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New core–shell hyperbranched chitosan-based nanoparticles as optical sensor for ammonia detection

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ABSTRACT

In this paper, preparation of new core–shell amino-terminated hyperbranched chitosan nanoparticles (HBCs-NH_2) NPs is described. The synthesized nanoparticles were characterized using ninhydrin assay, FTIR, TGA, and FESEM. The newly prepared (HBCs-NH_2) NPs were then used as a platform for facile and controlled synthesis of silver nanoparticles (AgNPs) which was confirmed using FTIR, UV–vis spectrometry, X-ray diffraction, SEM and HRTEM. Formation of the AgNPs was also noted upon changing the color of (HBCs-NH_2) NPs suspension from colorless into yellow as well as through the appearance of surface plasmon resonance (SPR) peak at 400 nm. HRTEM showed a uniform and spherical morphology of the resulting HBCs-NH_2 NPs with average size 400 nm, and the AgNPs were formed mainly on their surface with average size of 20–50 nm. The newly developed (HBCs-NH_2) NPs-AgNPs showed a great potential as optical sensor for efficient detection of the ammonia concentration in solutions based on the change in the SPR.

1. Introduction

Over the last few decades, hyperbranched polymers (HBP) became one of the most popular classes of polymers which extensively investigated due to their unique architecture and novel characteristics including the high density of functional groups [1–4]. Similar to dendrimers, the HBP have tree-like structures with the same enhancement in chemical and physical properties but with a considerable reduction in cost and time of synthesis [3]. Due to their unique properties, HBP have recently been used as templates for the controlled synthesis of different nanostructures, such as AgNPs, AuNPs, and ZnO NPs [5–8]. The synthesized NPs demonstrated, in most cases, small size with narrow size distribution and good stability [8]. Among the different types of HBP, the amino-terminated ones (HBP-NH_2) have showed good ability to capture and reduce metal ions to generate nanoparticles (NPs) [9].

Noble metal NPs have recently attracted tremendous attention because of their potential applications in a wide range of fields such as optoelectronics, optics, nanostructures fabrication, biochemical sensing, and catalysis [10]. AgNPs have been used in various biomedical, electrical, optical, and sensing purposes [11]. Different techniques have been explored for the synthesis of AgNPs such as chemical [12], electrochemical [13], photochemical [14], and biological methods [15–17]. AgNPs have characteristic SPR [18] which enables their use in various chemical and biological sensing applications such as colorimetric sensor for histidine [19], optical imaging of cancer [20], detection of herbicides [21], glucose biosensors [22], and optical ammonia sensors [23].

Because of its common use in industry and its high toxicity to humans and animals, the development of highly sensitive and reversible sensor of ammonia is of great importance. Ammonia sensors are beneficial in many fields such as air quality control as well as monitoring the ammonia level in biological, clinical, and environmental samples [24–30]. Numerous techniques have been reported to detect ammonia in gas samples. These include ion mobility spectrometry [25], metal oxide semiconductor detectors [31], electrochemical sensors [27], pH sensors [26], and optical sensors [28]. However, all these techniques could only detect ammonia gas and can't be used for the detection of ammonia content in solutions. To date, a few studies have reported the detection of ammonia in solution [24,32,33]. An equipment was developed recently by ATI analytical technology for dissolved ammonia sensing. This equipment uses chemical reactions to convert ammonia into monochloramine followed by measuring its concentration amperometrically. Optical sensors on the other hand show great potential due to their high sensitivity, simplicity, and low cost.

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In the current study, chitosan (Cs) has been selected due to its various superior properties such as non-toxicity, biodegradability and biocompatibility [34,35], to be as a nano-core for the synthesis of novel core–shell amino-terminated hyperbranched Cs nanoparticles, HBCs-NH_2 NPs after nanospray drying. The newly prepared HBCs-NH_2 NPs were characterized and investigated for the first time in literature as a platform for the controlled synthesis of AgNPs particularly on their surfaces due to their uniform spherical morphology and the large number of terminal amino groups, which can capture and reduce Ag^+ ions to generate AgNPs. Resulting (HBCs-NH_2) NPs-AgNPs were then used as an optical sensor of the detection of ammonia content in solutions based on the change in the SPR band intensity and peak position.

2. Experimental

2.1. Materials

Chitosan (Cs) of medium molecular weight was purchased from Aldrich (Germany). Acetic acid (CH_3COOH) and silver nitrate ($AgNO_3$) were provided by Fisher (UK). Methyl acrylate (MA) and ethylene diamine (EDA) 99+%, and ammonia (33%) were purchased from Acros (Belgium). Ninhydrin and sodium borohydride ($NaBH_4$) were obtained from Oxford (India). All of the other chemical reagents and solvents were of analytical grade and used as received.

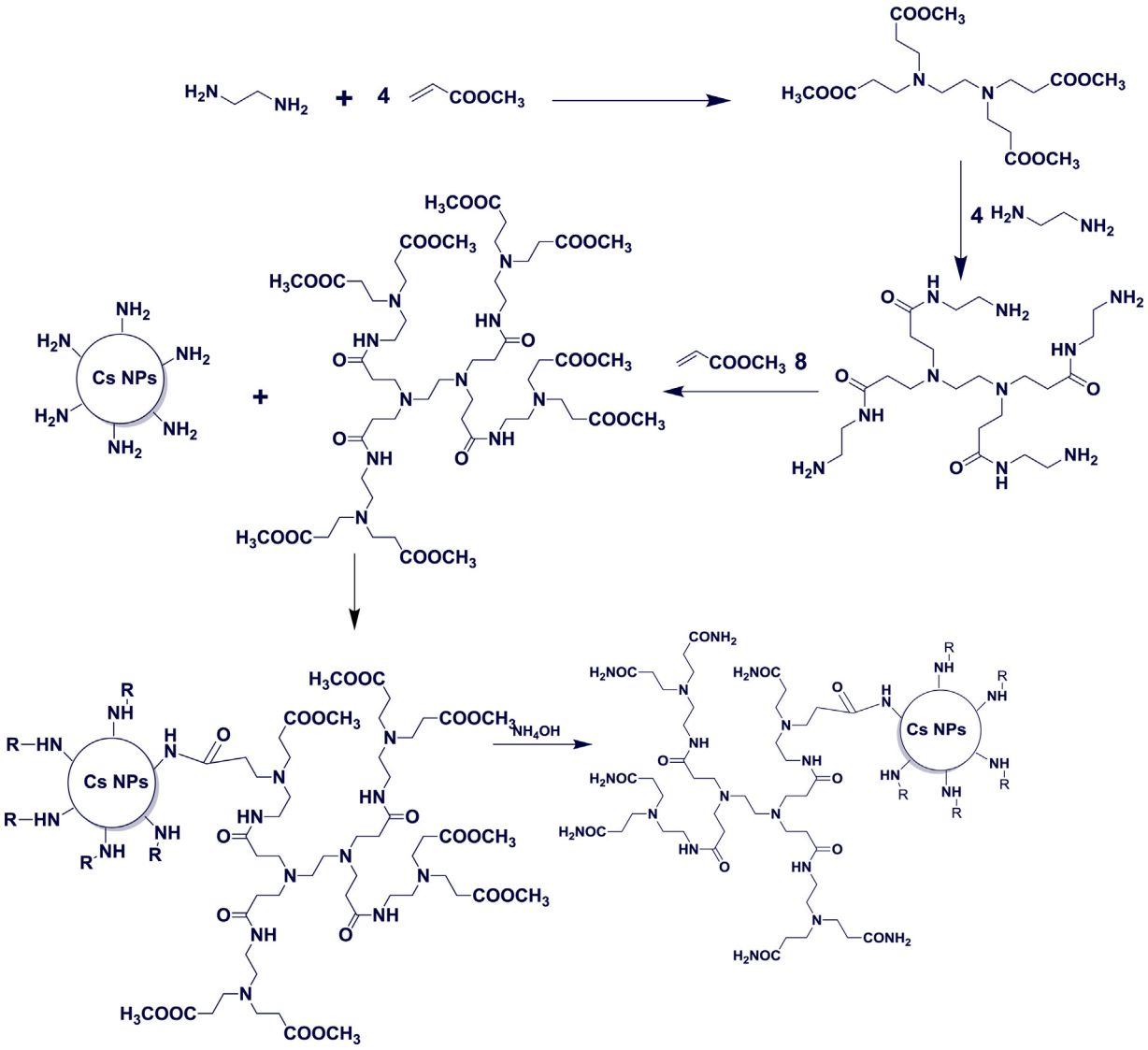
2.2. Methods

2.2.1. Characterization of Cs

The viscosity average molecular weight, Mw of the used Cs was found to be 372 kD as determined by the Mark-Houwink viscometry method [36], in a solvent mixture of 0.1 M acetic acid/0.2 M NaCl at 25 °C. The *N*-deacetylation (%) of the Cs under investigation was found to be 87.2% as estimated from FTIR using the following equation [37]:

$$N - \text{Deacetylation } (\%) = \left[1 - \left(\frac{A1655}{A3340}\right)\left(\frac{1}{1.33}\right)\right] \times 100$$

where, *A* is the absorbance value at the given wave number. The two absorption values at about 1655 and 3340 cm^{-1} are corresponding to the amide and the NH_2 groups of Cs, respectively. The factor (1.33) corresponds the ratio of A1655/A3340 for a fully N-acetylated Cs. FTIR (t_{max}, cm^{-1}) 3358 (O—H stretching and N—H extension vibration), 2806 (C—H stretching), 1623 (amide C=O stretching), 1418, 1392, 1311, 1158, 1035 and 548.



Scheme 1. Schematic illustration for the preparation steps of (HBCs-NH_2) NPs.