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Rapid communication

Incubating lead selenide nanoclusters and nanocubes on the eggshell membrane at room temperature

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Abstract

Lead selenide nanoclusters and nanocubes were successfully prepared on the eggshell membrane (ESM) through a room-temperature biosubstrate-directed approach. The nanoclusters were assembled by fine nanocrystallites, while single-crystalline nanocubes came into being through a ripen progress, and obtained lead selenide nanocrystallites were distributed homogeneously over the whole ESM. The morphology and the size were governed mainly by the configuration and chemical functional residues of the ESM and the synthesis conditions as well as their reciprocities. The functional groups such as amido groups and imido residues of the ESM macromolecules could not only direct the formation of 4–7 nm PbSe nanocrystallites and the assembly into nanoclusters and nanocubes, but act as a surfactant to well-distributed fine PbSe nanocrystallites. The as-prepared nanocrystalline PbSe exhibited single-crystalline, small-scaled and well-dispersed performances, which would offer more potential applications in semiconductors, lasers, optoelectronic devices and the like nanoelectronic fields.

Keywords: Biomimetic; Eggshell membrane; Lead selenide; Nanocubes; Na_2SeSO_3 solution

1. Introduction

Nature has so ingeniously succeeded in gestating various bioobjects with remarkable levers of morphological diversity and complexity. It could be a valuable source for constructing advanced materials with sophisticated hierarchical architectures and striking properties, which would been achieved either by employing the characteristic architectures of biomaterials [1,2] and the functional groups of biomacromolecules [3,4] or by adopting the life systems of bioassemblies [5]. The biomimetic strategy offers a novel and attractive alternative to conventional synthetic routines in preparing inorganic functional materials [3,4,6]. Plenty of biomaterials and biopolymers, such as oyster shells [7], cuttlebone [8], wood [9], sulfated polysaccharide PS_2 in coccoliths [10], multifunctional shellmatrix proteins, MSI60 and N16 [11], lustrin A [12], and collagen-binding proteins [13], can act as the excellent templates and substrates for directing the deposition, assembly and patterning of nanocrystalline structures, obtained inorganic materials will be successfully endowed with characteristic hierarchical bio-structure or intricate micro- or nanoscale organization, which are of great potential for application in a large variety of areas, such as microreactors, light and strong filler materials, nanotechnological devices, and so on.

Eggshell membrane (ESM) is a convenient biomaterial, which locates in the innermost layer of the eggshell and is composed of three-level tissues: the outer membrane (OM), the inner membrane (IM) and the limiting membrane (LM) surrounding the egg-white. Structurally, the OM and the IM are composed of randomly interwoven and coalescing fibers with the diameter ranging from 0.5 to 1.5 μm, and some of the broadest fibers form where two or more narrower ones join alongside each other for part of their length [14]. While the LM is revealed to form on a layer of spherical protein grains. Noticeably, each layer of ESM has the same ingredients containing collagen I, V, and X, glycoprotein, sialoprotein and proteoglycan [15], which play key roles in the formation of eggs and the development of chick embryo. Owing to having particular hierarchical architecture and chemical ingredients, ESM could be an attractive candidate for biomimetic synthesis. Liu and his coworkers have synthesized $BaWO_4$ crystals with different controllable morphologies and sizes by the function alliance of ESM and organic supramolecules [16]. Ishikawa epurated gold

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from electroplating waste water, based on the presence of amino, amido and carboxyl functional groups in the ESM ingredients [17]. More important, as an abundant, cheap, and environmental benign biomaterial, ESM has great advantages to synthesize inorganic functional materials through bio-inspired manufactures.

Nanosized PbSe with cubic rock-salt structure is a fascinating semiconductor with unique optical properties, which has potential applications in the IR spectral regime, biological labels, photovoltaic absorbers as well as electroluminescent devices and lasers [18]. It is necessary to prepare high-quality nanocrystalline PbSe which has high emission color purity resulted from the narrow size distribution and high photoluminescence quantum yield (PLQY) owing to the surface condition with deficient surface trap states [19]. Especially, PbSe/ESM nanocomposite may be more robust than PbSe nanocrystallites alone, since some properties, such as the tenacity and the adhesion of the semiconductors can be improved [20]. There reported a series of technologies for PbSe nanocrystallites, such as microwave radicalization [21], ultrasonic radiation and γ-irradiation two-step technique [22], sonochemical method [23], soft template technique [24], sol–gel route, solvothermal process [25], and so on. All above researches enlighten on the synthesis of nanocrystalline PbSe through mild approaches.

In this work, a facile, moderate and green biosubstrate-directed technique was designed to synthesize and assemble cubic PbSe nanocrystallites into nanoclusters and nanocubes on the ESM at room temperature, in which some functional residues such as amido and imido groups from glycoprotein mantle of ESM fibers, would provide chelation and location functions to the formation and the assembly of nanocrystalline PbSe, and could act as the surfactant and substrate to achieve fine nanocrystallites arraying well-distributed nanoclusters.

2. Experimental

The analytical grade reagents lead acetate, acetic acid, selenium powder and sodium sulfite were purchased from Shanghai Chemical Company. The Na_2SeSO_3 solution was prepared according to the literature [26].

Fresh eggs from the Shanghai local supermarket were softly broken, and the inner and the limiting membranes were easily removed from the eggshell by hand. After the remaining eggshell being immersed in 1.5 mol/L HCl solution, the outer membrane was isolated from the eggshell and subsequently was washed with distilled water. In our work, the clean outer membrane was used as the substrate to incubate lead selenide (PbSe).

The substrate ESM was firstly immersed into 30 mL mixed solution of 0.05 mol/L lead acetate and 0.02 mol/L acetic acid (v/v = 1:5) for about 10 h at room temperature, taken out and rinsed with deionized water, subsequently the following two processes went along, respectively, namely that the membrane was dipped for 16 h into fresh Na_2SeSO_3 solution (I); for adequate time (over 16 h) into ripen Na_2SeSO_3 solution laid still for 2 days (II). By the above processes, ESM became gradually dark, fished out of the solutions and dried naturally. The final samples I and II as dark gray were obtained with correspondence to process I and II, kept in a vacuum desiccator for further characterizations.

The X-ray powder diffraction (XRD) patterns of the ESM and PbSe/ESM hybrid were performed on a Bruker-AXS D8 Advance instrument operating at the voltage of 40 kV and the current of 40 mA with Cu Kα radiation (λ = 1.5406 Å). The morphology and the size were examined by a FEI Sirion 200 field-emission gun scanning electron microscope (FESEM). TEM images and electron diffraction (ED) patterns of PbSe nanoparticles in sample I were carried out on a JEOL-100CX transmission electron microscope operating at the accelerating voltage of 100 kV.

3. Results and discussion

Fig. 1 shows the XRD patterns of natural ESM, the composites PbSe/ESM (I) and (II), respectively. Fig. 1a indicates that the original ESM is totally amorphous, while all the reflection peaks in Fig. 1b and c can be indexed as cubic PbSe with the face-centered rock-salt structure (JCPDS No. 06-0354). The reflection peaks show markedly broadened, indicating that obtained products were small-sized nanocrystallites and sample I had smaller crystallite size than sample II.

The morphology and the configuration of the composite PbSe/ESM were investigated by SEM images shown in Fig. 2. Fig. 2a shows the rough surface of natural ESM, since there locates mammillary knobs on the surface of ESM fibers. It can be clearly seen the ESM presents characteristic macroporous meshworks of diverse interwoven and coalescing fibers [14]. Fig. 2b exhibits that PbSe nanocrystallites were stuck uniformly in ESM fibers while there was absent in the matrix among the membrane fibers. Fig. 2c shows that fine PbSe nanocrystallites with the average size of 5 nm were assembled into 25–30 nm smaller nanoclusters distributing uniformly on the ESM support. And herein some smaller nanoclusters would like to arrange for bigger nanoclusters. While PbSe nanocrystallites were finally prone to ripen into nanocubes with lower thermodynamic energy, the

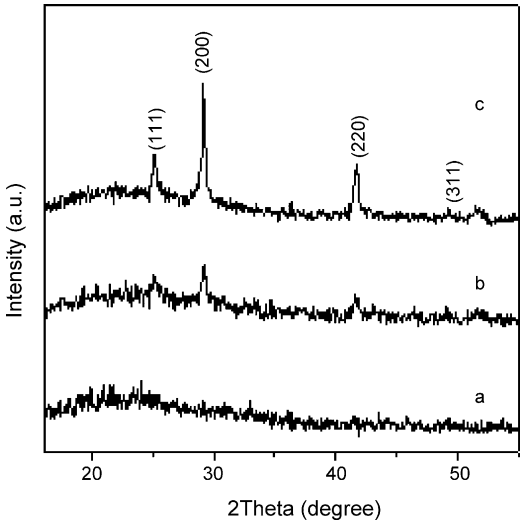

Fig. 1. XRD patterns of the samples: (a) the original ESM; (b) sample I (PbSe/ESM); (c) sample II (PbSe/ESM), respectively.