

doi:10.3969/j.issn.2095-4344.2013.34.016 [http://www.crter.org]

Tang SH, Li YQ, Wang J, Wang BY. Optical properties of gelatin/CdS bionanocomposite and its conformational change.

Zhongguo Zuzhi Gongcheng Yanjiu. 2013;17(34): 6166-6172.

# Optical properties of gelatin/CdS bionanocomposite and its conformational change\*\*\*◆

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## Abstract

**BACKGROUND:** The properties, integration mechanism and conformation change of protein are closely related with the biological effects of nanocomposites.

**OBJECTIVE:** To study the optical properties and integration mechanism of gelatin/CdS bionanocomposite, and to analyze the conformation change of gelatin macromolecule at pH 12.0.

**METHODS:** The gelatin/CdS bionanocomposites were synthesized *via* one-pot chemical route with the materials of gelatin, cadmium acetate and Na<sub>2</sub>S·9H<sub>2</sub>O through adding the Cd<sup>2+</sup> and S<sup>2-</sup> solution into the gelatin dilute solution at the temperature of 296, 302 and 308 K, and with the concentration of 8×10<sup>-6</sup> - 1.2×10<sup>-3</sup> mol/L. The shape, ζ potential and optical properties of samples were characterized by transmission electron microscope, dynamic light scattering, X-ray diffraction, ultraviolet-visible spectroscopy and Fourier transform infrared spectroscopy.

**RESULTS AND CONCLUSION:** Transmission electron microscopy images showed that the morphology of gelatin/CdS nanocomposites was mainly chain-shaped. The ultraviolet-visible spectroscopy showed that the gelatin/CdS nanocomposites band gap was decreased with the increasing in both the CdS concentration and temperature, and they showed an obvious quantum size effect. The dynamic light scattering showed that the ζ potential was negative and decreased slightly with the increasing in concentration of CdS. The Fourier transform infrared spectroscopy showed that level of α-helix and β-sheets in gelatin macromolecular conformation was decreased and the β-turns level was increased. The gelatin/Cd<sup>2+</sup> complex and gelatin/CdS nanocomposites were formed on the basis of various observations, the most plausible mechanism is proposed for the integration of gelatin/CdS nanocomposites, which includes the coordination (Cd<sup>2+</sup> with the oxygen of carbonyl group in gelatin molecular chain), vulcanization and surface coated.

**Key Words:** biomaterials; nanobiomaterials; gelatin/CdS nanocomposite; gelatin; cadmium acetate; sulfide; one-pot synthesis; optical properties; conformation change; National Natural Science Foundation of China

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Supported by: National Natural Science Foundation of China, No. 21067001\*; Guangxi Natural Science Foundation, No. 0991083\*

Received: 2012-10-19  
Accepted: 2012-11-30  
(20120702004/WLM · C)

## INTRODUCTION

Bionanocomposites are a new generation of hybrid nanostructured materials resulting from the assembly of inorganic nanosized solids with biopolymers. This kind of new material display interesting properties that is useful for advanced applications, either as functional or structural materials<sup>[1-2]</sup>. Some of these properties due to the inorganic component (mechanical reinforcement, electrical and optical behavior, *etc*)<sup>[3]</sup>, and the others are given by the biopolymer (biocompatibility, biodegradability, *etc*)<sup>[4]</sup>. The

study of bionanocomposites represents the development of an interdisciplinary knowledge placed in the frontier of materials sciences, life sciences, and nanotechnology<sup>[5]</sup>.

In a previous paper<sup>[6]</sup>, we have reported that biomimetic synthesis of gelatin polypeptide-assisted CdS nanoparticles and their interaction. This paper reports the results of the optical properties of gelatin/CdS bionanocomposites, and the conformational change of gelatin due to the effects of nano-CdS. The research results are interesting, not only because of the

potential beneficial applications, but also the potential risks to human health and the environment.

## MATERIALS AND METHODS

### Design

A synthesis and observation experiment of water soluble bionanocomposites.

### Time and setting

The experiments were performed in the Colloid and Interface Chemistry Laboratory, Guangxi University for Nationalities from June to December 2011.

### Materials

Gelatin (type B, chemically pure reagent, average molecular weight about 100 000) was purchased from Shanghai Chemical Reagent Company, China. Cadmium acetate ( $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) was analytical grade reagent, purchased from Guangzhou Chemical Reagent Factory, China.  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , NaOH and HCl, were all of analytical reagent grade. All the aqueous solutions were prepared with double-distilled water.

### Methods

#### Preparation of CdS/gelatin bionanocomposites

In a typical reaction, a matrix solution was prepared by adding different volumes (from 0 to 2.5 mL) of 0.010 mol/L cadmium acetate into 10.0 mL of the  $1.0 \times 10^{-4}$  mol/L gelatin aqueous solutions, respectively. Under moderate magnetic stirring, the pH value of the mixtures was adjusted to 12.0 using diluted NaOH or HCl solution. The solution turned transparent liquid indicating complete dissolution of cadmium acetate. Then, 0.5 mL of 0.10 mol/L  $\text{S}^{2-}$  solution was added, and the pH value of the mixtures was readjusted to 12.0. The solution containing the given amount of gelatin,  $\text{S}^{2-}$  ion and varied amount of  $\text{Cd}^{2+}$  was finally up to 25.0 mL with pH=12.0, and which was held in the thermostat water bath for at least 10 hours prior to the testing<sup>[6]</sup>.

#### Characterization methods of gelatin/CdS nanocomposites

The obtained sample was characterized by X-ray powder diffraction using D/max 2500 type (Rigaku Co., Japan) diffractometer with Cu K $\alpha$  radiation source ( $\lambda=1.5418 \text{ \AA}$ ) operated at 40 kV and 50 mA, in the range of diffraction angle  $10^\circ$ - $70^\circ$ .

Transmission electron microscopy images were taken on a JEM-1011 (JEOL, Japan) transmission electron microscope. The samples were prepared by placing a

drop of working solution on a carbon-coated standard copper grid (300 meshes) operating at 100 kV.

The ultraviolet-visible absorption spectrum of sample in aqueous solution was recorded on an UV-2802 PCS ultraviolet-visible spectrophotometer equipped with 10 mm quartz cells and a thermostat (AS-21P, Unico) at 296, 302, 308 K, respectively.

The Fourier transform infrared spectrograph spectra of the pure gelatin, gelatin/ $\text{Cd}^{2+}$  and gelatin/CdS were recorded on a Nicolet Magna 550 Fourier transform infrared spectrograph (Thermo, USA) at room temperature. The samples were prepared with potassium bromide (KBr) pellet method. For each spectrum, 256 interferograms were collected with a resolution of  $4 \text{ cm}^{-1}$  with 64 scans and  $2 \text{ cm}^{-1}$  interval from the 4 000 to  $400 \text{ cm}^{-1}$  region. In order to obtain detailed information about the change of the gelatin secondary structure, the shapes of the amide I band of the pure gelatin, gelatin/ $\text{Cd}^{2+}$  and gelatin/CdS were analyzed by derivatization, deconvolution and curve fitting techniques with OMNIC 8.0 software. After identifying the individual bands with the representative secondary structure, the percentages of each secondary structure of gelatin were calculated from the relative area of the component bands<sup>[7]</sup>.

$\zeta$  potential measurements were carried out using Malvern, ZS nano zetasizer. A Delta-320 digital pH meter was used for sample preparation.

### Main observation indexes

Major items were observed including ultraviolet-visible and Fourier transform infrared spectrograph spectra of gelatin, gelatin/ $\text{Cd}^{2+}$  and gelatin/CdS, respectively.

## RESULTS

### X-ray diffraction characteristics, ultrastructure and $\zeta$ potential of gelatin/CdS bionanocomposites

X-ray diffraction patterns of gelatin and the prepared gelatin/CdS bionanocomposites are presented in Figure 1A. Comparing with the broad peak of gelatin, the diffraction peaks of gelatin/CdS were broad and weak, and three main peaks at  $2\theta$  of  $26.30^\circ$ ,  $43.95^\circ$ , and  $52.03^\circ$  were characteristics to the (111), (220) and (311) directions of the face-centered cubic phase structure of CdS, respectively. It could be well matched with the standard values (JCPDS Card No. 10-454). The positions of the peaks were in good agreement with literature values<sup>[8]</sup>. This result confirmed the existence of CdS nanoparticle as final product in

gelatin. Microscopic observation showed that the size of gelatin/CdS bionanocomposites was uniform with average diameters around 25 nm, and they were chain-shaped (Figure 1B). The same conclusions have been found by Sreekumari *et al*<sup>[9]</sup> and Oluwafemi *et al*<sup>[10]</sup> for preparation of the polyacrylamide-PbS nanocomposites, and gelatin capped Ag nanoparticles, respectively.

When the concentrations of gelatin and  $S^{2-}$  ion were  $4.0 \times 10^{-5}$  and  $2.0 \times 10^{-3}$  mol/L, respectively, the  $\zeta$  potentials of the gelatin/CdS bionanocomposites were estimated to be circa  $-19.9$ ,  $-19.4$ ,  $-18.9$  and  $-17.6$  mV corresponding to the  $0.0$ ,  $1.0 \times 10^{-4}$ ,  $4.0 \times 10^{-4}$ , and  $1.4 \times 10^{-3}$  mol/L of  $Cd^{2+}$ . In another word, the  $\zeta$  potentials of the gelatin/CdS bionanocomposites were decrease with the increasing concentration of CdS.

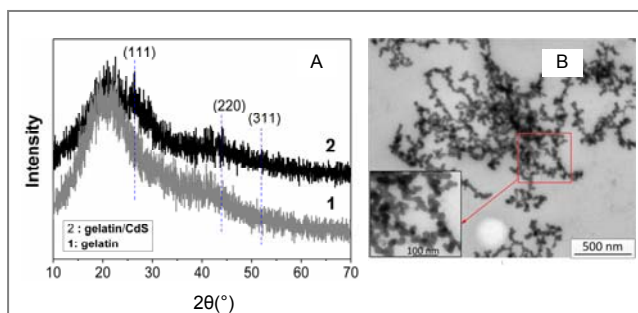


Figure 1 (A) X-ray diffraction patterns of gelatin and gelatin/CdS bionanocomposites: the diffraction peaks of gelatin/CdS has the characters of both the broad peak of gelatin and feature of crystal face of the face-centered cubic phase structure of CdS; and (B) transmission electron microscopy image of gelatin/CdS bionanocomposites: the synthesized gelatin/CdS bionanocomposites were chain-shaped

### Optical properties of gelatin/CdS bionanocomposites

Figure 2A shows the optical transmission spectra of gelatin/CdS bionanocomposites for different concentrations of  $Cd^{2+}$ . The optical transmittances of all the samples could reach to above 90% beyond the wavelength of 500 nm. It was observed that a shift toward longer wavelength with the increasing concentration of  $Cd^{2+}$ . According to the related theories of semiconductor materials, the relation connecting the absorption coefficient  $\alpha$ , the incident photon energy  $h\nu$  and optical band gap  $E_g$  obey Tauc's formula<sup>[11]</sup>:

$$\alpha h\nu = B(h\nu - E_g)^{1/2}$$

Where B was a constant. The band gaps have been calculated by extrapolating the linear region of the plots  $(\alpha h\nu)^2$  vs.  $h\nu$  on the energy axis, as shown in Figure 2B,

which were higher than that of the bulk CdS (2.42 eV at 27 °C)<sup>[12]</sup>. The decreasing of band gap with the increase in  $Cd^{2+}$  concentration at different temperatures was observed as shown in Figure 2C.

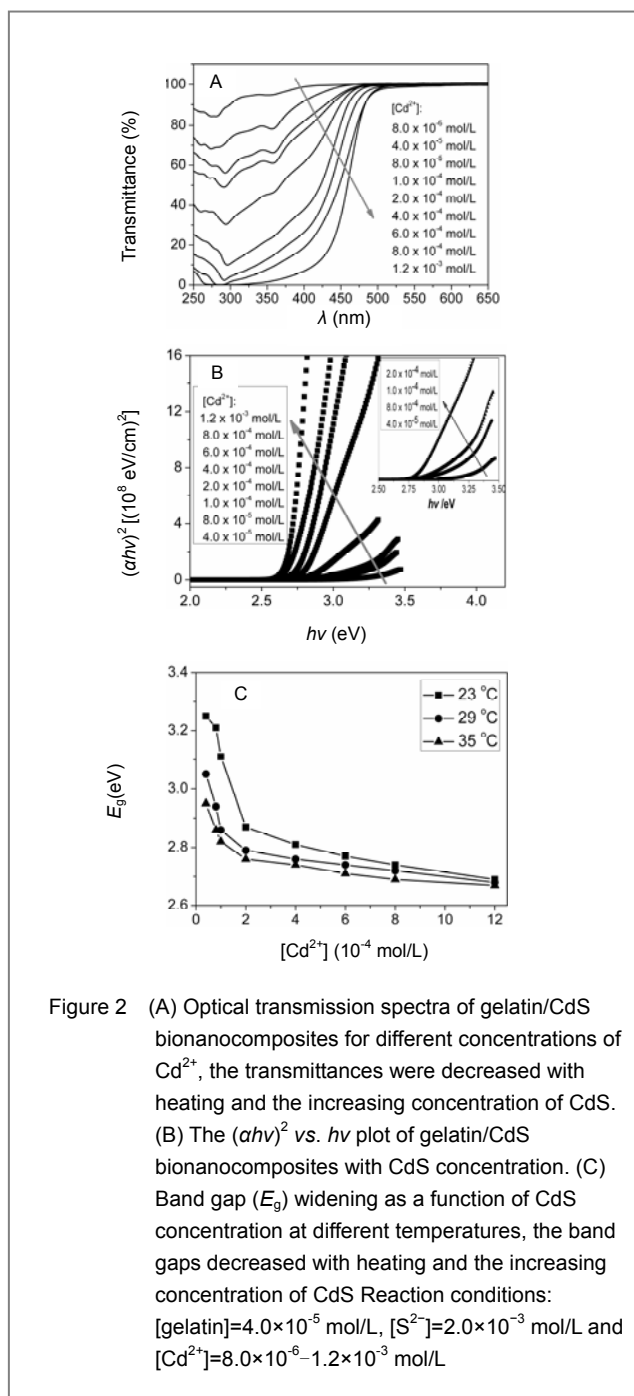


Figure 2 (A) Optical transmission spectra of gelatin/CdS bionanocomposites for different concentrations of  $Cd^{2+}$ , the transmittances were decreased with heating and the increasing concentration of CdS. (B) The  $(\alpha h\nu)^2$  vs.  $h\nu$  plot of gelatin/CdS bionanocomposites with CdS concentration. (C) Band gap ( $E_g$ ) widening as a function of CdS concentration at different temperatures, the band gaps decreased with heating and the increasing concentration of CdS Reaction conditions: [gelatin]= $4.0 \times 10^{-5}$  mol/L,  $[S^{2-}] = 2.0 \times 10^{-3}$  mol/L and  $[Cd^{2+}] = 8.0 \times 10^{-6} - 1.2 \times 10^{-3}$  mol/L

It was clear that the band gaps decreased due to an increasing of particle size with heating and the increasing concentration of  $Cd^{2+}$ , and this was known as the quantum size effect<sup>[13-14]</sup>. The lower  $E_g$  value corresponded to the higher temperature, which indicated that the increasing temperature was favorable to the increasing of particle size, as predicted by the kinetic and the thermodynamic behavior of growth of CdS nanoparticles<sup>[15]</sup>. The similar phenomenon was observed for the synthesis of the mercaptoacetic acid modified

CdSe quantum dots and the gelatin-PbS nanocomposites by Mi *et al*<sup>[16]</sup>, and Wang *et al*<sup>[17]</sup>, respectively.

### Conformational change of gelatin

The binding of protein to nanoparticles often induced significant changes in secondary structure, which made it essential to understand the effect of nanoparticles on fundamental biological process<sup>[18]</sup>. The amide I band (1 600–1 700  $\text{cm}^{-1}$ ) has been widely used for conformational studies<sup>[19]</sup>. To visualize the spectral changes more clearly, deconvolution of the amide I band was used for further analysis of the actual deformation on gelatin structure. The component peaks, their location and percentage of areas are showed in Figure 3 and Table 1. It was clear from the significantly differing band shapes and the shift of the peak maxima that the conformations of gelatin have changed due to its interaction with the  $\text{Cd}^{2+}$  and CdS.

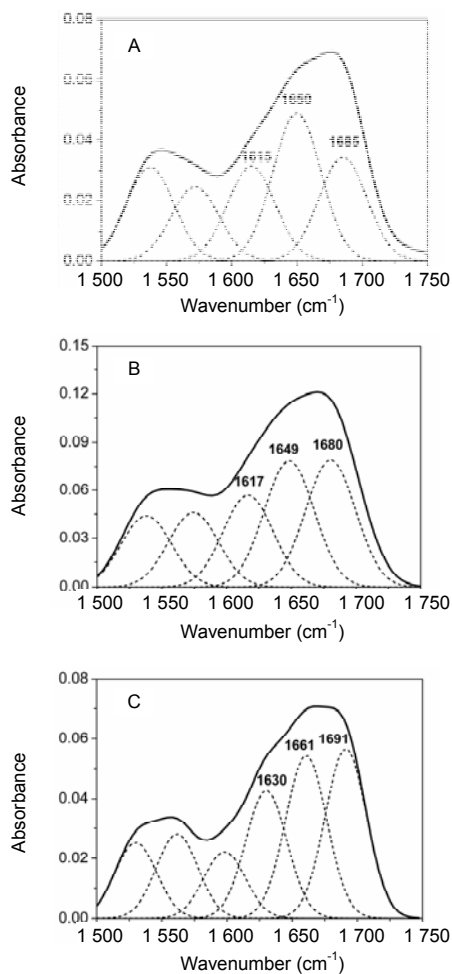


Figure 3 Curve fitting of amide I of free gelatin (A), gelatin/ $\text{Cd}^{2+}$  (B) and gelatin/CdS (C): experimental spectrum (solid line) and the fitting curve (dotted line)

Table 1 Secondary structure analysis (infrared spectra) from the free gelatin, gelatin/ $\text{Cd}^{2+}$  and gelatin/CdS solution at pH 12.0

Amide I components (%, $\text{cm}^{-1}$ ) <sup>[20-22]</sup>	Free gelatin	Gelatin/ $\text{Cd}^{2+}$	Gelatin/CdS
$\beta$ -sheet (%, 1 637- 1 615 $\text{cm}^{-1}$ )	27.3(1 615 $\text{cm}^{-1}$ )	26.6 (1 617 $\text{cm}^{-1}$ )	23.3 (1 630 $\text{cm}^{-1}$ )
$\alpha$ -helix (%, 1 660- 1 646 $\text{cm}^{-1}$ )	42.7(1 650 $\text{cm}^{-1}$ )	36.6 (1 649 $\text{cm}^{-1}$ )	35.5 (1 661 $\text{cm}^{-1}$ )
$\beta$ -turn (%, 1 695- 1 661 $\text{cm}^{-1}$ )	30.0(1 685 $\text{cm}^{-1}$ )	36.8 (1 680 $\text{cm}^{-1}$ )	41.2 (1 691 $\text{cm}^{-1}$ )

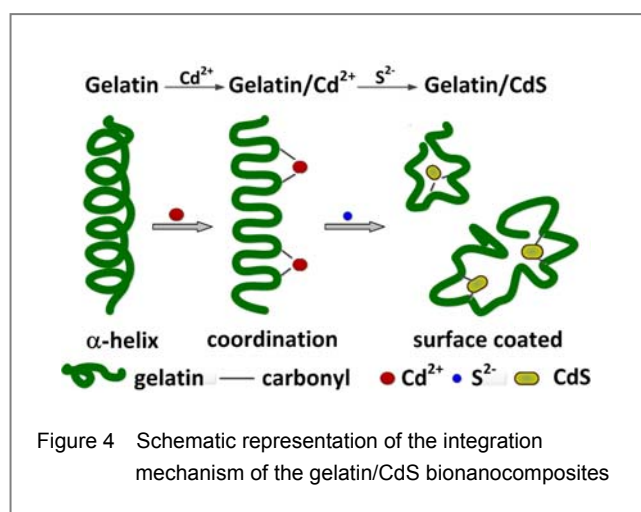
The data show that both contents of  $\alpha$ -helix and  $\beta$ -sheet were decreased, but that of  $\beta$ -turn was increased, which indicated that the secondary structure of gelatin was changed in the process of the formation of gelatin/ $\text{Cd}^{2+}$  and gelatin/CdS bionanocomposites.

Curve fitting analysis of component bands showed that gelatin lose a large percentage of its  $\alpha$ -helix and  $\beta$ -sheet characters<sup>[23]</sup>, showed by a decreasing in the percentage of area of the component band centered at 1 650 and 1 615  $\text{cm}^{-1}$ , respectively. In contrast, the fraction of  $\beta$ -turn was 30.0% in pure gelatin but increased up to 36.8% in gelatin/ $\text{Cd}^{2+}$  solution, and increased to 41.2% in gelatin/CdS solution (Table 1), respectively. These findings indicated that  $\text{Cd}^{2+}$  and CdS combined with gelatin, could weaken or break the hydrogen bond, respectively. In other words, the formations of gelatin/ $\text{Cd}^{2+}$  complex and gelatin/CdS nanocomposites resulted in that the secondary structures of gelatin were changed from  $\alpha$ -helix and  $\beta$ -sheet to  $\beta$ -turn, and the peptide chains of gelatin macromolecules were stretched. This changed conformation of the gelatin formed a configuration, which was well suitable for the formation of gelatin/ $\text{Cd}^{2+}$ , and also the growth of CdS nanoparticles in gelatin matrix<sup>[24]</sup>. Similar feature that has been previously reported for the formation of CdS nanocrystals in pepsin solution by Yang *et al*<sup>[25]</sup>. The conformational changes may affect the biological function of gelatin protein<sup>[26-27]</sup>.

### Integration mechanism of the gelatin/CdS bionanocomposites

Based on the results of discussion above, the schematic representation of the gelatin/CdS bionanocomposites formation is illustrated in Figure 4. It was speculated that the synthesis reaction of the gelatin/CdS bionanocomposites consisted of two steps as follows: First, there was a coordination interaction between the  $\text{Cd}^{2+}$  and carbonyl group (C=O) in gelatin macromolecular peptide chain to form initial precursor complexes (gelatin/ $\text{Cd}^{2+}$ ), and gelatin played the roles as oxygen source and structure-directing reagents<sup>[5]</sup>. At the same time, the interaction caused the gelatin

conformation change from  $\alpha$ -helix to  $\beta$ -turn, and the  $\beta$ -turn secondary structure formed a suitable conformation for the oriented growth of CdS nanoparticles. Second, when the  $S^{2-}$  was added to gelatin/ $Cd^{2+}$  solution, the gelatin/ $Cd^{2+}$  interacted with  $S^{2-}$  to form gelatin/CdS bionanocomposites, and the excess  $S^{2-}$  could be adsorbed on the surface of CdS nanoparticles<sup>[18, 28]</sup>. In this reaction process, gelatin macromolecular conformation was changed from  $\alpha$ -helix and  $\beta$ -sheets to  $\beta$ -turns, and coated on the surface of CdS nanoparticles, which may foreshadow the biological functional change of protein.



## DISCUSSION

In this study, water-soluble gelatin/CdS bionanocomposites were directly synthesized by simple "one-pot" chemical route involving the reaction of  $Cd^{2+}$  with  $S^{2-}$  in dilute aqueous solution of gelatin at pH 12.0, and the produced particles have good water solubility and stability. The X-ray powder diffraction analysis confirmed that the sample is the gelatin/CdS bionanocomposites. The results obtained from transmission electron microscopy showed that the synthesized gelatin/CdS bionanocomposites are chain-shaped.

The quantum size effect of the gelatin/CdS bionanocomposites has been studied by the ultraviolet-visible absorption spectra. The results indicate that the values of band gaps are decreased with the increasing in both the CdS concentration and temperature.

The effect of  $Cd^{2+}$  and CdS on gelatin and the change of gelatin conformation were studied through Fourier transform infrared spectrograph spectroscopy. Both

contents of  $\alpha$ -helix and  $\beta$ -sheet are decreased but that of  $\beta$ -turn is increased, due to the binding of gelatin with  $Cd^{2+}$ , and binding of gelatin/ $Cd^{2+}$  with  $S^{2-}$ . These changes indicate the conformation of gelatin become more flexible and more exposed to the solvent, and may affect the biological function of protein.

The possible integration mechanism involves the coordination ( $Cd^{2+}$  with the oxygen of carbonyl group in gelatin molecular chain), vulcanization and surface coated was also discussed. The better understanding of the structural changes induced by nanoparticles can help to study the mechanism of therapeutic action, which denoted great importance in pharmacy, pharmacology and biochemistry<sup>[29-30]</sup>. In addition, the gelatin-assisted route is fast, simple, and environmentally friendly, and the research results can provide theoretical basis to design and widely use of this kind of bionanocomposites.

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## 明胶/CdS 纳米生物复合物光学性质和构象变化\*\*\*◆

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### 文章亮点:

1 采用一釜化学反应法合成链状明胶/CdS 纳米生物复合物, 该复合物量子尺寸效应显著。

2 纳米 CdS 在明胶上的原位结合, 导致明胶大分子的  $\alpha$ -螺旋结构被破坏, 进而使其构象中  $\alpha$ -螺旋和  $\beta$ -折叠含量降

低,  $\beta$ -转角含量增加。

3 文章结果揭示了明胶/CdS 纳米生物复合物的形成机制, 即  $\text{Cd}^{2+}$  与明胶大分子肽链上的羧基氧络合生成明胶/ $\text{Cd}^{2+}$  配合物, 继而与  $\text{S}^{2-}$  反应生成明胶/CdS 纳米复合物。

4 研究所提出的实验方法为有机/无机复合材料的设计提供必要的理论基础; 生物纳米复合物的形成机制及蛋白质构象变化的研究结果, 对无机纳米材料的临床应用具有重要的指导意义。

关键词:

生物材料; 纳米生物材料; 明胶/CdS 纳米生物复合物; 明胶; 醋酸镉; 硫化钠; 一釜合成; 光学性质; 构象变化; 国家自然科学基金

### 摘要

背景: 纳米生物复合材料的性质、形成机制和蛋白质构象变化与其生物学效应密切相关。

目的: 观察  $\text{pH}=12.0$  时, 明胶/CdS 纳米复合物的光学性质和结合机制及明胶大



分子的构象变化。

**方法:** 以明胶、醋酸镉和  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  为原料, 采用一釜化学反应法, 即将  $\text{Cd}^{2+}$  和  $\text{S}^{2-}$  依次加入明胶稀溶液中, 分别在温度为 296, 302, 308 K, CdS 浓度为  $8\times 10^{-6}$ – $1.2\times 10^{-3}$  mol/L 下原位生成明胶/CdS 纳米复合物。利用透射电子显微镜、动态光散射、X 射线衍射、紫外-可见和傅里叶变换红外光谱等技术测定其形貌、 $\zeta$  电势及其光谱性质。

**结果与结论:** 透射电镜显示, 所合成的明胶/CdS 纳米生物复合物为链状。紫外-可见光谱结果表明明胶/CdS 纳米复合物的带隙宽度随 CdS 浓度和反应温度的增加而降低, 量子尺寸效应显著; 动态光散射结果显示所合成的明胶/CdS 纳米生物复合物  $\zeta$  电势为负值, 且随 CdS 浓度增加而略有降低。傅里叶变换红外光谱显示

明胶大分子构象中  $\alpha$ -螺旋和  $\beta$ -折叠含量降低,  $\beta$ -转角含量增加。形成机制可表述为络合-硫化-表面包覆, 即  $\text{Cd}^{2+}$  与明胶大分子肽链上的羧基氧络合生成明胶/ $\text{Cd}^{2+}$  配合物, 继而与  $\text{S}^{2-}$  反应生成明胶/CdS 纳米复合物, 明胶大分子在 CdS 表面的包覆增大了其水溶性。

**基金资助:** 国家自然科学基金项目 (21067001), 广西自然科学基金项目 (0991083)。

**作者贡献:** 第一作者进行实验设计, 实验实施为第一、二作者, 第三、四作者参与实验评估和资料收集, 第一、二作者成文并对文章负责, 第一作者审校。

**利益冲突:** 课题未涉及任何厂家及相关雇主或其他经济组织直接或间接的经济或利益的赞助。

**学术术语:** 一釜化学反应法-将多步反应集成在一个釜式反应器中进行, 省去了中间体的分离步骤, 直接获得结构复杂的分子。

**作者声明:** 文章为原创作品, 数据准确, 内容不涉及泄密, 无一稿两投, 无抄袭, 无内容剽窃, 无作者署名争议, 无与他人课题以及专利技术的争执, 内容真实, 文责自负。

中图分类号: R318 文献标识码: B

文章编号: 2095-4344(2013)34-06166-07

唐世华, 黎幼群, 王军, 王白杨. 明胶/CdS 纳米生物复合物光学性质和构象变化[J]. 中国组织工程研究, 2013, 17(34):6166-6172.

(Edited by Han WB/Chen X/Wang L)