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Observation of luminescent gold nanoclusters using one-step syntheses from wool keratin and silk fibroin effect

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ABSTRACT

Highly fluorescent, water-soluble and green Au nanoclusters (AuNCs) have been synthesized by one-step method with wool keratin as reducer and silk fibrion as stabilizer. Understanding of AuNCs syntheses mechanism and luminescent property is essential for the syntheses of biocompatible AuNCs. This report demonstrates the thiol groups' dependent syntheses with wool keratin (WK) and silk fibroin (SF) solution with different component ratios. Significantly, it was found that the percentage of SF was critical in determining the size of AuNCs. Interestingly, the fibrils of SF, which is made of stick shaped β sheet crystals, contributes to the cage of AuNCs, while the WK dedicates the thiol groups to synthesize WK@AuNCs. Using the transmission electron microscopy, we show that the WK&SF@AuNCs can grow due to the degradation of protein or particle coalescence from the electron beam irradiation. Through the combination of these two processes, the dynamic growth of nanocrystals involves the variation of Au nanocrystals with a bimodal distribution.

1. Introduction

Gold nanoclusters (AuNCs) is made up of a few tens of atoms, which has been developed in response to optics, physics, chemistry, materials science, and biosciences because of their characteristic physicochemical properties compared to those of metallic nanoparticles [1,2]. Au nanoparticles can be classified as regime I and II, with the size of sub-nanometer to ~2 nm and ~3 nm to ~100 nm, respectively. For the regime II there is the opportunity for obtaining strong plasmon resonance(s), a collective excitation mode of the conduction electrons in the particle, which dominate the optical properties. The regime I exhibits unique quantum confinement effects such as the loss of plasmon resonance characteristic of relatively large gold nanocrystals (3–100 nm) and emergence of a molecular-like properties (discrete electronic states and size-dependent fluorescence), which result in enhanced photoluminescence, and these particles are usually called Au nanoclusters [2–5]. Moreover, AuNCs are nontoxicity and can be used for biolabeling and bioimaging applications compared with semiconductor quantum dots which are larger in size and usually contain toxic metal species [6–10]. There are several types of AuNCs: (1) Au nanoclusters protected by thiols (e.g., glutathione) through chemical reduction [4,11–14]. (2) Au nanoclusters templated by dendrimers and DNA [15–18]. (3) Au nanoclusters directed by proteins and peptides [6,19–22].

There have been major research advances in the syntheses of thiolated gold clusters, in which $Au_{25}(SR)_{18}$ cluster system has been served as the first excellent model for one to appreciate the detailed cluster structure–property relationships [4,5,23,24]. X-ray crystallographic analysis shows that the Au_{25} cluster features a centered icosahedral Au_{13} core, which is further capped by a second shell comprised of the remaining twelve Au atoms [25]. Until now, diverse proteins such as BSA, lysozyme, trypsin, chicken egg white (CEW), etc., are exploited for the preparation of AuNCs, applied to nanoelectronics and optics, biosensing and catalysis [19–21]. Xie et al. first reported the green synthetic route of AuNCs with highly red fluorescent by using bovine serum albumin (BSA) as template [6]. Following this report the insulin@AuNCs was synthesized and showed excellent biocompatibility [26].

Herein, we report environmental friendly one-step syntheses of AuNCs using aqueous solution of wool keratin (WK) and silk fibroin (SF). WK is unique in that it has a great predominance of cysteine and high disulfide bonds, which possesses thiol groups as tethering moiety and a hydroxyl group as ligand moiety in AuNCs system [27–29]. There are kinds of amino acid residues in SF protein molecule, leading to great capping and reducing capabilities [30–35]. The wool keratins at different thiol groups levels could affect the structural nature and strength of interaction between the WK and SF chains and the gold ions, leading to the formation of AuNCs with different fluorescence intensity in

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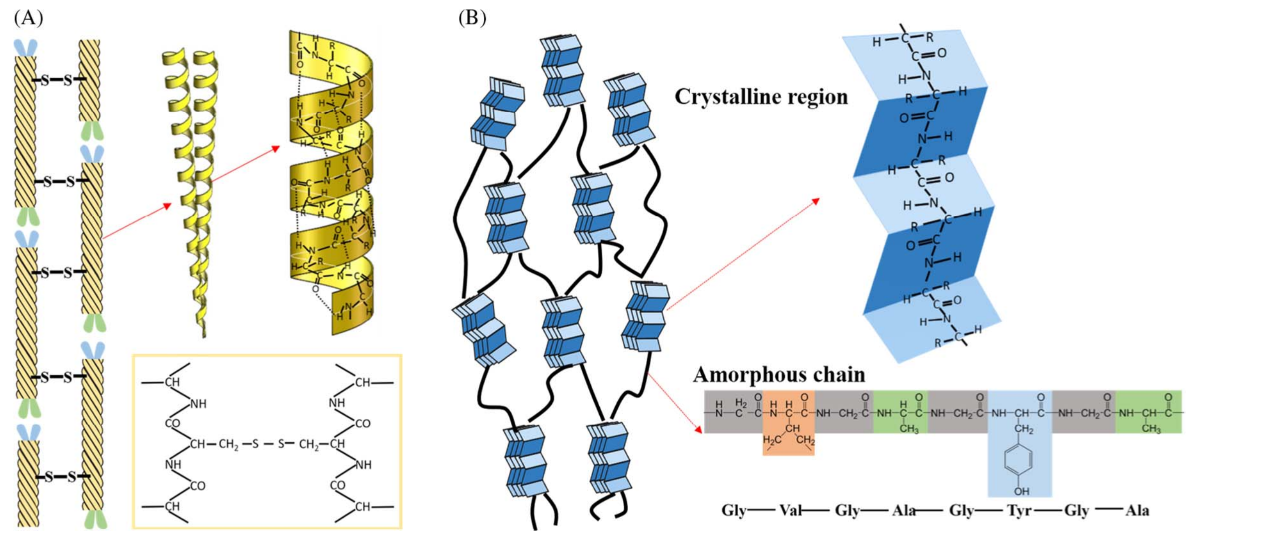

Fig. 1. (A) Protofilament structure of α keratin in wool fibers is composed of dimers (two α helix chains) connected by disulfide bonds) and (B) *β* crystals molecular networks in silk materials are crosslinked by hydrogen bonds.

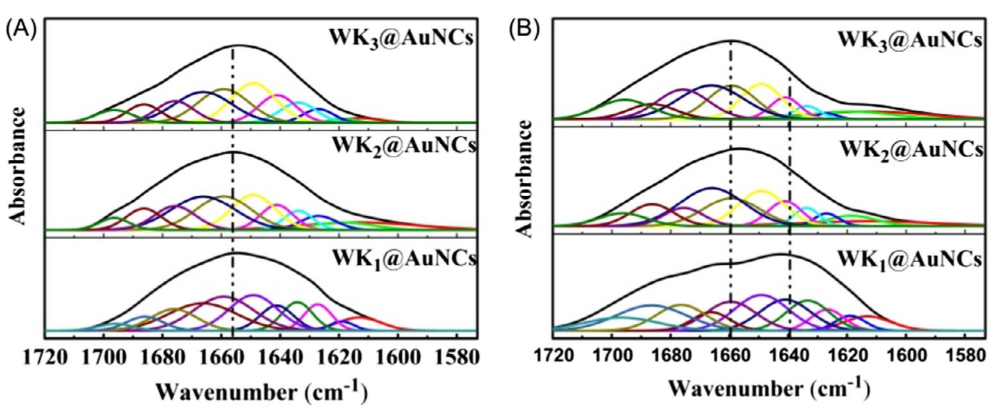

Fig. 2. FTIR spectra of three types of WK@AuNCs (A) without SF (B) with SF (60%) in the regions at 1720–1573 cm^{-1}. According to the literature [39], the 1697, 1627 and 1619 cm^{-1} are assigned to intermolecular *β*-sheets, while the 1633 cm^{-1} components are associated and attributed to intramolecular *β*-sheets. The 1659 cm^{-1} component is contributed to the *α* helix, the bands of 1665, 1675 and 1686 cm^{-1} are assigned to *β*-turns and the 1642 and 1650 cm^{-1} component are contributed to random coils, respectively.

Table 1
Results of deconvolution of three WK@AuNCs solution without SF and with SF (60%).

Sample	β sheets	α helix	β turns	Random coils	Side chains	
WK_1@ AuNCs	19.62	19.82	32.63	23.18	4.75	
WK_2@ AuNCs	17.11	17.29	36.13	21.89	7.58	
WK_3@ AuNCs	17.87	17.78	33.24	29.08	2.03	
WK_1	&SF@ AuNCs	26.62	11.41	29.41	27.21	5.35
WK_2	&SF@ AuNCs	17.67	14.87	38.55	23.22	5.69
WK_3	&SF@ AuNCs	18.90	14.51	40.09	18.87	7.63

various ratios of WK and SF. Therefore, it is of interest to investigate the syntheses of WK&SF-mediated AuNCs.

2. Materials and methods

2.1. Materials and instruments

Chloroauric acid tetrahydrate ($HAuCl_4{\cdot}4H_2O$) and Sodium dodecylsulfate (SDS) were obtained from Sinopharm Chemical Reagent. Sodium sulfide nanahydrate ($Na_2S{\cdot}9H_2O$), urea and acetone were

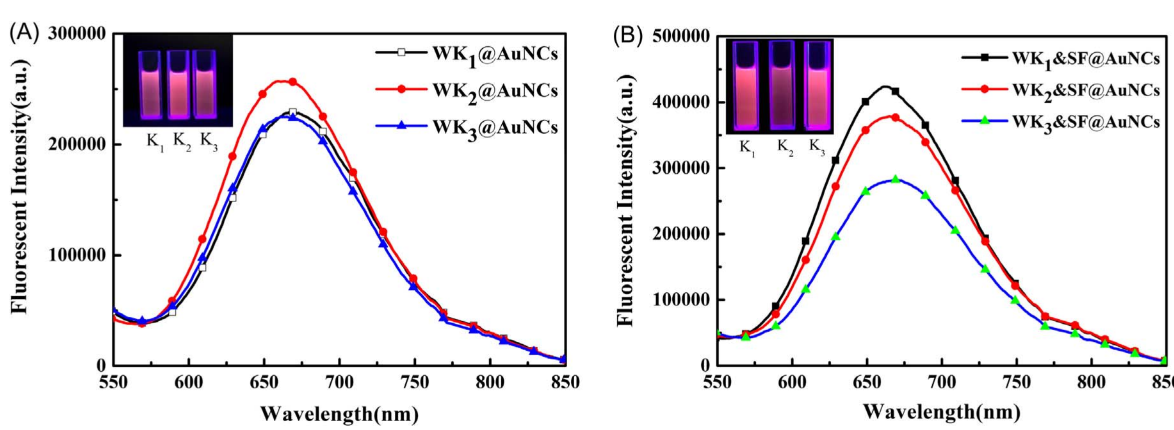

Fig. 3. The fluorescent spectra of (A) WK@AuNCs (B) WK&SF@AuNCs, the inset includes photographs of AuNCs solution under UV light (λ = 365 nm).