. Specimens

The Lepidoptera specimen used for these biomorphic mineralisation replication studies was the east African sunset moth *Urania Croesus* from Mafia Island, Tanzania.

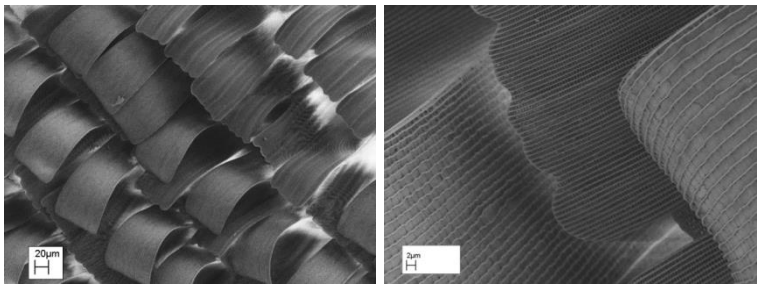
2.2. Chemicals
Yttrium and europium oxides (Neomaterials, UK, 99.99%), nitric acid (Merck, UK, AnalaR), ethanol (Merck UK, AnalaR 99.5%) and titanium ethoxide (Sigma Aldrich, UK). All chemicals were used without further purification.

2.3. Preparation of Y_2O_3:Eu^{3+} Precursor Infilling Solutions, infilling and annealing of Moth Wing Scales
An in-depth description of the preparation, infilling and annealing of the moth wing scales (and butterflies) is described elsewhere [46].

2.4. Electron microscopy
The original *Urania croesus* moth wing scale samples (before any treatment) and the post-annealed Y_2O_3:Eu^{3+} (moth) replicas were imaged using a field emission gun scanning electron microscope (FEGSEM), (Zeiss, Germany). The samples were mounted on carbon tabs fixed to aluminium pin stubs and coated with a sputter coated layer of gold to eliminate charging of the specimens.

3. Results and Discussion

FEGSEM images from a topside forewing section of the natural *Urania Croesus* specimen's green wing scales before replication treatment are presented in figure 1. The iridescent curved cover scales formed at their base by air-cuticle multilayers are apparent in figure 1 (a) (to the left) to the right of the image the flatter dentated terminated ground scales that in this species produce the black or darker scales are apparent. In figure 1 (b) a higher magnification study illustrating the extreme curvature of the iridescent cover scales.

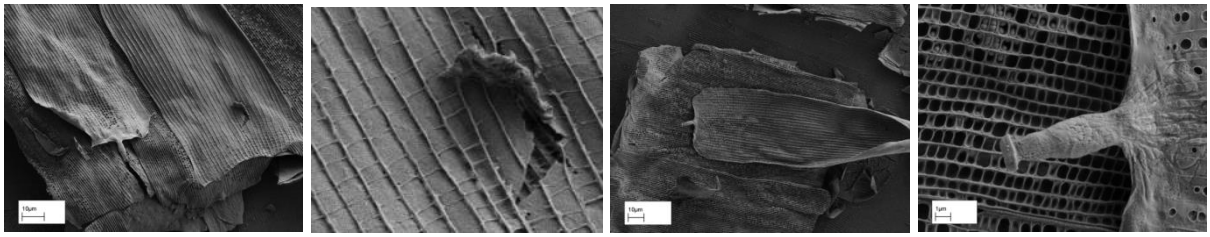


(a) (b)

Figure 1: FEGSEM images of *Urania Croesus* topside forewing scales (a) scale bar 20 µm, (b) scale bar 2 µm.

In figure 2 FEGSEM studies showing faithful Y_2O_3:Eu^{3+} *Urania Croesus* topside forewing scale replicas that are overlaying one another are shown. In figure 2 (a) are cover scales on top of ground scales, that have had their curvature flattened due to the pressure applied during infilling the scales with Y_2O_3:Eu^{3+} precursor solutions. The upper scale to the left of the image has a complete pedicel replica which had become detached from the epithelial wing membrane before infilling, the uppermost scale to the right has a small tear on its surface. In the higher magnification study in Figure 2 (b) it is possible to see through the tear to the scale below which has been replicated indicating that the Y_2O_3:Eu^{3+} precursor solution has permeated through the entire wing scale section. From these initial studies it can be seen that there is some shrinkage between groups of scales whilst the scales themselves appear to be intact, there is minor wrinkling upon their surfaces. The curling at some edges observed in figure 2 (a) and (c) may be due either to the separating of the quartz slides after infilling with the precursor solutions or the flattening of the curved cover scales, if it was due to the heat treatment more scales would display this feature. Also in figure 2 (c) is another Y_2O_3:Eu^{3+} replication of a complete scale pedicel of which a higher magnification is presented in figure 2 (d), fine radiating vein-like structures and flat bottomed furrows can be seen as the pedicel starts to

transform into the scales longitudinal ridges (it is normal that they are not fully formed at this position). Also the crossribs are not mature at this transformation zone, they form circular openings that lead into the scale interior instead of rectangular voids [12].



(a) (b) (c) (d)

Figure 2: FEGSEM images showing Y_2O_3:Eu^{3+} replicas of *Urania Croesus* topside forewing scales (a) stacks of ground and cover scales, scale bar 10 µm, (b) expansion of previous image showing faithful replication of ground scale below tear in cover scale, scale bar 1 µm (c) is another group of wing scales, scale bar 10 µm, and (d) an intact pedicel, scale bar 1 µm.

4. Conclusions

The work described here has shown that the nanostructures of Lepidoptera can be replicated using precursor solutions of europium-doped yttrium nitrate solution, by a faithful replacement of the chitin structures forming the wing scale. We have previously shown that it is possible to look at a range of spectral properties of such casts [18-22].

5. References

[1] Michael G P 2009 Biodiversity of Lepidoptera – in *Insect biodiversity: Science and society* (Foottit R G and Adler P H, Wiley-Blackwell, Oxford, UK)
[2] MacRae I J 2007 *Can. J. Environ. Ed.* **13** 11-29
[3] Herbert P D N and Gregory T R 2005 *Syst. Biol.* **54** 852-59
[4] Wiemers M and Fiedler K 2007 *Front. Zool.* **4** (8) 1-16
[5] Hammer T J, McMillan W O and Fierer N 2014 *PLoS ONE* **9** (1) 1-8
[6] Goldstein PZ and DeSalle R 2011 **33** 135-47
[7] Scoble M J 1992 *The Lepidoptera: Form, function and diversity* (Oxford University Press, Oxford, UK)
[8] Boggs C L, Watt W B and Ehrlich P R 2003 *Butterflies: Ecology and evolution taking flight* (University of Chicago Press, Chicago, USA)
[9] Ghiradella H and Radigan W 1976 *J. Morph.* **150** 279-98
[10] Ghiradella H 1991 *Appl. Opt.* **30** 3492-500
[11] Ghiradella H 1998 Hairs, bristles and scales – in *Microscopic anatomy of invertebrates* **11A:** Insecta (ed. Locke M Wiley-Liss New York) pp 257-87
[12] Vukusic P, Sambles J R and Ghiradella H 2000 *Photonic Sci, News* **6** 61-6
[13] Merzendorfer H and Zimoch L 2003 *J. Exper. Biol.* **206** 4393-412
[14] Dutta P K, Dutta J and Tripathi V S 2004 *J. Sci. Ind. Res.* **63** 20-31
[15] Ghiradella H and Butler M W 2009 *J. R. Soc. Interface* **6** S243-51
[16] Morris R B 1975 *J. Ent. (A)* **49** 149-54
[17] Biró L P, Bálint Z, Kertész K, Vértesy Z, Márk G I, Horváth Z E, Balázs J, Méhn D, Lousse V and Vigneron J P 2003 *Phys. Rev. E* **67** 021907
[18] Silver J, Ireland T G and Withnall R 2005 *J. Modern Opt.* **7** 999-07
[19] Withnall R, Ireland T G, Martinez-Rubio M I, Fern G R and Silver J 2002 *J. Mod. Opt.* **49** 965-76
[20] Withnall R, Martinez-Rubio M I, Fern G R, Ireland T G and Fern G R 2003 *J. Opt. A-Pure Appl. Opt*. **5** S81-5
[21] Silver J, Withnall R, Ireland T G, Fern G R and Zhang S 2008 *Nanotechnology* **19** 095302
[22] Withnall R, Silver J, Ireland T G, Zhang S and Fern G R 2011 *Opt. Laser Technol.* **43** 401-9