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An ancient method-inspired route for fast fabrication of 'PbS bird feathers'

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Abstract

Many studies have been carried out to thoroughly understand the colorization mechanisms of bird feathers. However, most of the methods used so far are time-consuming (in days) and involve rather complicated steps (5 to 12). Here, we report a rapid way of producing 'PbS bird feathers'; this method is inspired by a hair-dyeing method used in ancient Egypt 4000 years ago. The complete synthesis route comprises only two steps and can be completed within 2 h, with the original morphologies of bird feathers well preserved. This method has potential to be extended to the fast fabrication of other functional sulfides which are too complicated to fabricate otherwise.

Introduction

For the past several decades, structural coloration mechanisms of bird feathers,[1] which bear various short-range-ordered microstructures,[2] have attracted much attention, especially with the rapid development of photonic crystals.[3–5] To date, the relationship between feather structures and coloration[6,7] has not yet been fully clarified, hindering the development of novel feather-inspired applications in controlling light propagation. Since coloration behaviors are drastically related to the refractive index (RI) of materials, some groups have attempted to directly replicate the original feather structures of β-keratin into high-RI materials (e.g., SiO_2,[2] TiO_2,[2] ZnO,[8] and CdS[9]) to test a broad range of present-day theoretical hypotheses. However, these sol–gel methods are time-consuming (in days)[8] and contain many steps (5 to 12).[2,8,9] Inspired by a cosmetic preparation route developed in ancient Egypt more than 4000 years ago,[10] we report in this paper a rapid way of producing 'PbS bird feathers'; this method comprises only two steps (sulfhydrylation plus in situ PbS formation) and can be completed within 2 h. Since the cations of Pb, Cd, Ag, and Cu can easily combine with sulfur to form sulfides with small solubility products, our 'feather-dyeing' methods have potential to be extended to the fast fabrication of other sulfide replicas of feathers with RI ranging from 3.92 (PbS) to 1.45 (CuS).

Experimental

To synthesize PbS feathers, 50 mg cleaned white flight feathers[11] of domestic pigeons (*Columbia livia domestica*) were first immersed in a 50 mL 2,3-dimercaptosuccinic acid (DMSA)[12] and ethanol solution (20:1, w/v) for 30 min in a water bath with the temperature kept at 80 °C, and were then thoroughly rinsed in ethanol and water. The feathers were then transferred into the saturated PbO solution in calcium hydroxide (1:1, w/v)[10] in the water bath at 80 °C for 60 min. The as-synthesized PbS feathers were then taken out and subjected to ultrasonic cleaning for 3 min. It was easily seen that the color of the feathers changed from white to black, as shown in Fig. 1.

Scanning electron microscopy (SEM) images were taken using an FEI FEG 250 scanning electron microscope, which was operated at an acceleration voltage of 20.0 kV and equipped with the capability for energy-dispersive X-ray spectrometry (EDS) analysis (Oxford Instruments, UK 80 mm^2 detector). Samples were subjected to Au sputtering before observation. A high-resolution transmission electron microscopy (HRTEM) study was conducted using an FEI Jeol JEM-2100 (Jeol JEM-2100: JEOL Ltd., Japan) transmission electron microscope (200 kV). X-ray diffraction (XRD) results were recorded using a Rigaku D/max 2550 (Rigaku D/max 2550 (CuKa): Rigaku, Japan) ($Cu_{K\alpha}$) instrument at a scan rate of 4°/min. Fourier transform infrared spectroscopy (FTIR) analyses were conducted using a Perkin Elmer Spectrum 100 instrument (Perkin Elmer Spectrum 100 instrument: Perkin Elmer, Inc.) using samples ground to powder and compressed into KBr pellets.

Results and discussion

It has been reported that ancient Egyptians used to apply PbS nano-particles to dye hair dozens of centuries ago.[10] Although such a method has been discarded previously because

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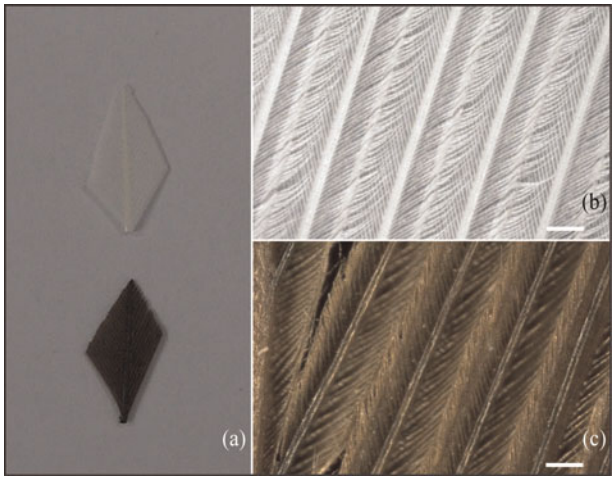


Figure 1. Optical micrograph of original pigeon feathers and PbS feathers. (a) Digital camera image of original pigeon feathers (white) and PbS feathers (black). (b) Optical micrograph of original feathers. (c) Optical micrograph of PbS feathers. Scale bars: 100 μm.

of its toxicity,[13] the facile and time-saving nature of 'hair-dyeing' can still benefit state-of-the-art applications owing to the similarity of the composition (keratin) of human hair and avian feathers.[14] Similar to human hair, bird feathers have a filament–matrix texture.[15] The conformation of the polypeptide chain in the ordered filaments is based on the β-pleated sheet, with the inner surface densely covered by hydrophobic residues and the outer surface populated by charged residues and cysteine ones.[15,16] At a molecular level, there is a high concentration of cysteine residues (7–20% of the total number of amino acid residues).[17] Although sulfur-rich peptides in the matrix that surrounds supramolecular-organized keratin proteins can serve as nanoscale reactors, achieving 'intact PbS feathers' requires more reactive sites to generate continuous PbS layers as compared with a simple hair-dyeing process.[10] In Ref. 10, the sample was simply treated for 3 days. Hence, to improve efficiency, our synthesis route contains a sulfhydrylation process followed by PbS deposition via in situ reaction in solution. For arousing more sulfhydryl sites on the β-keratin of avian feathers, we first chose DMSA dissolved in ethanol as a precursor for sulfhydrylation. Pb^{2+} ions were then provided by the PbO saturated solution in calcium hydroxide.[10] Generally, Pb^{2+} transforms into $Pb(OH)_2$ deposits and impedes the reaction. For the saturated calcium hydroxide solution, it is easy to maintain a constant pH, ensuring stability of the reaction system.

Figure 2 compares the morphologies of as-synthesized PbS feathers with their original counterparts. The main components of the artificial feather were confirmed to be PbS [XRD results, Fig. 3(a)], with an average crystallite size of ~15.6 nm

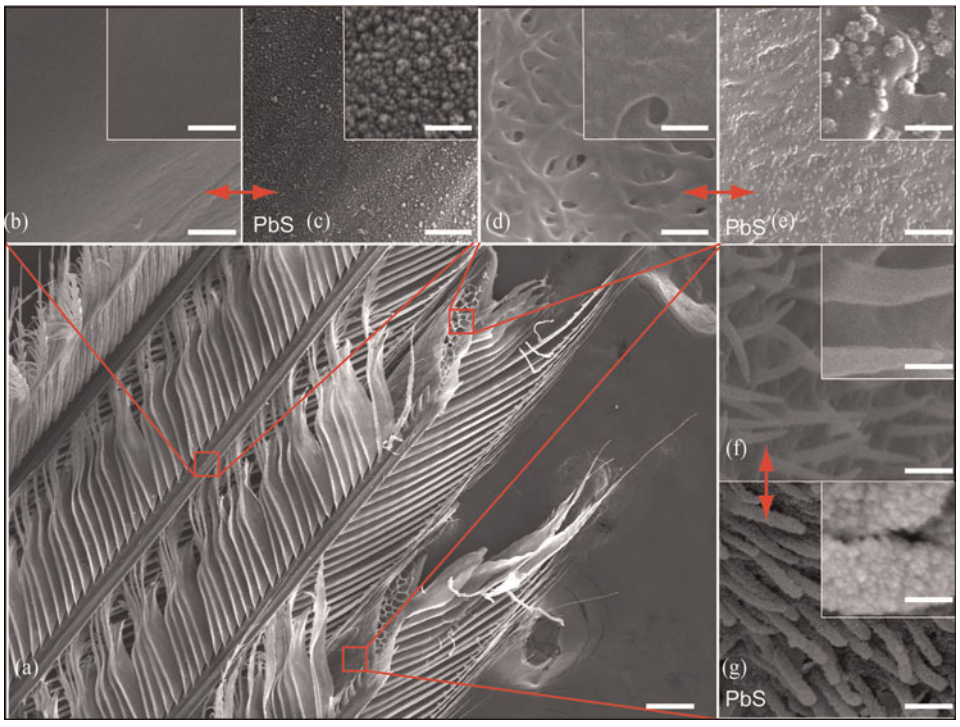


Figure 2. Comparison of the morphologies between original pigeon feathers and PbS feathers. (a) Pigeon feather. (b), (d), (f) Close-up view of the original pigeon feather at (b) barbs, (d) the inner part of medulla, and (f) barb ramus. (c), (e), (g) The corresponding areas of (b), (d), (f) on PbS feathers. Continuous and uniform PbS layers were formed therein. Scale bars: (a) 80 μm; (b)–(g) 800 nm and (insets) 200 nm.

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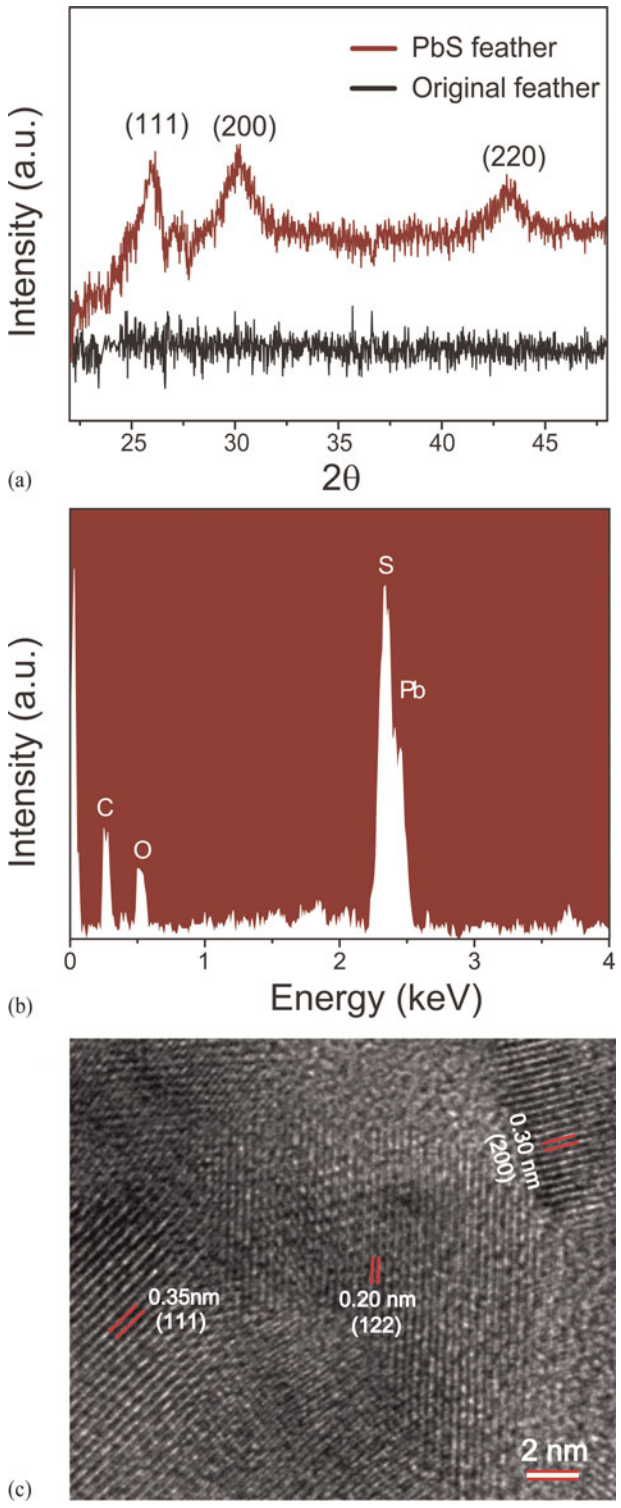


Figure 3. Characterization of as-synthesized PbS feathers. (a) XRD results confirmed the generation of PbS. The average crystallite size of PbS was calculated to be 15.6 nm. (b) EDS results. (c) HRTEM observation of the PbS nano-particles.

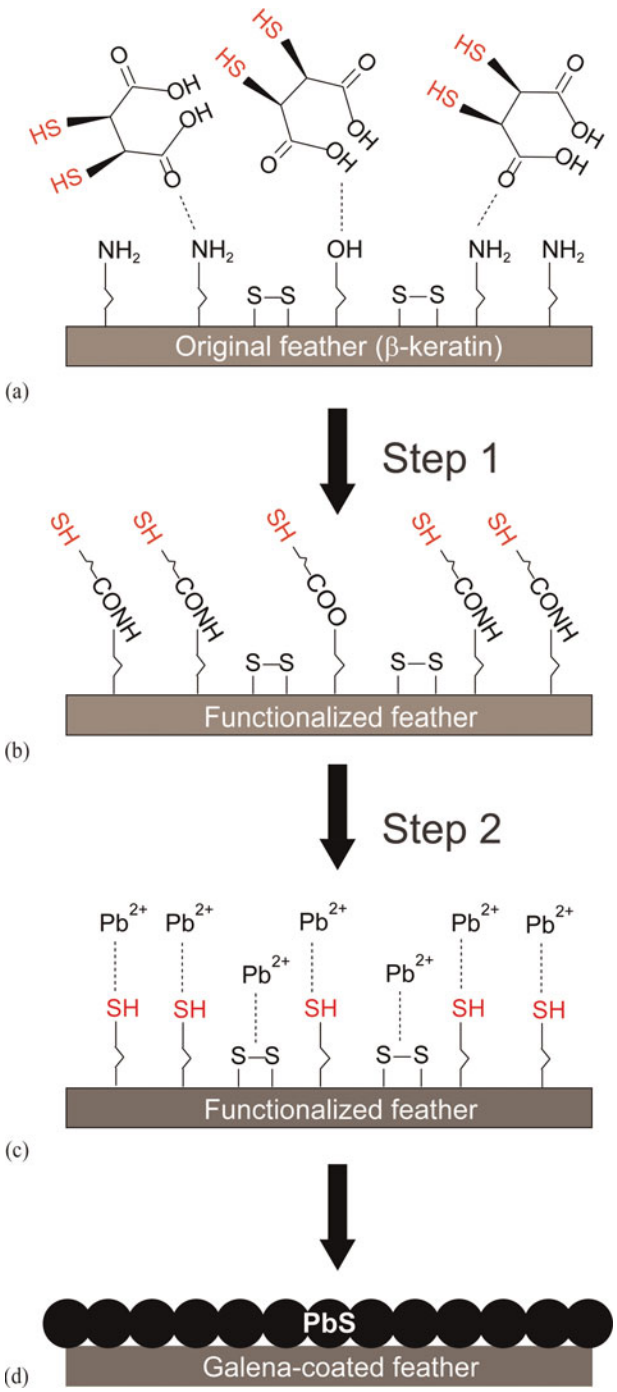


Figure 4. Schematic illustration of the synthesis route. (a) DMSA molecules introduced to original feathers; (b) sulfhydrylated feathers; (c) high affinity of Pb^{2+} for sulfhydryls; (d) as-synthesized PbS feathers. Steps 1 and 2 denote the processes of sulfhydrylation and in situ PbS formation, respectively.

(calculated with the Scherrer formula). Such results were also confirmed by the EDS results [Fig. 3(b)] and also the HRTEM analysis [Fig. 3(c)]. These continuous PbS nano-particles were formed across the feather surface and the PbS

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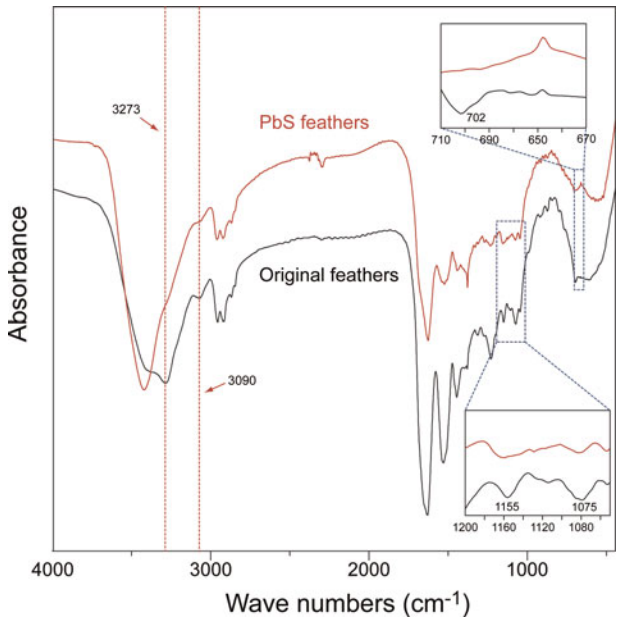


Figure 5. FTIR analyses of original feathers and their PbS counterparts.

feathers faithfully inherited the morphologies of different feather parts. Such conformality could even be observed in the inner parts of the feather structures,[18–20] which were manually cut open for observation after the PbS formation [Fig. 2(e)].

The fabrication mechanism is demonstrated in Fig. 4. We observed the morphologies of the feathers processed under different times and found that it took ˜60 min for the formation of a continuous PbS layer (Supplementary Fig. S1 online). Compared with the reaction time (3 days) reported in Ref. 10, the entire reaction time presented here was only 2 h owing to the sulfhydrylation process and the higher reaction temperature (80 °C versus room temperature in Ref. 10). In step 1 [Fig. 4], amino groups of β-keratin combined with carboxyls of DMSA and thus activated the original feather with sulfhydryls [Fig. 4(b)]. This process could be identified in the FTIR spectra (Fig. 5), where absorption peaks at 3273 and 3090 cm^{-1} that correspond to the vibration of the groups $–NH_2$ and $–NH_3^+$ decreased for the PbS feathers as compared with their original counterparts. Moreover, DMSA contains many carboxyls that tend to react with hydroxyls of feathers [Fig. 4(b)]. As proved by the FTIR spectra (Fig. 5), the peaks at 1155 and 1075 cm^{-1} that correspond to the vibration of the C–OH group decreased for PbS feathers. Such a reaction also helps in the settling of sulfhydryls. In general, the sulfhydryls formed in step 1 presented a large number of reactive positions for in situ PbS formation (Step 2) owing to the high affinity of lead for sulfhydryls [Fig. 4(c)]. As shown in Fig. 5, the peak at 702 cm^{-1} (vibration of C–S) drastically decreased for PbS feathers, which indicated that the element of S in β-keratin reacted with the Pb^{2+}, yielding the PbS nano-particles observed in Figs. 2 and 3.

Conclusions

We have demonstrated a simple two-step process for producing 'PbS bird feathers' inspired by an ancient hair-dyeing method; this method can be completed within 2 h just like what happened in the daily life of the ancient Egyptians. Compared with the methods of previous works, the number of synthesis steps (5 to 12) and time consumption (in days) are significantly lower. The morphologies of original feathers are well preserved owing to the continuous and uniform PbS nano-particle layers. Our method has potential to be extended to the fast fabrication of other functional sulfides with hierarchical microstructures of avian feathers. As one of the bio-templating strategies,[21–25] this work may help promote research into the optical applications inspired by these nature-constructed fine structures, which are effective in controlling light but are too complicated to fabricate otherwise.

Acknowledgments

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Y.T., F.Z. and P.O. have contributed equally to this work.

Supplementary materials

For supplementary materials of this article, please visit http://dx.doi.org/10.1557/mrc.2013.2

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