

A control Fabrication of Hydroxyapatite Using Chemically Modified Polycation Stabilized Gold Nanoparticles

Remant Bahadur K.C.^a, Shanta Raj Bhattarai^a, Myung Seob Khil^b, Hak Yong Kim^{c*}

^aDepartment of Bionanosystem Engineering, ^bCenter for Healthcare Technology Development, and ^cDepartment of Textile Engineering, Chonbuk National University, Jeonju 561-756, Republic of Korea

Introduction

The application of chitosan is somewhat limited by its poor solubility and reactivity and its physical properties, a direct result of strong intra- and inter-molecular hydrogen bonding. To overcome these chemical modifications could be an easy and convenient way. Here we dealt the hydrophobic modification of chitosan and its use to stabilize gold nanoparticles for the control fabrication of hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] (HAp). Aliphatic hydrophobic groups of different chain lengths were first grafted onto the backbone of chitosan [1]. Gold nanoparticles stabilized by native and *N*-acylated chitosan (*Nac*-6-Au and *Nac*-8-Au) were prepared by graft-onto approach. The stability of *Nac*-6-Au was significantly higher so it was selected for further study. HAp crystals were chemically fabricated using *Nac*-6-Au as a matrix and characterized by various physicochemical techniques (FT-IR, UV-vis, XRD, SEM and TEM) [2]. Here, three different types of *Nac*-6-Au-HAp were prepared by varying the nucleation time viz: *Nac*-6-Au-HAp (I), *Nac*-6-Au-HAp (II), and *Nac*-6-Au-HAp (III) for 1, 2, and 3 h, respectively.

Materials

Chitosan-10 [M_v = 2.1 × 10⁵ [DD=78%] (Wako Pure Chemical Industries), fatty acyl chlorides (hexanoyl and octanoyl chloride), HAuCl₄, NaBH₄ (Sigma-Aldrich Co.) were used without any further purification.

Results and Discussion

The characteristic bands, amide I (1656 cm⁻¹), amide II (1593 cm⁻¹), and amide III (1373 cm⁻¹) of *Nac*-6 were shifted to 1635, 1525 and 1404 cm⁻¹ after its insertion on gold surface, respectively. The broad band at 3432 cm⁻¹ was modified and shifted to a more intense band at 3342 cm⁻¹. Further, the C-O stretching vibration at 1075 cm⁻¹ corresponding to the saccharine moiety was well intense into a broad band (850-1159 cm⁻¹). This increase in intensity with significant peak broadening is due to the coupling effect of ν₁ and ν₃ stretching modes of PO₄³⁻ at 960 cm⁻¹ and 1115 and 1010 cm⁻¹, respectively [2]. Interestingly, an additional band at 566 cm⁻¹ attributed to the excited ν₄ mode of PO₄³⁻ groups was well resolved in all the cases. It implies the ceramic modification of *Nac*-6-Au was through the oxygen atom of polymer due to ionic interaction.

SEM images of *Nac*-6-Au-HAp show well-dispersed, quasi-spherical structured particles of sizes ranging from 1 to 5 μm with a significant surface roughness [2]. The quantitative analysis of HAp crystals fabricated on *Nac*-6-Au was performed from the intensity of Ca and P signals in the EDX spectra. Ca/P ratio was varied with the nucleation time. It was only 1.25 in *Nac*-6-Au-HAp (I) and 1.55 in *Nac*-6-Au (III) nearly in agreement with the expected stoichiometry based on the

chemical structure of HAp. Further, depending on Ca/P ratio, aggregation of particles was varied. Aggregation was significant in *Nac*-6-Au-HAp (III) as compared to *Nac*-6-Au-HAp (I) and *Nac*-6-Au-HAp (II). The individual platelets *Nac*-Au-6-HAp particles were well resolved in the form of needle shaped nanocrystals in *Nac*-Au-6-HAp (III) (Fig. 1D) as compared to the *Nac*-Au-6-HAp (I) (Fig. 1B) and *Nac*-Au-6-HAp (II) (Fig. 1C).

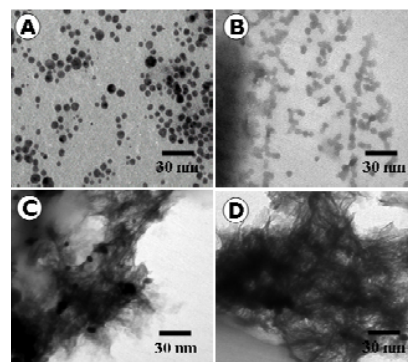


Figure 2. TEM micrographs of *Nac*-6-Au-HAp dispersed in triple distilled water at pH 7.4; *Nac*-6-Au (A), *Nac*-6-Au-HAp (I) (B), *Nac*-6-Au-HAp (II) (C), and *Nac*-6-Au-HAp (III) (D).

Conclusions

Gold nanoparticles stable in physiological condition could be fabricated by using hydrophobically modified chitosan (*Nac*-Au). Surface characteristics of *Nac*-Au were modified by ceramic material HAp in the form of nanocrystal via in-situ nanoprecipitation. Nucleation of HAp nanocrystals was initiated through the oxygen atom of polymer and dependent on the nucleation time. It was concluded that the *Nac*-Au played a key role to induce and direct the growth of HAp crystals.

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References

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