# Chapter 2
# Toward Metallic Butterfly Wing Scales

## 2.1 Introduction

Till now, natural biostructures have already been converted to a broad range of oxides. To prepare these replicas, metal ions were first coordinated on the surface of biological templates via an impregnation process. The hybrids were subsequently sintered in *air* under high temperatures to form desired oxides, with the original biological skeletons simultaneously removed [1–5].

However, preparing metallic structures based on biotemplates is a rising field. Metal nanoparticles (NPs) have comparatively high-surface energies and low-melting points [6–10]. These natures can cause severe particle aggregation and growth during the sintering process. Additionally, since some metals are prone to oxidation, such an approach of impregnation plus calcinations in air is unsuitable to preparing hierarchically structured metals. Researchers thus coated metal particles onto biostructures using physical vapor deposition (PVD) and chemical vapor deposition (CVD) [11, 12]. Nevertheless, the line-of-sight nature of these vapor deposition methods prevented a complete inheritance of the original three-dimentional (3D) biomorphologies [13].

Hence, all the approaches introduced in this book are based on wet-chemical methods. Some routes were conducted under high temperatures (e.g., $H_2$ reduction) while others were at mild temperatures (e.g., photoreduction). In this chapter, two strategies including $H_2$ reduction and photoreduction will be introduced. Experimental parameters, degrees of morphology preserving, and related mechanisms will be discussed in details to evaluate these two methods.

We select copper (Cu) and silver (Ag) as two target components. These metals have been widely applied due to their good electrical and thermal properties. Presently, different preparation routes for Ag and Cu materials with subwavelength features have been widely reported [13–19]. These methods include calcinations in reducing atmospheres and chemical syntheses conducted under mild temperatures. For example, Z. H Bao et al. first converted the bio-$SiO_2$ of diatom cell walls to Si by application of Mg steam under 650 °C [13, 19]. Then, Ag, Au, and Pd were deposited onto the Si diatoms. The as-prepared metals well-kept the 3D characteristics

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of original biological structures down to a nanometer scale [13]. Therefore, this work has a certain reference for preparing metals with submicrometer superstructures gleaned from butterfly wing scales.

## 2.2 Biotemplate Selection

Lepidopterans (butterflies and moths) have ~174,500 identified species, and their colorizations may be achieved by two ways [20]. One results from wing pigments. Colors generated in this way are also known as pigment colors or chemical colors. The other is aroused by specific optical reflections, which is mainly determined by the interactions between submicrometer-textured wing scales and incident lights. Colors induced by this process are also known as structural colors [21, 22]. For butterfly wings, typical structural colors are usually shining blue and green, while pigment colors are mainly black, white, red, and yellow, etc. In many cases, these two colorization mechanisms can coexist on butterfly wings. Figure 2.1 shows some species of butterflies and moths. Wing colors in Fig. 2.1a–e are structural, while those in f–l are caused by pigments.




**Fig. 2.1** Typical species of butterfly and moth

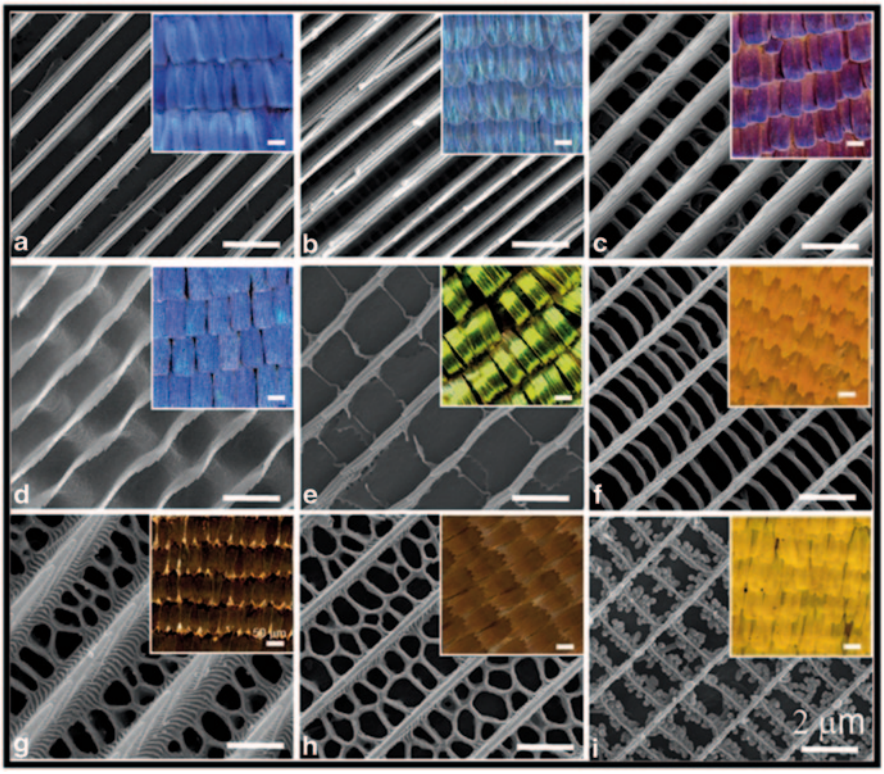



**Fig. 2.2** Scanning electron microscopy (SEM) images of different kinds of butterfly and moth scales are shown in Fig. 2.1. Insets are the corresponding optical microscopy images. Scale bars: 2 μm. (50 μm for inset)

Surface textures of wings exhibited in Fig. 2.1a–e are shown in Fig. 2.2. These scanning electron microscopy (SEM) images were taken from the rectangular areas marked in Fig. 2.1. As shown in Fig. 2.2, the surfaces of butterfly wings are covered with numerous small and flat scales, with a typical size of 100–200 μm in length and 50–100 μm in width. Different scale structures result in deferring structural colors shown in the insets of Fig. 2.2a–e, which are in association with different biological functions. The morphology diversity in wing scales presents researchers enough freedom in selecting appropriate butterfly wing structures as biotemplates to fulfill specific functions.

Herein, two species of butterflies (*Euploea mulciber* and *Papilio paris*) with different microstructures are selected as biotemplates to replicate. These butterflies are widely distributed and easy to collect. The forewing scales of *E. mulciber* have a 3D photonic structure, while those of *P. paris* have a honeycomb structure.

Figure 2.3 shows the digital photo and optical microscopy image of an *E. mulciber* (*Cramer*) butterfly. The dorsal side of its forewing exhibits blue-violet with a metallic luster. When the butterfly dances, its wings may reflect dull purple, bright purple, and bright blue of sunlight in different directions. Previous studies indicated

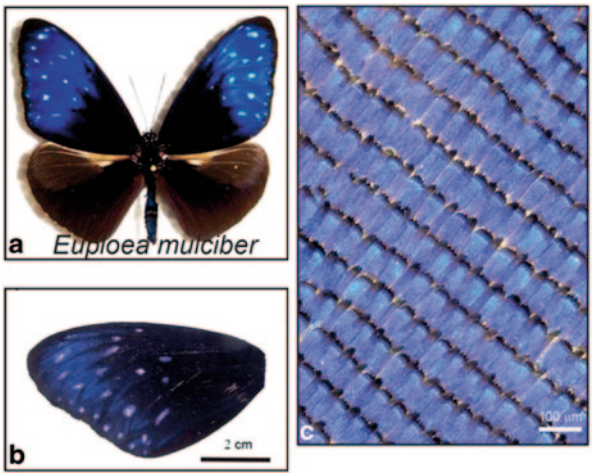



**Fig. 2.3** *E. mulciber*. **a** Whole wing. **b** Forewing of **a**. **c** Optical microscopy image of wing scales on the dorsal side of **b**

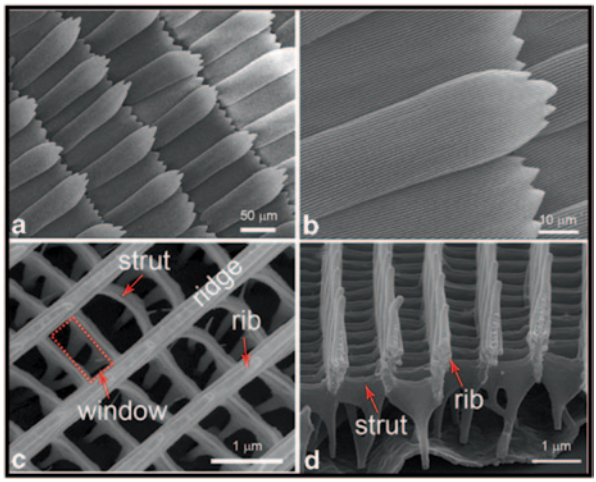



**Fig. 2.4** Scanning electron microscopy (SEM) images of blue scales on the dorsal side of *E. mulciber* forewing. Structural features are denoted in **c** and **d**. (Reproduced with permission [24]. Copyright 2013, American Chemical Society)

that such blue-violet colors come from the photonic structures of scales rather than pigments [23]. These tiling scales are shown in Fig. 2.3c. In comparison, the colors of *E. mulciber* hindwings do not change with the observation directions, suggesting that the brown colors come from pigments.

The surface morphology of individual single scale was further observed using SEM. Since original wings are not conductive, Au sputtering is needed to treat the wing surface before SEM observations. As shown in Fig. 2.4a, the wing surface is uniformly covered by many scales that are orderly arranged in a certain direction, just like tiles on a roof. The size of an individual scale is about $50 \times 100$ μm.

Under higher magnifications, it can be observed that these scales have complex microstructures. There are parallel main ridges with a period of ~1 μm and short

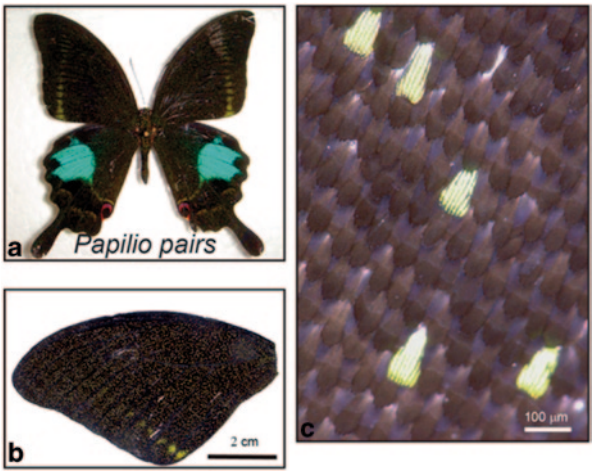



**Fig. 2.5** *P. paris*. **a** Whole butterfly. **b** Forewing of (**a**). **c** Optical microscopy image of wing scales on the dorsal side of (**b**)

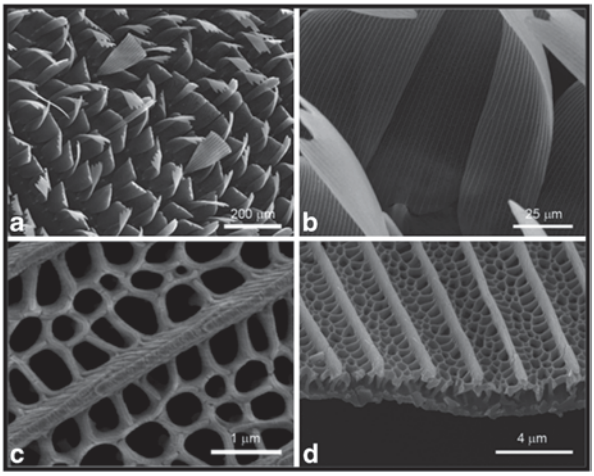



**Fig. 2.6** Scanning electron microscopy (SEM) images of the black scales on the dorsal side of *P. paris* forewing. **c** and **d** are the top-view and side-view SEM images of (**b**), respectively

struts vertical to main ridges, forming the "window" structures marked in Fig. 2.4c. Figure 2.4d shows a cross-sectional view of the scale. Overlapped thin rib structures locate on each individual ridge, with a certain angle against the scale surface. The spacing between adjacent ribs is about 100–200 nm.

The digital photo and optical image of a *P. paris* butterfly are shown in Fig. 2.5. Since its hindwing contains various types of scales, we mainly deal with its forewing (Fig. 2.5b). The dorsal side of the forewing is mainly covered by black scales, with some bright yellow/green scales sparsely distributed within. These yellow/green scales have different contours and shapes to their black counterparts (Fig. 2.5c).

The structure of black scales of *P. paris* were studied with SEM. As shown in Fig. 2.6, fine microstructures of the black scale can be observed. The spacing between two adjacent ridges is about 2.5 μm. Disorderly arranged holes with several

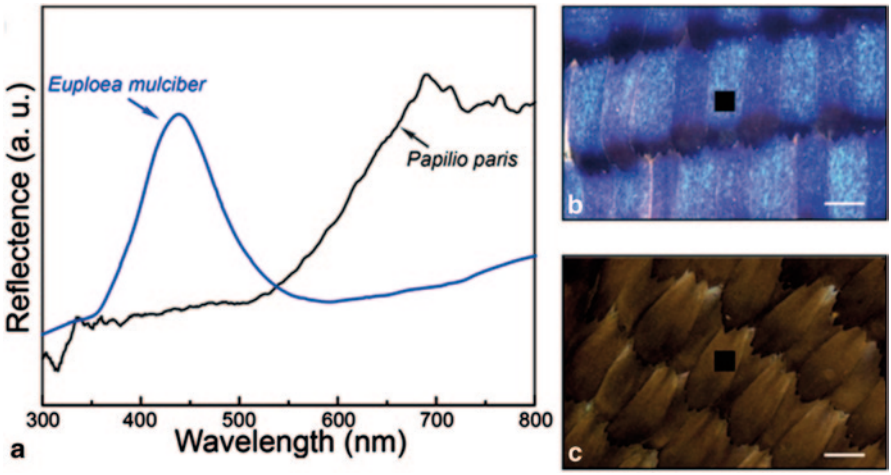



**Fig. 2.7** **a** Reflectance spectra of two natural butterfly wing scales with different microstructures. (**b**) and (**c**) are optical microscopy images of **b** the blue scales of *E. mulciber* and **c** the black scales of *P. paris*. The *black rectangles* denote the selected areas for spectra collection. Scale bar: 50 μm. To prepare these samples, the original butterfly wings were first washed in alcohol for 20 min and dried in air. The treated wings were then placed on a black substrate for measurement. The reflectance spectra was recorded with vertical incidence and reflection

hundred nanometers in diameter are distributed between main ridges (Fig. 2.6c). This "quasi-honeycomb" structure is beneficial to the multiple scatterings of light in scales, making the scales appear darker [25]. In addition, there are no other ordered periodic structures except main ridges (Fig. 2.6c), which might explain why structural colors are not observed on this type of scales.

Both scale structures are important for the survival of the corresponding butterflies and are hard to be manually reproduced. The scales of *E. mulciber* make its forewing surface shine with a blue luster, which is beneficial to courtship and intraspecies communication. In comparison, the quasi-honeycomb structures of black scales can help *P. paris* to absorb solar energy much more effectively, which helps to balance the heat of butterflies [26, 27]. Figure 2.7 shows visible reflectance spectra of the forewings of *E. mulciber* and *P. paris*, respectively. For *E. mulciber* scales, there is a strong reflection peak at ~450 nm, while no reflection peak can be found in reflectance spectra of *P. paris*.

## 2.3 Cu Scale Replicas Prepared via $H_2$ Reduction Under High Temperatures

The first route toward metal scale replicas is via $H_2$ reduction. This strategy can be divided into two steps. First, specific oxide scales as intermediates are prepared via calcinations. Then, these oxide scales are reduced in $H_2$ atmosphere to form

metal replicas. Cu is selected herein as a target component for demonstration. This method can be extended to prepare other transition metals that can be reduced by $H_2$.

### 2.3.1 Sample Preparation

The CuO butterfly wings can be fabricated using an impregnation method described in Ref. [3]. A precursor with $Cu^{2+}$ ions was first prepared. Twenty gram $Cu(NO_3)_2$ $5H_2O$ was dissolved in 50 mL ethanol and stirred for an hour. Ethylene glycol was then added into the $Cu(NO_3)_2$ ethanol solution to form a precursor. Butterfly wings pretreated using the method reported in Ref. [3] were then immersed in this precursor for 24 h. After that, the wings were taken out, rinsed in deionized water, placed on a silicon wafer, and dried in air for 12 h. The wings were then moved into a muffle furnace and heated up to 500 °C with a heating rate of 1 °C/min to remove the biological wing skeletons. CuO butterfly scales were thus obtained.

These CuO scales were then reduced in a $H_2$ atmosphere to obtain Cu wing replicas. To achieve this, CuO wings were put in a furnace with $H_2$ atmosphere. Mixed flowing gas of hydrogen/argon (volume ratio of 4:1) was adopted therein, with a gas flow rate of 200 mL/min and a sintering temperature of 250 °C. After 1 h, the Cu butterfly wings were fabricated.

### 2.3.2 Characterizations

Figure 2.8a and b show SEM images of an as-prepared CuO scale. This CuO scale has a spatial periodic structure that retains the original ridges and the periodic window structures (see Fig. 2.4c). Figure 2.8c shows an energy-dispersive X-ray spectroscopy (EDS) result on the CuO scale. This spectrum suggests that the sample mainly contained Cu, O, and Si, while the detected Si signal originated from the Si wafer. X-ray diffraction (XRD) analysis (Fig. 2.8d) indicates that the synthesized film was mainly composed of crystallized CuO. Based on the Scherrer equation, the CuO grain size was estimated to be ~12 nm by measuring the half-width of the (002) diffraction peak.

Transmission electron microscopy (TEM) analyses on the obtained CuO butterfly wings are provided in Fig. 2.9. Figure 2.9c reveals the lattice fringes of a single NP with a lattice spacing of ~0.252 nm, which corresponds to the (002) plane of CuO. Corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 2.9d. The diffraction rings are well consistent with those of CuO and can be indexed as (110), (002), (200), $(\bar{2}02)$, and (020), respectively.

Figure 2.10 compares a CuO wing with its Cu replica obtained via $H_2$ reduction. The CuO wing exhibits an iridescent characteristic, suggesting that the original photonic biostructures were well-preserved. In comparison, the sample color became

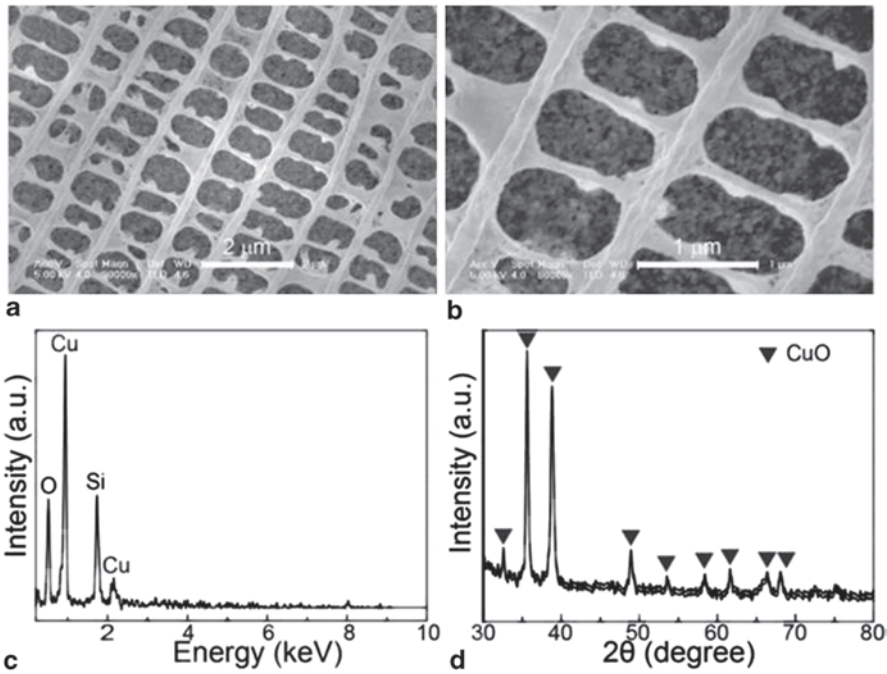



**Fig. 2.8** **a** and **b** scanning electron microscopy (SEM) images of CuO replicas. **c** Energy-dispersive X-ray (EDS) result of CuO replicas. **d** X-ray diffraction (XRD) result of CuO replicas

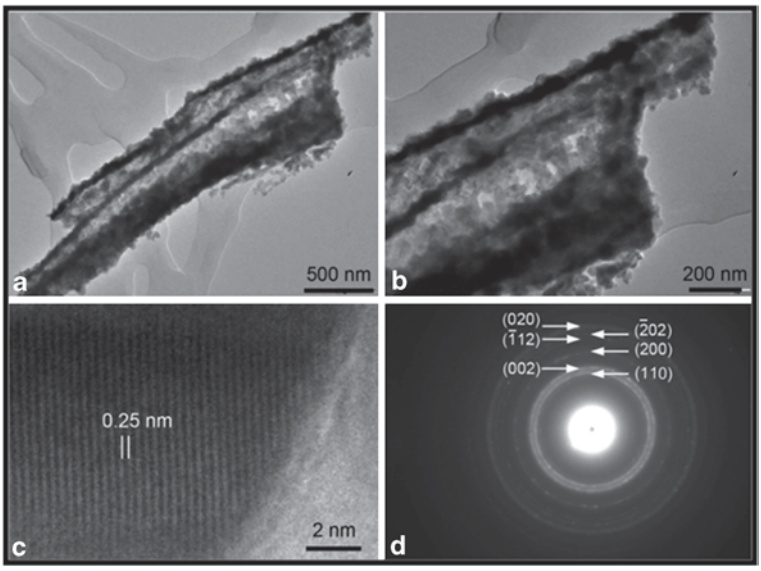



**Fig. 2.9** **a** and **b** transmission electron microscopy (TEM) images of CuO replicas. **c** Lattice fringes of a CuO NP. **d** Selected area electron diffraction (SAED) pattern of the corresponding areas

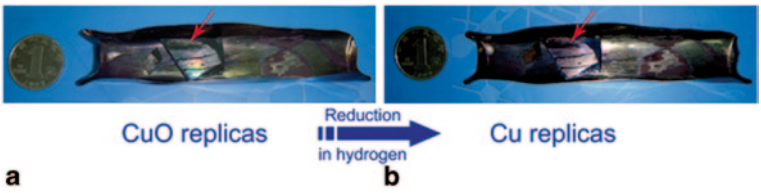



**Fig. 2.10** Optical images of **a** CuO and **b** Cu replicas

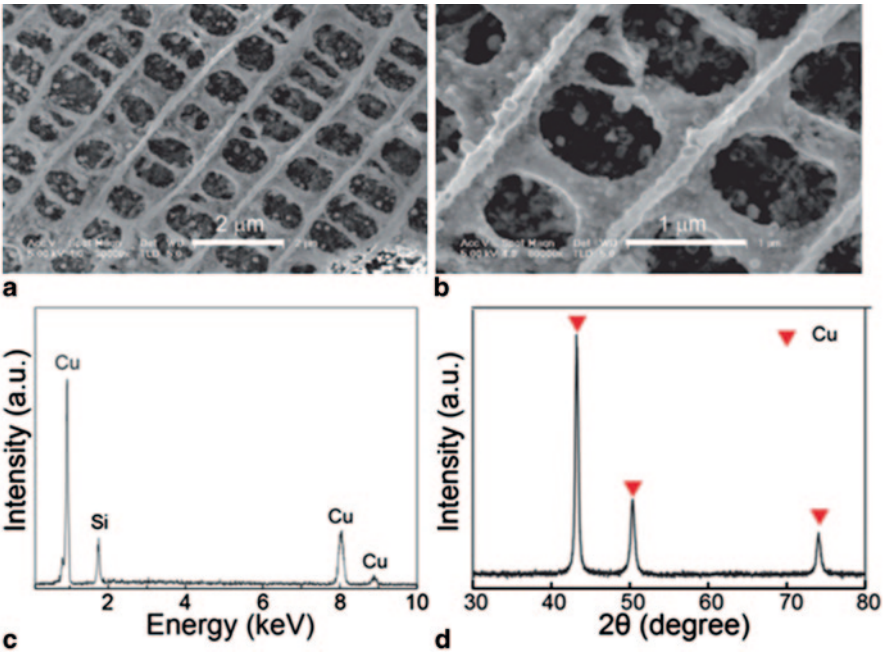



**Fig. 2.11** **a** and **b** scanning electron microscopy (SEM) images of Cu replicas prepared by the reduction of CuO intermediates in $H_2$ at 250 °C. **c** Energy-dispersive X-ray spectroscopy (EDS) result of Cu replicas. **d** X-ray diffraction (XRD) result of Cu replicas

dark red after the calcination in $H_2$, indicating that the CuO has been reduced to metal Cu.

Figure 2.11a and b show the SEM images of an as-reduced Cu scale. As shown in this figure, the Cu scale basically retains the original morphology of wing scales (e.g., main ridges and window structures). However, finer scale structures are not well preserved. Compared with the CuO scale, the surface of the Cu replica becomes rough. Cu NPs grow larger and some parts of the ridges even collapse. Figure 2.11c gives the EDS results of the Cu replicas, which indicates that the sample only contains Cu and Si that originates from the Si substrate. XRD results (Fig. 2.11d) indicate that the synthesized film is crystallized Cu. Using the Scherrer equation, the average grain size of Cu is calculated to be ~30 nm.

These results confirm that CuO scales with the structures inherited from butterfly scales may be obtained with the impregnation plus calcination route. These scales as intermediates can be reduced into Cu in $H_2$ atmosphere. Although the reduced Cu film retained the basic morphology of original wing scales, finer submicrometer superstructures of the scales were destroyed as the Cu grains rapidly grew up under the high-reduction temperature. Hence, it is necessary to find an alternative method to prepare metal butterfly wings under mild temperatures.

## 2.4 Ag Scale Replicas Prepared via Photoreduction Under Mild Temperatures

### *2.4.1 Sample Preparation*

Figure 2.12 illustrates the route towards Ag scale replicas via photoreduction. The method described in Ref. [28] was first used to activate the original butterfly wing template. Selected butterfly wings were immersed in an activation solution (ethylenediaminetetraacetic acid (EDTA) in N, N-dimethylformamide (DMF) with a volume ratio of 1:10) at a temperature of 110 °C for several hours. After that, butterfly wings were washed with an ammonia/ethanol solution. The activated wing templates were then immersed in a $AgNO_3$ water solution. The butterfly wing scales with $AgNO_3$ loaded upon were irradiated under an ultraviolet source (30 W) for 12 h in a closed box. After the photoreduction process, composites of Ag/wing were obtained. A fine needle with a tip diameter of ~30 μm was used to transfer the single wing scale to a Si wafer under a stereomicroscope. We finally removed the chitinous template by dripping a $H_3PO_4$ aqueous solution onto the scale surface, keeping the sample at room temperature for 72 h, and rinsing it with distilled water.

### *2.4.2 Formation Mechanisms*

The original butterfly wing is mainly composed of chitin and a small amount of proteins [29]. Chitin is a polymer of 2-(acetylamino)-2-deoxy-D-glucose ($C_8H_{13}NO_5$).

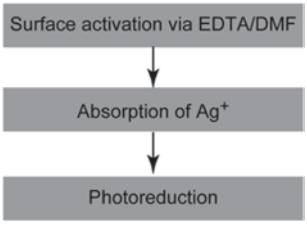



**Fig. 2.12** Fabrication processes for Ag butterfly wing scales

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