Composite Biomimetic Nanomaterials

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Introduction

Tagging an object it makes it easier to identify and those who have come into contact with it. These can be best designed with biotemplates. 20-100mm pollen grains (found in seed plants) appeared over 300 million years ago and allowed reproduction. The wall of the pollen is designed to protect it from desiccation and contains biopolymer – sporopollenin and an outer exine structure. Another bio-template to use is butterfly wings. The wings of *Thaumantis diores* are naturally occurring platelet structures and their photonic properties have been fine-tuned by TiO_2 overcoating and replication.

TiO_2 has been used to overcoat polymer [1] and silica spheres [2]. The former templates have been removed [3] by heating the composites at 500°C in air for 2 h.

Experimental

In 2007 some of the present authors discussed sol-gel routes to stable bio-templated oxide replicas [4]. Here we wanted to explore the thermal stability of CVD-derived TiO_2-overcoated samples. The pollen of *lilium longiflorum* was treated with the vapour of titanium isopropoxide under reflux for 0h (i.e. uncoated), 0.5h, 1h or 2h, after which the surface alkoxides were allowed to react with moisture in the atmosphere to give surface layers of TiO_2. Immersion of the pollen grains in the alkoxide ($0.5cm^3$) in ethanol ($50cm^3$) was also assessed. In this the mixture was then shaken vigorously for 10 s and then allowed to stand for 0.5 h. The composite nanotags were then filtered out of the solution and dried in a vacuum oven at 40° C overnight.

Results and Discussion

The thermal stability of the uncoated and coated pollen was examined by thermogravimmetric analysis (TGA; TGA Q500 Version 6.7 Build 203) during heating at 10°C/min to 800°C. SEM-EDX was undertaken on a Hitachi S-3200N fitted with an Oxford Instruments energy-dispersive X-ray detector on samples (1mg; uncoated or coated with TiO_2 by CVD for 0.5h) held in well in

2mm deep wells in 1 cm^2 brass plates and heated to 20, 100, 200, 300, 400 and 500° C for 45min. EDX showed that the host pollen grain templates contained significant K.

TGA showed that the untreated pollen grains lost significant weight up to 550^{o}C, but that 0.5h TiO_2 overcoating retarded the high temperature weight loss of the pollen a little. Interestingly, higher levels of TiO_2 overcoating seemed to accelerate the weight-loss of the pollen grains at lower temperature.

Figure 1 shows the symmetric TiO_2-repliacs of the pollen grains emerged after treatment at 500^{o}C in air and retained the original characteristic reticulated structure of the pollen. The uncoated pollen did not survive intact.

The use of butterfly wings in producing asymmetric TiO_2 replicas is also explored. The wings of *Thaumantis diores* are naturally occurring platelet structures and their photonic properties have been fine-tuned by overcoating and replication with TiO_2 using immersion methods [5]. Here a reflux CVD method was preferred. The overcoated wings lost weight in heating in air up to 580^{o}C leaving a titania replica.

References

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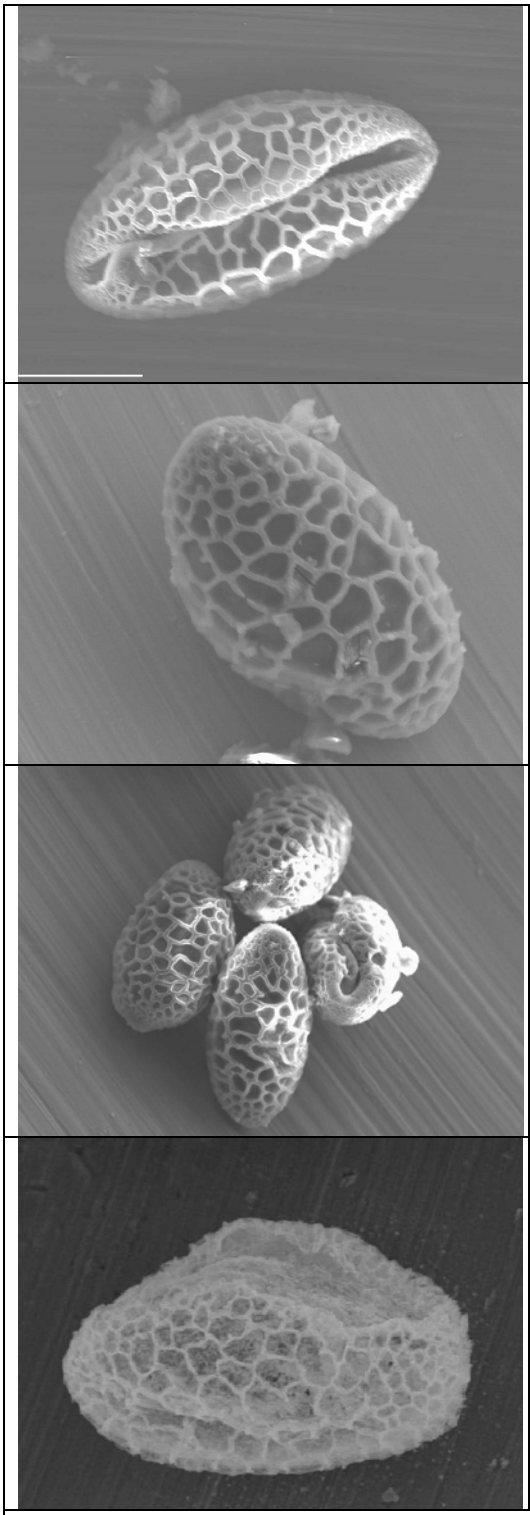

Figure. 1 Micrographs of pollen grains overcoated with TiO_2 (0.5h) during heating in air to various temperatures. Scale bar 30μm