



Chitosan/silver nanocomposites for colorimetric detection of glucose molecules

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ABSTRACT

This study was about the simple method for the rapid colorimetric and visual detection of glucose molecules in water medium. Silver nanoparticles were spread on the chitosan surface (CS/Ag NCs) and it was characterized by UV–visible spectroscopy, fourier transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). The CS/Ag NCs displayed a strong surface plasmon resonance band at 429 nm which disappears in the addition of accelerative concentrations of glucose molecules and it was attended by color alteration from yellow to colorless. The interaction of glucose molecules on the CS/Ag NCs was displayed through TEM technique. Glucose molecules was detected not only by naked eyes (from yellow to purple grey) but also by UV–vis spectrophotometer in the concentration range between 0 and 100 μM , with limit detection of 5 μM and a good linear relationship of R^2 value = 0.99. The proposed paper was used for the application of the detection of glucose molecules in water sample with adequate outcome. This CS/Ag NCs was very simple and low cost system without using any other enzymatic catalyst and organic chromogenic agents for glucose molecules detection.

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1. Introduction

Glucose is an essential carbohydrate in biological metabolisms that been reasoned as a two-sided molecule owing to its physiological and pathological effects. Moreover, glucose is an essential power source for human cells and a metabolic intermediary, acting as a risk messenger in average cellular signal transduction activities. Diabetes is an international public health difficulty, and its complications consider higher endangerment of heart illness and kidney failure problems and have been discovered as any of the leading reason of death in the world. All these indications can be reflected by anomalous glucose concentration in human blood [1]. Hence, it was extremely desirable to produce a simple biosensor platform to sensitive observation device for monitoring the concentration of glucose on a regular base [2].

Between many reported sensing methods, colorimetric biosensors have been attracting more attention due to their simple, cost efficient, expediency and independently classy equipment [3]. Nowadays, numerous nanoscale materials were demonstrated to purpose as natural biomolecules impersonate that can catalyze oxidation reactions. On the starting point of biomolecules detection, these nanomaterials appeared as a sort of colorimetric tool for the detection of glucose. Very recently, it has been reported that some metal oxide nanomaterials such as Fe_3O_4 magnetic nanoparticles (NPs), Co_3O_4 , CuO and CeO_2 NPs obsessed constitutional glucose molecules detection [4]. In addition, carbon nanomaterials with novel electronic, mechanical, and chemical properties, such as graphene, graphene oxide, carbon dots and single wall carbon nanotubes are favorite in constructing hybrid nanocomposites materials used for glucose molecules detection [5,6]. In specific, these hybrid nanocomposites showed cooperatively demonstration for colorimetric detection of glucose molecules [7–9].

Recently, the specific optical properties of noble metal nanoparticles such as silver and gold have been highly appreciated by researchers for numerous applications including biosensing [10], catalysis [11], imaging [12] and drug therapy [13]. Fast detection, cost efficient, superficial function, and the quality to overlap with other on chip devices that

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require low sample quantity have preferably considered these metallic nanoparticles for medical use. Biosensing exploitation plasmonic nanoparticles was frequently accomplished to direct the sensitivity of the decentralized surface plasmon resonance (SPR) to modifications in the refractive index at the nanoparticle surface where binding of biopolymers occurs. Moreover, the interaction of the nanoparticles with a biopolymer can affect the placement between nanoparticles, neutering the plasmonic coupling between the two nanomaterials, which frequently results in large SPR shifts and enhanced sensitivity. Although progress was made in recent years toward the enhancement of commercial devices which can be used with analyzable medical samples, biofouling of the nanoparticle surface with discarded species in analyzable biological solutions, such as urine and blood remains a faultfinding problem [14]. Biological molecules, such as enzymes, circumvent the problem of biofouling through an active site which possess shape complementary and specificity. The sensitive detection of glucose molecules based on chitosan covered palladium and platinum (Pd@Pt) core–shell NCs delivers extraordinary chances for scheming low-cost biosensors [15]. Fabrication of Ag NPs/Graphene quantum dots (GQDs) nanocomposite for colorimetric detection of glucose molecule sensor achieves good sensitivity and selectivity with a low detection limit [16]. Highly stable and reproducible fabrication of Ag NPs used for detection of glucose molecules in human body fluids such as sweat and saliva was achieved with excellent sensitivity, low detection limit and appropriate linear range [17].

We proposed a facile synthesis of chitosan/Ag nanocomposites (CS/Ag NCs), which were functionally and morphologically characterized by UV visible spectroscopy, FTIR, XRD, SEM and TEM. The synthesized chitosan/Ag nanocomposites for sensitive approach to colorimetric sensor of glucose molecules in aqueous medium. Attaching the different functions of chitosan, the CS/Ag NCs was used to notice its specific interactions with glucose molecules. Glucose molecules were directly detected through the exposed eye and a UV–vis spectrometer. Effective sensing capacity was obtained with values ranging from 5 to 100 μM of glucose.

2. Materials and methods

2.1. Materials and chemicals

Chitosan and acetic acid were obtained from Aladdin Industrial Corporation and from Richjoint Chemicals, China respectively. Highly pure

analytical grade silver nitrate (AgNO_3) and glucose were purchased from Sinopharm Chemicals (China) and were used as received without further purification. All the glassware was thoroughly washed with deionized water.

2.2. Synthesis of CS/Ag NCs

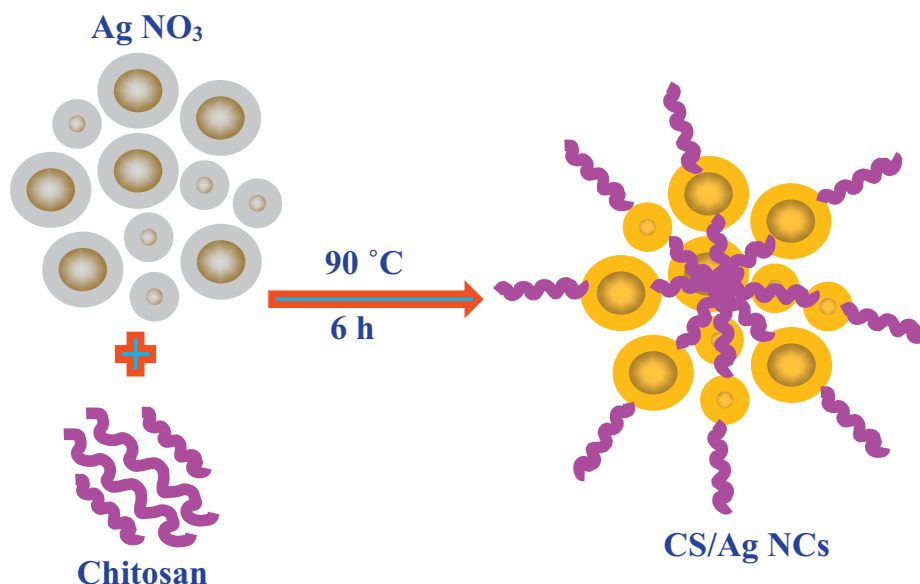
The synthesis of CS/Ag NCs was carried out by stirring 100 mL of 0.7% (w/v) chitosan in 0.1 M glacial acetic acid and attained chitosan solution pH was 2.6. The viscous solution was stirred continuously overnight to dissolve chitosan. About 0.05 M concentrations of silver nitrate was used for the synthesis. A volume of 40 mL of AgNO_3 solution was added to the viscous solution of chitosan and stirred. The colorless solution was heated at 90 °C for 6 h to obtain an orange yellow CS/Ag NCs colloid (Scheme 1). This color change indicated the formation of CS/Ag NCs and evidence for colorless to orange yellow color change was measured using UV–vis spectroscopy (Model: Shimadzu UV-1750). After reaching room temperature, it was centrifuged at 9000 rpm for 30 min for eliminating undesired biggest CS/Ag NCs. The supernatant constitutes the CS/Ag NCs stock solution and before use 10 mL of stock solution was diluted in 90 mL of distilled water.

2.3. Characterization of CS/Ag NCs

The synthesized CS/Ag NCs was first characterized by fourier transform infrared (FTIR) spectroscopy. The spectra were recorded using a Nicolet FTIR (NEXUS-870) spectrometer in the wavenumber range of 4000–400 cm^{-1} . The UV–Vis absorption spectra were recorded (Shimadzu UV-2450 spectrophotometer). Powder X-ray diffraction (XRD) measurements were conducted on an advanced Rigaku D/max-RA X-ray diffractometer equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology of CS/Ag NCs was determined using scanning electron microscopy (SEM, Hitachi S-4800). The surface morphology and size of the CS/Ag NCs was investigated by transmission electron microscopy (TEM, Hitachi JEM-2100).

2.4. Colorimetric detection of glucose by UV–vis spectrophotometry

5 mL test tubes containing ~400 μL of diluted CS/Ag NCs were used as blank. About 100 μL of different concentration between 5 and 100 μM of glucose molecules were added in to newly prepared CS/Ag NCs. Different concentrations of glucose molecules were added in to CS/Ag NCs



Scheme 1. Schematic representation for the synthesis of chitosan/silver nanocomposites.

samples and sample were incubated at 35 °C for 30 min. UV–vis absorption spectra were recorded against water at room temperature and the experiment was conducted by five times.

3. Results and discussion

3.1. Characterization of CS/Ag nanocomposites

The synthesis of CS/Ag NCs was obtained by reduction of AgNO_3 in the chitosan solution at 90 °C and there is a color change associated to the reduction, which was monitored using UV–vis spectrophotometry. The absorption spectra of the consequent CS/Ag NCs solution peaks are shown in Fig. 1a. The CS/Ag NCs sample was prepared at 90 °C and the final mixture initiated its color change from colorless to light yellow color within 1 h of reaction. Further color change from light yellow to permanent dark yellow color was observed within 6 h (Fig. 1b). As expected, all spectra reported in Fig. 1a show absorption peaks in the visible range and exhibit their distinctive SPR maximum peaks at a wavelength of ~420 nm. This result suggests the arrangement of spherical, morphological Ag NPs on the chitosan surface [18]. Furthermore, Fig. 1a shows that as the reaction time increased, a progressive increase in the intensity of the SPR peak was observed along with an addition of Ag NPs density in the chitosan mixture. The concentration of acetic acid in CS and temperature show an essential function in the reduction procedure. These results were found to be consistent with previous reports of silver NPs prepared by acetic acid employed as reducing agent and CS as intermediate of the response [19]. CS is a perishable polymer and it has different bewitching properties including superior film forming ability, non-toxicity, good adhesion, high permeability toward water and biocompatibility [20]. Moreover, CS can be used as a reducing and stabilizing agent for Ag NPs and so prevents Ag NPs from accumulation. In the present study, CS was used as a stabilizing agent for the synthesis of Ag NPs owing to its nonpoisonous nature. The prepared CS/Ag NCs was found to be stable for more than five months as reported in Fig. 1b. The CS/Ag NCs supported assay is extremely desirable for the detection of glucose molecules. Owing to its very simple use, economic synthesis method and long stability, CS/Ag NCs were found to provide equivalent performance when compared to some other metal-based nanocomposites.

Fig. 2 reports FTIR spectra for CS/Ag NCs providing information on the molecular interactions between Ag NPs and chitosan. The FTIR spectrum of CS/Ag NCs display common peaks at wavenumber positions of ~3436, 1645, 1381, 1075 and 557 cm^{-1} . The wide peak positioned at a wavenumber of ~3370 cm^{-1} corresponding to stretching vibration of —OH. The peak positioned at a wavenumber of ~1645 cm^{-1} is related

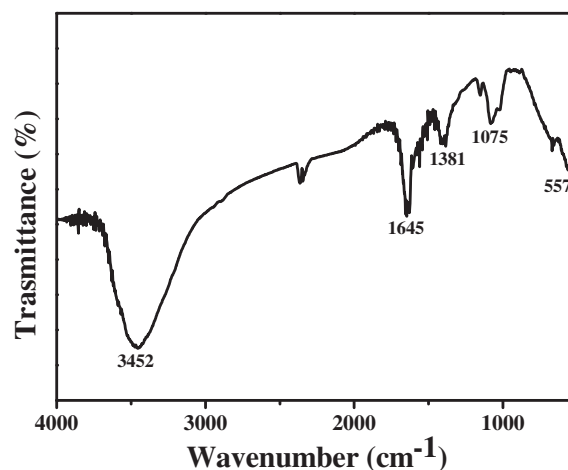


Fig. 2. FTIR spectra of chitosan/silver nanocomposites and the spectral region between 4000 and 400 cm^{-1} .

to vibrational motions of amide I moieties. Other transmittance peaks located at wavenumber positions of ~1381 cm^{-1} belonged to CH_2 wagging vibration, ~1075 cm^{-1} related to COO^- group of carboxylic acid salt and stretching vibration of C—O—C. The peak located at a wavenumber position of ~557 cm^{-1} confirmed the presence of Ag NPs in the NCs [21]. This peak has been associated to Ag NPs soldering with O_2 from hydroxyl group [22]. Hence, the FTIR spectra displayed the interaction from the CS to Ag NCs in the polymeric compound. From the FTIR spectrum of CS/Ag NCs, the shifting of the CS peaks was determined which may be due to the interaction of Ag NPs on the CS surface in the NCs [23]. The peak of ~1075 cm^{-1} corresponding to the vibrational motions of hydroxyl groups belong to the backbone structure of CS, which is in agreement with the FTIR results obtained by Raveendran et al. [22], Ishihara et al. [24].

The structural properties of the synthesized CS/Ag NCs were investigated by powder X-ray diffraction. Fig. 3 reports XRD patterns of CS/Ag NCs. The broad peak located at a diffraction angle 2θ value of 23.6° corresponds to chitosan molecules [25]. The CS molecules peak matched well with the reported literature [26–28]. The broadening of the peaks was due to the amorphous nature of the biopolymer [29]. From the XRD pattern of the CS/Ag NCs reported in Fig. 3, it was noticeable that the Ag NPs were in a crystallized form. This was supported by the presence of diffraction peaks located at 2θ values of 38.1°, 44.1°, 64.4° and 77.9° that correspond to the typical (111), (200), (220) and (311)

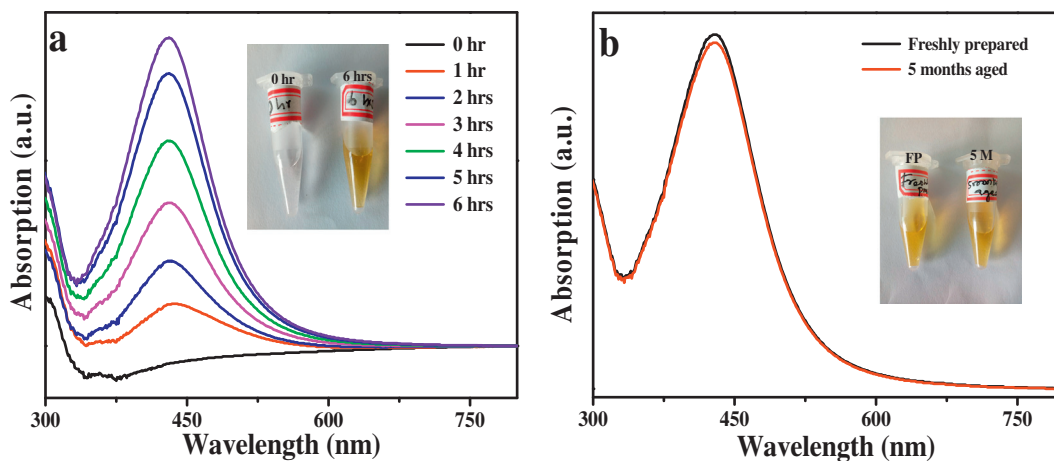


Fig. 1. UV–Vis absorption spectra of CS/Ag NCs prepared at 90 °C between 0 and 6 h (a). Inset: Photographs (a) indicated that color change of precursor (CS, AgNO_3) at 0 h and formation of CS/Ag NCs after 6 h. Absorption spectra of CS/Ag NCs (b), Freshly prepared (black line) and after 5 months aged CS/Ag NCs (red line). Inset Photographs (b) freshly prepared and 5 months aged CS/Ag NCs.

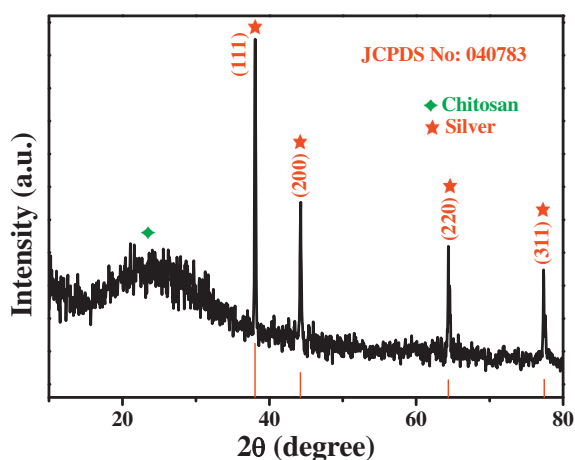


Fig. 3. Powder XRD pattern of chitosan/silver nanocomposites, 2θ range between 10° and 80° , operated voltage of 40 kV and a current of 30 mA.

reflections of Ag NPs, respectively. The diffraction pattern obtained was well correlated with JCPDS No. 040783, corresponding to the typical monoclinic structure of Ag NPs on the chitosan molecules. In the XRD pattern, no additional diffraction peaks were observed, meaning that no impurities were present within the CS/Ag NCs. The intensity of the contemplation owing to the presence of Ag NPs was decreased with CS concentration. Nevertheless, the interaction between CS molecules and Ag NPs induced a loss of Ag NPs crystallinity.

SEM images of CS/Ag NCs are shown in Fig. 4a and b. The CS/Ag NCs showed a sheet like morphology and small dot like particles on the surface of chitosan sheet are observed (Fig. 4b). The synthesized Ag NPs are present within the CS matrix as small particles gathered together into clumps having spherical shape. The SEM images of CS/Ag NCs demonstrated a mixture of CS and Ag NPs, which confirms the binding of chitosan biopolymer to the surface of Ag NPs [30]. The SEM images suggest that Ag clumps were relatively well dispersed in the CS matrix

and that CS stabilized the synthesized Ag NPs at its surface. It was ascertained that the Ag NPs were basined in an arrangement of CS and also that the size of the Ag NPs was confined to the nano size range. The decrease of agglomeration of Ag NPs was found to occur when the CS was allowed to dissolve for a longer duration of time, followed by the dispersion of Ag NPs in the CS solution for about an hour before the reduction process.

TEM images of CS/Ag NCs are reported in Fig. 4c and d. TEM results revealed that the arrangement of spherical morphology of Ag NPs with size ranging from 6 to 18 nm were distributed in the CS matrix (Fig. 4c and d). It was established that the NPs size and structure can be modified by applying reducing conditions and capping factor at correct quotient. The size of the Ag NPs was found to range from 6 to 18 nm. The Ag NPs accumulated at the CS surface with a invidious placement on the CS boundary. The Ag NPs were relatively well separated from each other, therefore confirming the previous observation supported by UV absorption spectra and XRD pattern [31]. The CS/Ag NCs possess a layered structure instead with glassy surface structure and where Ag NPs were poly dispersed in nature [32].

3.2. Colorimetric detection of glucose

The interaction of glucose molecules with CS/Ag NCs generated a significant decrease in the interparticle space (Fig. 5b, c) when compared to CS/Ag NCs that was not exposed to glucose molecules (Fig. 4c, d). The consequence of TEM analysis distinctly displayed the forum of CS/Ag NCs in the existence of glucose molecules (Fig. 5b, c). The glucose molecules were adsorbed onto the surface of CS/Ag NCs and could efficiently carry the Ag NPs close to each other. A modification in the electron compactness on CS/Ag NCs was proposed due to the electronic interaction between the adsorbed glucose molecules and the CS/Ag NCs surface leading to a reduction in the SPR absorbance of CS/Ag NCs consequent in an alteration in the electronic existence of the surface bed [33]. Such interaction leads to a reduction in the SPR band of the CS/Ag NCs upon the interaction of glucose molecules. The interaction of glucose molecules with CS/Ag NCs leads to a small reduction in the

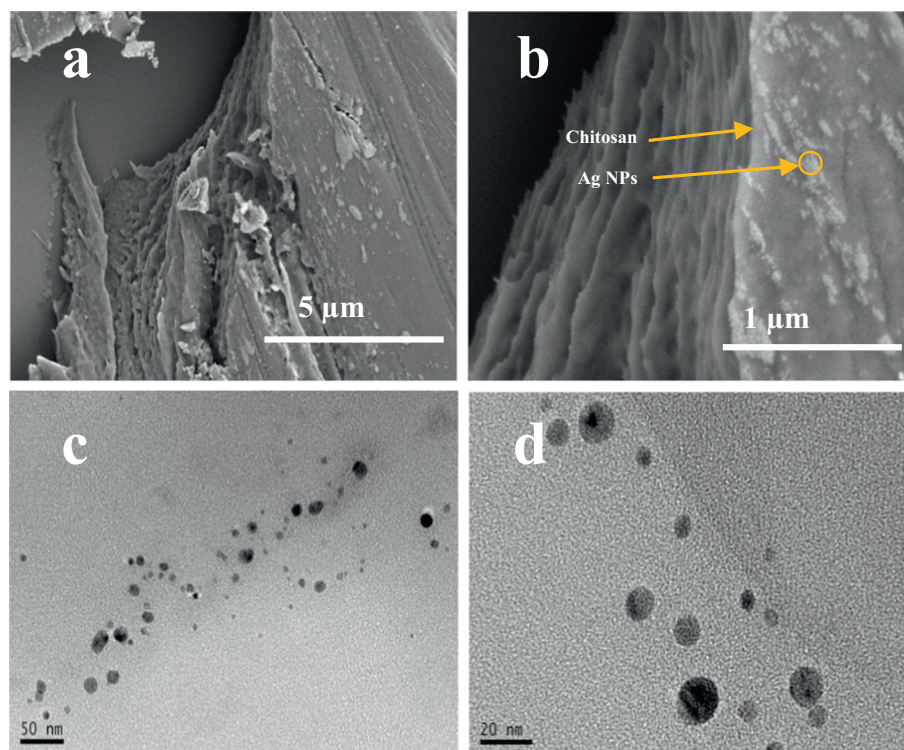


Fig. 4. SEM (a,b) and TEM (c,d) images of synthesized CS/Ag NCs obtained at various magnifications.

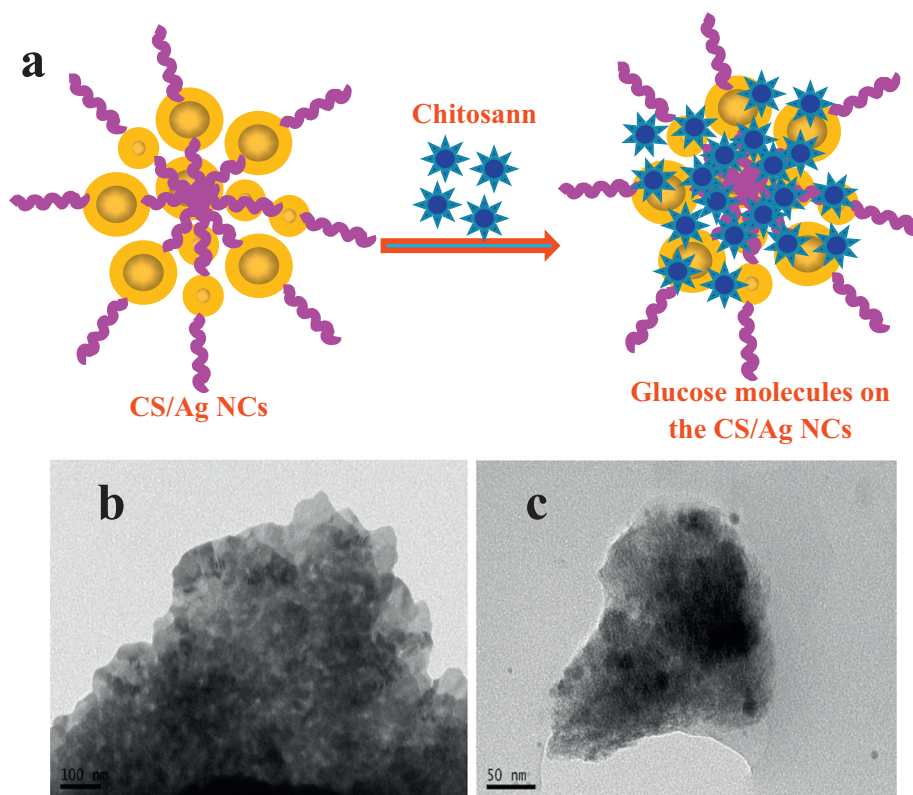


Fig. 5. Schematic representation of addition of glucose molecules on the CS/Ag NCs (a). Low (b) and high (c) magnifications of TEM images of the assembled CS/Ag NCs upon the addition of 5 μM glucose molecules.

NPs morphology and size due to the absorption of glucose molecules on the CS/Ag NCs directing to demetallization of the overhead silver atoms [34]. This causes a change in the Ag NPs size and in this study an alteration from 18 to 13 nm was detected (Fig. 5c).

Fig. 6 showed that after addition with various concentrations of glucose molecules between 0 and 100 μM , CS/Ag NCs mixture color showed a conversion from yellow to purple grey. Similarly to some other glucose molecules colorimetric detection ranging between yellow and pale

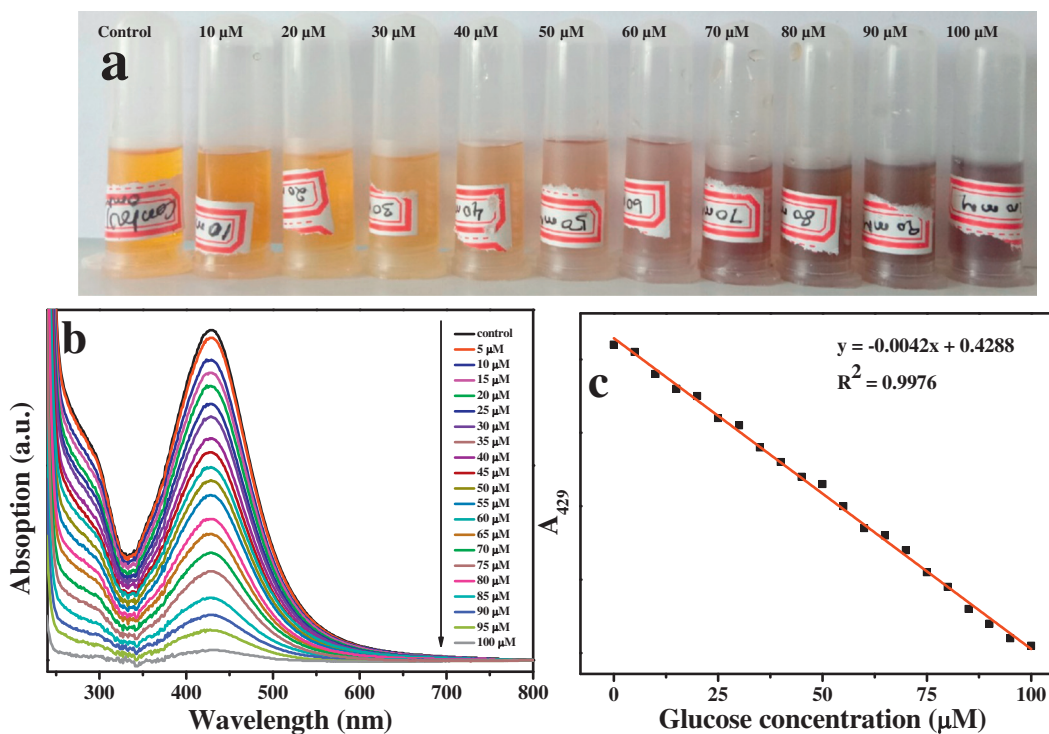


Fig. 6. Color change photographs of CS/Ag NCs solution in the addition of different concentration of glucose molecules between 0 and 100 μM (a). Absorption spectral changes observed for CS/Ag NCs upon the addition of 5 μM of glucose (b). Related calibration plot of absorbance against glucose concentration (c).

grey. The UV–Visible absorption spectra were recorded for CS/Ag NCs in the presence and absence of glucose and the spectra are shown in Fig. 6a. A reduction in the SPR peak was detected for CS/Ag NCs upon the addition of glucose molecules (Fig. 6b). The SPR absorption intensity of the CS/Ag NCs reduced significantly by the addition of 5 μM glucose molecules (Fig. 6b) owing to the adsorption of glucose molecules on the surface of CS/Ag NCs. The mainstay of glucose molecules on the CS/Ag NCs surface can be expected and supported on the existence of N–Ag binding between the NPs and glucose molecules [35,36]. With every addition of 5 μM glucose molecules to the CS/Ag NCs, the SPR absorption peak of the CS/Ag NCs reduced significantly (Fig. 6b). The reduction in the SPR absorption intensity of CS/Ag NCs was attributed to the glucose molecules elicited forum of CS/Ag NCs. The standardization plot of absorption of CS/Ag NCs against the glucose molecules concentration demonstrated a straight line (Fig. 6c). The observational limit of detection (LOD) was established and found to be 5 μM . A good linear relationship (R^2 value = 0.99) between the absorption of CS/Ag NCs and the glucose molecules concentration at 429 nm was acquired in the range of 5–100 μM .

The accompanying color variation from yellow to orange and then to red was sufficient for the naked eye to distinguish this color change as reported in Fig. 6a. Compared with previously reported colorimetric sensing based on silver materials, the two responsive phenomena including the SPR band decline and red-shift, and color change were superior to single color fading (e.g. ranges from yellow to pale), and were more sensitive for the naked eye. Benefiting from these outstanding colorimetric properties, this approach achieved a low detection limit for glucose as low as 5 μM and good linearity of the calibration curves at different glucose concentration regions between 0 and 100 μM . Furthermore, this CS/Ag NCs was further exposed to the glucose molecules colorimetric sensing and a detection value of 5 μM was obtained. The glucose molecules were adsorbed on the surface of CS/Ag NCs and can efficaciously carry the Ag NPs ambient to each other. The absorption spectral modifications of CS/Ag NCs were not discovered in the existence of other biological molecules such as fructose, lactose, sucrose and maltose. On further addition of controlled amounts of other biological molecules in the observational solution, the absorption spectrum of the CS/Ag NCs remained unaffected. The constipating activity of glucose molecules were well assorted when compared to other molecules showing the existence of constipating of the amine groups with the surface of biopolymer mediated metal NCs [37,38].

Table 1 shows the detection of glucose molecules in the existence of other metal and metal oxide NPs mediated composites under similar experimental conditions. There were many reports available worldwide

involving the use Ag NPs to sense glucose molecules but only limited reports available for CS/Ag NCs mediated colorimetric detection of glucose molecules. The synthesis of DNA-embedded Au/Ag core shell NPs with and without addition of various concentrations of glucose molecules between 0.01 and 200 μM were undergone for selective colorimetric detection [39]. Jiang et al. [40] reported that Au NPs based colorimetric assay allow easy and impressive detection of glucose molecules in a rat brain using from 0 to 50 mM concentration. Gao et al. [41] investigated the selectivity of the Au NPs–Ag NPs scheme for glucose molecules detection in the concentration between 0 and 70 μM . Lin et al. [42] demonstrated the Au NPs SPR displacement had a linear correlation with the concentration of glucose molecules in the range between 0 and 1 mM. Chen et al. [43] have reported that much more sensitive colorimetric system detection of glucose molecules concentration between 0.5 and 400 μM using the GODs/Ag NPs hybrid. Pham et al. [44] have demonstrated that the 4-MPBA incorporated GO@SiO₂@Ag NPs used for optical sensor of glucose molecules in PBS. Xia et al. [45] studied a uniform scheme corresponding Ag nanoprisms and glucose molecules for cost-efficient, easy and highly sensitive colorimetric detection of glucose molecules in serum. The existing Ag NPs enclosed in CS matrices based colorimetric sensing system displayed the lowest sensing limits at 5 μM concentrations for the detection of glucose molecules in the existence of meddling molecules such as fructose, lactose, sucrose and maltose. The detection of glucose molecules was the lowest when compared to other reports [46,47]. The existing CS/Ag NCs based colorimetric detection can be used for the detection of glucose molecules. It was fascinating to billet that the existing CS/Ag NCs integrated in functionalized CS matrix allow easy development of a colorimetric sensor for the detection of glucose biomolecules.

In the present system, glucose molecules can be adsorbed on the surface of CS/Ag NCs and then generate —OH radicals. The generated —OH radicals might be stabilized by CS/Ag NCs via partial electron exchange interaction, which may contribute to the detecting ability of CS/Ag NCs, leading to react with glucose to produce an intense color reaction. The interaction of the Ag with a chitosan can affect the placement between nanoparticles, neutering the plasmonic coupling between the two nanomaterials. This frequently results in large SPR shifts and enhanced sensitivity. The colorimetric detection of glucose molecules is governed by a mechanism where glucose precisely regulates the colorimetric reactivity of CS/Ag NCs through potentially physical interaction between Ag and chitosan. The porous nanostructures of Ag NPs and large surface areas of chitosan enhanced the interactive sites between CS/Ag NCs and glucose molecules, contributing to accelerated electron transfer of Ag and the high sensitivity of the biosensor.

Future of sensing is based on the key factors of simplicity, cost-effectiveness and rapid response. CS/Ag NCs based colorimetric detection method is significant while analyzing its ideal characteristics of glucose molecules. Previous reports of colorimetric detection are meant to be a bulk and complex one, requiring different functional blocks such as transducer, processing unit, a detection unit etc. leading to a delayed sensor response. Current system of CS/Ag NCs based calorimetry detection is all about the miniaturization of size, cost, in-situ and without any additional instruments. A calorimetric sensor is used for rapid detection of glucose molecules and shows a color change, which can be detected visually.

4. Conclusion

Stable CS/Ag NCs were successfully synthesized by using Ag⁺ as the precursor and CS as a reducing and stabilizing agent. Exclusive AgNO₃ and CS were essential in the synthesis procedure of the CS/Ag NCs. The CS/Ag NCs display respective benefits such as separation, high detection efficiency, disperse and stability. Due to these benefits, they provide an easy, low-cost, extremely sensitive and selective performing for colorimetric detection of glucose molecules. The method was found to be useable and could be easily implemented, especially for the farming population in third world countries.

Table 1

Detection of glucose molecules in the presence of different metal and metal oxide NPs mediated composites using colorimetric sensor system.

Sensing materials	Analytical method	Linear range (μM)	LOD (μM)	Reference
DNA-embedded Au@Ag core shell NPs	Colorimetry	0–200	0.01	[39]
Au NPs	Colorimetry	0–5000	0.01	[40]
Ag NPs	Colorimetry	270–4440	130	[46]
Au NPs–Ag NPs	Colorimetry	0–700	100	[41]
Au NRs	Colorimetry	0–1000	10	[42]
CH–Ag NPs	Colorimetry	5–200	0.1	[47]
GQDs/Ag NPs	Colorimetry	0.5–400	0.17	[43]
PB–Fe ₂ O ₃	Colorimetry	1–80	0.16	[48]
Fe ₃ O ₄ @MSN	Colorimetry	10–500	4	[49]
Pt–MnO ₃ nanomaterials	Colorimetry	5–500	0.18	[50]
CF nanocubes	Colorimetry	8–90	2.47	[51]
G–Ag NPs	Electrochemistry	2000–10,000	100	[52]
GO–Ag NPs	Electrochemistry	2000–12,000	310	[53]
rGO–Ag NPs	Electrochemistry	32–1890	4.5	[54]
CeO ₂ NPs	Fluorimetry	10–200	8.9	[55]
PEI–Ag NCs	Fluorimetry	10–1000	0.8	[56]
CS/Ag NCs	Colorimetry	0–100	5	Present study

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