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Bioinspired fabrication of magneto-optic hierarchical architecture by hydrothermal process from butterfly wing

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ABSTRACT

We developed a green solution to incorporate nano-Fe_3O_4 into the hierarchical architecture of a natural butterfly wing, thus obtaining unique magneto-optic nanocomposites with otherwise unavailable photonic features. Morphological characterization and Fourier Transform Infrared–Raman Spectroscope measurements indicate the assembly of Fe_3O_4 nanocrystallites. The magnetic and optical responses of Fe_3O_4/wing show a coupling effect between the biological structure and magnetic material. The saturation magnetization and coercivity values of the as-prepared magneto-optic architecture varied with change of subtle structure. Such a combination of nano-Fe_3O_4 and natural butterfly wing might create novel magneto-optic properties, and the relevant ideas could inspire the investigation of magneto-optical devices.

1. Introduction

Biological structures on the external surfaces of animals, insects, and plants are remarkably sophisticated, with amazing abilities to perform multiple functions and comply with numerous, often conflicting demands. For example, adhesive force provided by gecko foot-hairs [1,2], self-cleaning effect on the lotus leaves [3], and the striking optical effects caused by beetles [4], are all related to the unique micro- and nanostructures on the surfaces [5–7]. Inspired by nature, these fascinating structures have been employed as templates to create exquisite replicas from a variety of metal oxides and noble metals.

Butterfly wing is one of the best examples, which owns the largest number of species and each species possess the unparalleled structure and color. The wings are made of small scales forming two or more layers over the wing membrane like rooftiles [8]. The subtle microstructures of the scales form two main optical effects, multi-layers that produce thin-film interference colors and lattices that produce diffraction colors. Studies show that iridescent butterfly scales are structurally colored, relying upon the interaction of light with detailed architecture to produce their color [9]. The diversity of colors and subtle hierarchical structures on the butterfly wing boom the biotemplating investigation. In 2003,Cook et al. [10] synthesis silica wing by chemical vapor deposition. Later, phosphor wing [11], ZnO microtube wing [8,12], Al_2O_3 hollow wing [9], SnO_2 wing [13], and CdS/wing [14] were developed using solution casting, dipping process, atomic layer deposition, sol–gel process, and hydrothermal process, respectively. However, to the best of our knowledge, little work has been done for combine magnetite with butterfly wings.

As a natural magnetic material, magnetite (Fe_3O_4) has attracted a great deal of research interest due to its extensive applications in various fields, such as biomedicine [15], catalysts, high density magnetic recording media, and medical diagnosis [16]. Inoue et al. [17] reported that one-dimensional magneto-photonic crystals composed of dielectric and magnetic materials exhibit remarkable magneto-optical properties accompanied by a huge enhancement in their Kerr and Faraday rotations,and giant enhancement of nonlinear magneto-optical response [18] was observed. The magneto-optical effect is crucial, which determines the read-write speed of the magnetic recording materials [19] and sensitivity of the magnetic switch [20]. A series of natural photonic crystals based on natural butterfly was reported [9,21], where it was shown that natural butterfly wings have unique features that modulate visible light. In comparison with known natural photonic crystals, we consider magnetic material with natural photonic crystals more effective because their photonic properties are sensitive to magnetic and electric fields and they have the potential for use in a variety of optoelectronic devices.

Herein, two species of butterflies with different wing scale patterns are chosen as template for the fabrication of magnetite magneto-optic architecture. We studied two conventional biotemplate oxide synthesis routes for magnetite architecture fabrication: Air Oxidation Method (AOM) and Vacuum Reduction Method (VRM). However the oxidation of ferrous ion in atmosphere can be hardly control in AOM and the adsorption ferric ion in ethylene glycol solution is extremely low. On the basis of summarizing the failed experiences, we present a significant

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advance on the up two method using ferrous sulfate heptahydrate as the only iron source and hydrogen peroxide as the oxidant. We develop the one-step synthesis of hierarchical microstructures of magnetite magnetic optical architecture from butterfly wing via Hydrothermal Method (HM). The as-synthesized sample exhibits increase magnetic properties with the ultrafine structure. Since hierarchy porous structure could participate in tuning nano-Fe_3O_4 magneto-optical properties, the combination of nano-Fe_3O_4 and wing scales would be promising and significant. This investigation may also provide helpful information for the synthesis of other magnetic materials with peculiar structures.

2. Experimental

2.1. Materials

The butterfly wing scales chosen as biotemplates are butterflies Euploea mulciber (subfamily Danainae of the family Danaidae) and Papilio paris (subfamily Papilioninae of the family Papilionidae), which were purchased from a butterfly garden in Shanghai. All reagents used in this experiment were of analytical grade without further purification.

2.2. Fabrication process

We developed three different methods for the fabrication of magnetic wings as shown in Table 1.

Air Oxidation Method (AOM): the natural wings were treated by dipping in 8% NaOH ethanol solution at 60 °C for 1 h, then the specimen were immersed into a closed vessel containing a solution of the precursor, which were prepared similar to the work reported in [22], after that, the specimen were heated at the temperature range 250–300 °C.

Vacuum Reduction Method (VRM): the pre-processing of natural wings were the same as in the first method. Afterwards, the treated wings were dipped into 2 mol/L $Fe(NO_3)_3 \cdot 9H_2O$ ethylene glycol solution for 10 h at room temperature, finally the specimen was annealed at 400 °C under vacuum for 2 h.

Hydrothermal method (HM): First, the wings were dipped in an activation medium, which was prepared by dispersing ethylenediaminetetraacetic acid (EDTA) in dimethylformamide (DMF) with a volume ratio of about 1:10, for 6 h at 110 °C to get the EDTA/DMF activated wing. Second, $FeSO_4 \cdot 7H_2O$ (2.502 g) was dissolved in 20 ml deionized water, 10 ml of polyethylene glycol 20,000 solution (50 gL^{-1}) was added to the $FeSO_4 \cdot 7H_2O$ solution and stirred, followed by 10 ml of diluted ammonia (2.5%). After that, 0.27 ml H_2O_2 was added into the solution slowly while stirring. The mixture was stirred for 5 min to obtain a homogeneous solution. The final procedure was carried out as follows: the activated wing was immersed into the above solution, then transferred the system into an autoclave, and stored in a sealed autoclave at 160 °C for 5 h. When finished, the autoclave was naturally cooled down to room temperature. The treated wing was taken out and rinsed thoroughly and dried to harvest the target sample Fe_3O_4/wing.

2.3. Sample characterization

The as-synthesized samples were examined by FTIR measurements using a Bruker EQUINOX 55 instrument. X-ray diffraction (XRD) measurements were carried out with a Bruker-AXS X-ray diffractometer system by applying CuKα radiation. The investigations of the morphologies and microstructures of the products were carried out using a FESEM (FEI XL30). The FESEM was operated under 5.0 kV (Acc.V). Transmission electron micrographs (TEM), high-resolution transmission electron micrographs (HRTEM), and selected area electron diffraction (SAED) patterns were obtained on a JEOL JEM-2100F instrument. Reflection spectra were measured on a UV spectrometer (Cary 500) and an integrating sphere. The magnetization measurements were performed using a Vibrating Sample Magnetometer (VSM, Lakeshore 7407) at room temperature to investigate the magnetic properties.

3. Results and discussion

According to the thermodynamics of Fe_3O_4 synthesis, a complete precipitation of Fe_3O_4 takes place when a molar ratio of Fe^{3+}:Fe^{2+} is 2:1. As ferrous ions can be easily oxidized in air, scientists adopted various protective measures in the process of synthesis Fe_3O_4, such as feeding with inert atmosphere [23], annealing under vacuum [24], and using poisonous as protective layer [25]. Herein, we tried three different harmless and environmentally friendly methods for the preparation of magnetic wings.

In the Air Oxidation Method (AOM), we designed partial oxidized ferrous chloride by air to get magnetite oxide according to the work [22]. The X-ray diffraction patterns of the samples heated at different temperature was shown in support information (Figure. S1 supporting information). Obviously, there is no Fe_3O_4 diffraction peaks and the samples appears dark brown, which is not consistent with the results displayed in the work [22]. This may be owing to the instability of ferrous chloride, which was gradually oxidized by the air in the 10 h dipping process. Considering it is hard to control air oxidation, we adopted the vacuum environment and cut off the influence of atmosphere. In the Vacuum Reduction Method (VRM), we seriously control the ratio of reducing agent and oxidant. We immerse the pre-treated wings into $Fe(NO_3)_3 \cdot 9H_2O$ ethylene glycol solution for the in situ synthesis of magnetite nanoparticles. As revealed in Fig. 1(a), the diffraction peaks at $2\theta = 35.32$, 56.72, and 62.24 were assigned to (3 1 1), (5 1 1), and (4 4 0) planes of Fe_3O_4. The peaks of the spectrum in Fig. 1(a) are broadened and it can be explained by the carbon residues and the thin coating layer of magnetite in the final product, which can be confirmed by the FESEM results show in Fig. 3(b). The two routes mentioned above were typical methods for biotemplate oxide synthesis, unfortunately, the results turned out to be frustrating. Remarkably, we demonstrated a novel hydrothermal method based on the previous experiment failure to achieve unique magneto-optic nanocomposites as shown in scheme 1. In this route, ferrous sulfate heptahydrate was used as the only iron source and hydrogen peroxide as the oxidant, and the aqueous solution provides a golden condition for preventing oxidation of ferrous ion from air. According to the diffraction peaks measured by X-ray diffraction (XRD) exhibited in Fig. 1(b), the as-prepared magnetite had a spinel structure with a

Table 1
Procedure factor of different method synthesis magnetic butterfly wing.

Methods	Pre-processing	Medium ingredients	Final treatment
AOM	8% NaOH ethanol solution 60 °C, 1 h	0.1 mol $FeCl_2 \cdot 4H_2O$,0.1 mol citric acid monohydrate, 100 ml ethanol	sintering under air
VRM	8% NaOH ethanol solution 60 °C, 1 h	2 mol/L $Fe(NO_3)_3 \cdot 9H_2O$ ethylene glycol solution	vacuum sintering
HM	EDTA/DMF 110 °C, 6 h	0.009mol $FeSO_4 \cdot 7H_2O$, 20 ml deionized water, 10 ml of PEG 20000 solution (50 gL-1), 10 ml of (2.5%) ammonia 0.27 ml H_2O_2	hydrothermal method