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Preparation and characterization of keratin and chicken egg white-templated luminescent Au cluster composite film

Yao Xing, Hongling Liu, Weidong Yu*

Key Laboratory of Textile Science & Technology, Ministry of Education, College of Textiles, Donghua University, Shanghai 201620, China

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ABSTRACT

The characterization of keratin-chicken egg white-templated luminescent Au cluster composite films were studied using fourier-transform infrared spectroscopy (FTIR) to demonstrate and quantify the secondary transformation of composite films. The results showed that the secondary structure of treated films was transformed from disordered structure to ordered conformation including α-helix conformation and β-pleated-sheet conformation due to the increase of protein-templated luminescent Au cluster. The absorption features of treated films were exhibited by the UV–vis spectra. The bule-shift and decreased intensity indicated the change of microenvironment due to the concentration of protein-templated luminescent Au cluster. The transmission electron microscopy images of composite films supported the aggregation resulting from microenvironment. The effect of protein-templated luminescent Au cluster was characterized by the laser scanning confocal microscope (LSCM) images which showed the gradually intensive luminescence with increasing Au cluster and the transformation from the whiskers to nanoparticle.

1. Introduction

Wool waste is a keratin fiber, which has been developed in response to technical, environmental and economic challenges. It is composed of large quantities of the sulfur-containing amino acids, particularly cysteine, which can be used as surface reconstruction material [1]. Keratin is naturally hydrophilic, non-burning, biodegradable, biocompatible and can be mechanically or chemically processed and regenerated in different forms [2]. The extraction of keratin is mainly used by reduction or oxidation method to damage the disulfide bonds. The main forms of keratin can be classified as powders [3,4], films [5,6], and fibers [7,8]. However, the neat keratin solution without additive is instable and the keratin film has poor mechanical property so that it is difficult to satisfy the demand for produce and application. Many researchers have suggested that natural or manmade polymers are added to enhance the mechanical performance of neat keratin. Tanabe et al. [9] prepared keratin-chitosan composite film by casting the treated solution of both biopolymers in 75% acetic acid to adjust the mechanical properties of keratin film and decrease bacteria number. Similarly, Liu et al. [10] carried out a series of research about bio-inspired designing composite, in which wool fibrils at micro scales used as reinforcement to blend with keratin matrix. Pena [11] used skin multiphoton microscopy to record one-photon excited fluorescence (1PEF) and two-photon excited fluorescence (2PEF) in order to analyze keratin structure.

Recently, the progress of metallic nanoparticles in nanoscience has opened new fields of application for these nanosystems, including biological labeling, biosensing and catalysis [12–14]. In this respect, the optical properties of noble metal nanoparticles are the most interesting because their UV–vis absorption spectra is dominated by a very intense resonance due to the collective motion of the *S—valence* electrons, the so-called surface plasmon resonance (SPR) [15]. Chemical and biological methods are used to synthesize these amazing materials. The precise clusters were successfully obtained from the “12 principles of developing green chemistry” by chemical method [16]. The biological method is usually referred to the template method, which is simulated by biomineralization behavior in nature such as DNA [17], peptides [18] and protein [19]. A paper written by Min Li [20] has been reported which synthesize noble metal cluster (Au and Pt) by “a real green way” using chicken egg white as template. The resulting products show high luminescence and stability both in the form of liquid and solid states.

* Corresponding author.
E-mail addresses: 1142015@mail.dhu.edu.cn (Y. Xing), hlliu@dhu.edu.cn (H. Liu), wdyu@dhu.edu.cn (W. Yu).

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The aim of this study is to explore the microstructure of keratin/protein-templated luminescent Au cluster by the means of FTIR spectroscopy. The maximum volume of protein-templated luminescent Au cluster was 15 dots composited with neat keratin in these experiments. To investigate the variations of the absorption features of the treated films, the UV spectroscopy were also measured. The LSCM has been employed to show the intense luminescence and the size of particles. The TEM has been carried out to monitor the size and the number of Au particle in composite film.

2. Materials and methods

2.1. Materials

Merino 64's wool fibers were degreased by Soxhlet extraction with ethyl alcohol and then with acetone for further 4 h, respectively. After that, the fibers were rinsed with distilled water for three times and then dried in drying oven for 12 h.

Urea and acetone are obtained from Shanghai Lingfeng Chemical Reagent Ltd. (Shanghai, China). Sodium dodecyl sulfate (SDS), ethyl alcohol and glycerol are purchased from Sinopharm Chemical Reagent co. Ltd. (Shanghai, China). Sodium sulfide (Na_2S) is done using Shanghai Tongyang Chemical Development Ltd. (Shanghai, China).

2.2. Preparation of keratin solution

Keratin was extracted according to the reduction method reported previously [21]. Briefly, 5 g pretreated wool was immersed in 100 ml of water solution containing 42 g urea, 1.9 g Na_2S and 0.8 g SDS. The mixture was stirred at 50 °C for 14 h and then filtered through vacuum suction filter. The filtrate was dialyzed against deionized water using dialysis bag (molecular cut-off about 8 kDa−10 kDa, diameter 2.5 cm) for 3 days. The dialyzate was concentrated at 60 °C for 8 h and then the protein concentration was 200 mg/ml in average. Thus, obtained keratin solution was stored at 4 °C before next step.

2.3. Fabrication of keratin/protein-templated luminescent Au cluster composite film

Egg protein-templated luminescent Au cluster solution was kindly supplied by Da-Peng Yang [20]. Three different volumes (5, 10 and 15 dots) of egg protein-templated luminescent Au cluster solution were added to the 5 ml aqueous keratin solution, which was mixed with appropriate volume of glycerol. The original samples including neat keratin and the chicken egg white-templated luminescent Au cluster were called S_k film and S_l solution respectively. The treated samples were recorded as S_5, S_{10}, and S_{15} film respectively. The mixture was dispersed for 2 h using ultrasonic disperser. The keratin/illuminant was cast onto the polyfluortetraethylene (PTFE) plate (300×300 cm^2) and dried at air for 24 h. The thickness of obtained film was 0.3 mm on the average.

2.4. Characterization

FTIR measurement was performed using Thermo Nicolet Omnic sampler. A total of 64 scans were taken for each sample between 650 and 4000 cm^{-1} with a resolution of 8 cm^{-1}. Four samples were used. The average spectra for the fibers of various chemical treatments were used for the evaluation.

UV–vis spectra of composite films and Au cluster solution was carried out at room temperature by UV–VIS–NIR spectrometer U-4100 with a resolution of 1 nm. The films were sampled at regular gripping objective with a 2 × 1 cm hole, and the solution is sampled in a quartz cell of 4 × 1 × 1 cm.

Laser scanning confocal microscope (Carl Zeiss LSM 700, Jena, Germany) was employed for multi-color fluorescence images. In LSCM observation, series of two-dimensional sliced images in the depth direction can be obtained by moving the motorize observation stage along the light axis. A laser (λ = 298 nm) was emitted to excite fluorescein molecules.

Transmission electron microscopy (TEM) measurements were carried out on a JEM-2100 microscope at 200 kV. The sample were dispersed in H_2O, then deposited on a copper grid coated with a perforated carbon film, and air-dried at room temperature.

3. Results and discussion

3.1. Morphology of the keratin/luminescent Au cluster composite films

Fig. 1 showed the keratin films with 0. 3 mm thickness

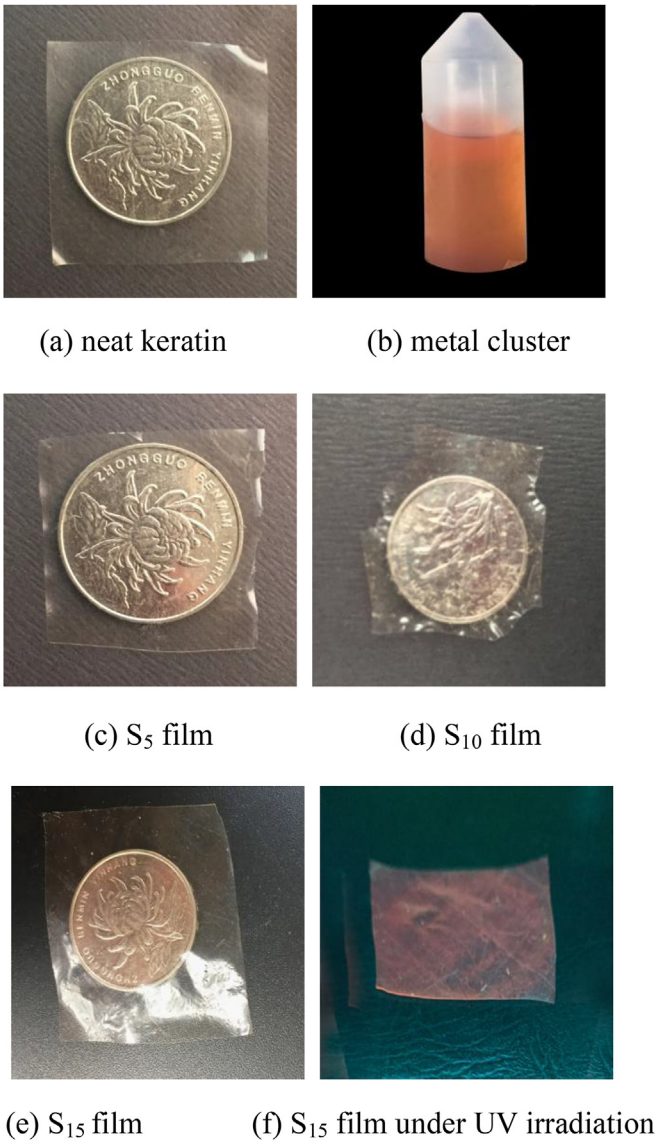

Fig. 1. Visual appearance of (a) neat keratin; (b) luminescent metal cluster; (c) S_5 film; (d) S_{10} film (e) S_{15} film (f) S_{15} film under UV irradiation (λ = 365 nm).