

Au@SiO₂ Core-shell Nanoparticles: DNA Binding Studies

K.L.DHANALEKSHMI¹, K.S.MEENA²

¹Associate Professor, ²PG& Research, Department of Chemistry,

¹BIST, BIHER, Bharath University, Chennai-73,

²Queen Mary's College, Chennai - 04

ghanamveni88@gmail.com

Abstract

Core-shell type Au@SiO₂ nanoparticles were prepared by Stober's method. They were characterized by FT-IR, AFM and HR-TEM techniques. High resolution transmission electron microscopy measurements revealed that their size is below 30 nm. The binding affinity of CT-DNA with Au@SiO₂ core-shell NPs surface is studied in this work. The data indicate that the strength of interaction between CT-DNA and core-shell NPs surface is closely related to the particle size, with smaller particles producing the most pronounced effects. From the observed studies showed that SiO₂ supported on the surface of Au NPs not only prevent aggregation, but also proved to have enhanced DNA binding activity than the free nanoparticles.

Keywords: Core-shell nanoparticles; Stober's method; DNA binding study.

1. Introduction

In recent years, many researchers have focused on the studies of interaction of small molecules with DNA [1–5]. DNA is generally the primary intracellular target of anticancer drugs, so the interaction between small molecules and DNA can cause DNA damage in cancer cells, blocking the division of cancer cells, and resulting in cell death [6,7]. DNA is generally the primary intracellular target of anticancer drugs, so the interaction between small molecules and DNA can cause DNA damage in cancer cells, blocking the division of cancer cells and resulting in cell death [8,9]. Small molecule can interact with DNA through the following three noncovalent modes: intercalation, groove binding, and external electrostatic effects. Among these interactions, intercalation is one of the most important DNA-binding modes, which is related to the antitumor activity of the compound. This unusual binding mode is not only important in many biological processes, like replication and transcription, but is also significantly exploited as one of the drug design strategies in the development of new chemotherapeutic agents against

different types of cancer and malaria and various kinds of bacterial, viral and fungal infections [10,11]. In this regard, noble metal nano particles were found to be particularly useful because of their potential to bind DNA.

Among the noble metal nanoparticle, gold nanoparticles with diameters between 10 and 100 nm have been extensively used in biomedical applications such as biosensors, drug and gene delivery, and novel photodynamic therapies [12]. In this respect, not only gold seems very useful but also due to its superior physical - chemical properties, e.g.: corrosion resistant, low toxicity, conformational flexibility which all make this noble metal very attractive for biomedical applications [13,14]. Gold in particular, have attracted great attention since ancient times [15]. This is due to their promising new applications in fields such as materials science, medicine, catalysis, and fluorescence spectral engineering based on surface enhancement effects [16,17]. The surface of nanoscaled materials is very reactive, and needs to be protected by surface ligands to avoid irreversible growth and agglomeration.

Silica is an inert, robust and optically transparent material. The silica shells not only enhance the colloidal stability, but also control the distance between core particles within assemblies by the thickness of the shell. Furthermore, this shell is hydrophilic, biocompatible and easy to functionalise with several groups using different silane coupling agents. These unique characteristics and the possibility of bio-conjugation made silica coating an attractive route for bio-analytical and medical applications of metal nanoparticles [18]. The concentric silica shell formation around metal NPs would provide a means to further tune the functional and interfacial properties of the NPs and thus make them more stable, processable and versatile. While a thin dielectric silica coating has the potential to modify and stabilize the plasmonic properties [19-26].

2. Materials and methods

2.1. Reagents

Tetraethoxysilane (TEOS) was purchased from Sigma Aldrich. Tetrachloro auric acid was obtained from CDH chemicals and all the other chemicals used were of Analar grade. Milli-Q water was used.

2.2 Synthesis of Au@SiO₂ core-shell nanoparticles

Silica particles were prepared by adding dropwise the mixture of 18ml of ethanol and 6ml TEOS to the mixture of 42ml ethanol and 9ml NH₄OH (25% NH₃) under constant stirring. The titration speed was controlled at 20 sec per droplet and after the titration, the stirring was performed continuously for 1 hr. The obtained silica colloid was aged for 24 hrs and no purification treatment was carried out[27-31].

7.5ml of the one-day-old silica colloid was mixed with a water-ethanol (1:9) solution containing 0.3mmol HAuCl₄.3H₂O with stirring. A dilute ethanol solution containing excessive formaldehyde was added dropwise at a titration speed of 14 sec per droplet under constant stirring. The obtained red colour solution was aged for 24 hrs and then was centrifuged and washed with water three cycles to remove residual reactants[32-34].

2.3 Characterization

In the present study IR spectroscopic measurements were carried out with a Perkin Elmer FTIR Spectrum RXI spectrometer. AFM images were taken in a VECO/Digital instruments Nanoscope III atomic force microscope. High resolution transmission electron microscopy (HRTEM) photographs were captured using a JEOL JEM-3010 electron microscope operated at 300 keV with the magnification of 600 and 800 k times. Samples were prepared for transmission electron microscope characterization by dispersing the sample in highpurity ethanol, followed by sonication. A drop of this suspension was then evaporated on a copper TEM grid[35-39].

2.4 DNA binding study by electronic absorption spectral titration method

CT-DNA was purchased from Bangalore Genei (India). A solution of CT-DNA in the buffer (5 mmolL⁻¹ Tris-HCl/50 mmolL⁻¹ NaCl buffer (pH 7.2)) gave a UV absorbance ratio at 260 and 280 nm of about 1.89:1, indicating the CT-DNA sufficiently free from protein contamination. The CT-DNA concentration was determined by the UV absorption spectroscopy using the molar absorption coefficient of 6600 M⁻¹ cm⁻¹ at 260 nm. Stock solutions were kept at 4 °C[40-45].

Electronic absorption titrations were performed in Tris-HCl/NaCl buffer (5 mmolL⁻¹Tris-HCl/50 mmolL⁻¹NaCl buffer pH 7.2) using DMF (10%) solution of nanoparticles at room temperature. Absorption titration experiments were made using different concentrations of CT-DNA, keeping the nanoparticles concentration constant. Core-shell nanoparticles-DNA solutions were allowed to incubate 5 min before the absorption spectra were recorded.

2.4.1 Calculation of binding constant (K_b)

In order to quantify the binding affinity of core-shell nanoparticles with CT-DNA, the intrinsic binding constant, K_b were calculated from Wolfe–Shimer Eq. (1) [27], through a plot of $[DNA]/\epsilon_a - \epsilon_f$ vs $[DNA]$,

$$[DNA]/\epsilon_a - \epsilon_f = [DNA]/\epsilon_b - \epsilon_f + 1/K_b |\epsilon_b - \epsilon_f| \quad (1)$$

Where, $[DNA]$ represents the concentration of DNA, Where ϵ_a is the extinction coefficient observed for the charge transfer absorption at a given DNA concentration, ϵ_f the extinction coefficient at the nanoparticles free in solution, ϵ_b the extinction coefficient of the nanoparticles when fully bound to DNA and K_b the equilibrium binding constant. A plot of $[DNA]/(\epsilon_a - \epsilon_f)$ versus $[DNA]$ gives K_b as the ratio of the slope to the intercept.

3. Result and Discussion

3.1 Fourier transform infrared spectroscopy (FTIR)

Fig.1. shows the FTIR spectrum of Au@SiO₂ core-shell NPs. In FTIR spectra, band observed at 3190 and 1660 cm⁻¹ corresponding to O-H stretching and O-H bending vibrations of water molecules. The bands seen at 1056 and 943 cm⁻¹ are assigned to the asymmetric stretching vibrations of the Si-O-Si and Si-O bonds respectively. The bands at 792 and 449 cm⁻¹ are attributed to the symmetric stretching and bending vibrations of the Si-O-Si bonds.

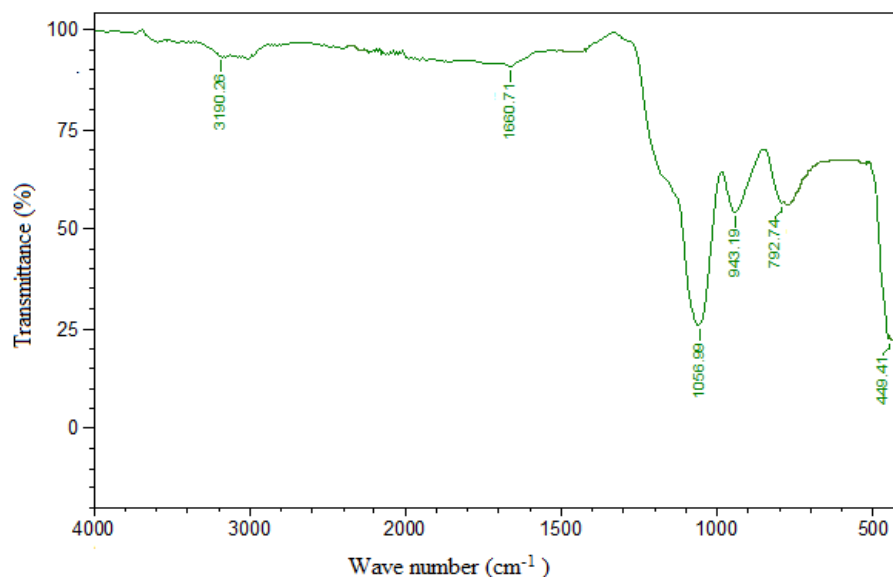


Fig.1. FTIR spectrum of Au@SiO₂core-shell NPs

3.2 Atomic force microscopy (AFM)

Two-dimensional (2D) and three - dimensional (3D) AFM images of Au@SiO₂core-shell nanoparticles are shown in Fig.2. (a & b). The particles appears to have different sizes. The average roughness (Ra) and root mean square (RMS) roughness (Rq) for Au@SiO₂core-shell NPs are 3.844 and 8.425 nm. The calculated value of ten-points mean height roughness (Rz) of Au@SiO₂core-shell NPs is 173.626 nm. The Roughness skewness (Rsk) for Au@SiO₂core-shell NPs is - 5.532 nm. Negative skew is a criterion for a good bearing surface. This negative value indicates that the valleys are dominant over the scanned area. The calculated value of Rku for Au@SiO₂core-shell NPs is 30.098 nm. The Rku values shows that the surface of Au@SiO₂core-shell NPs is spiky surface.

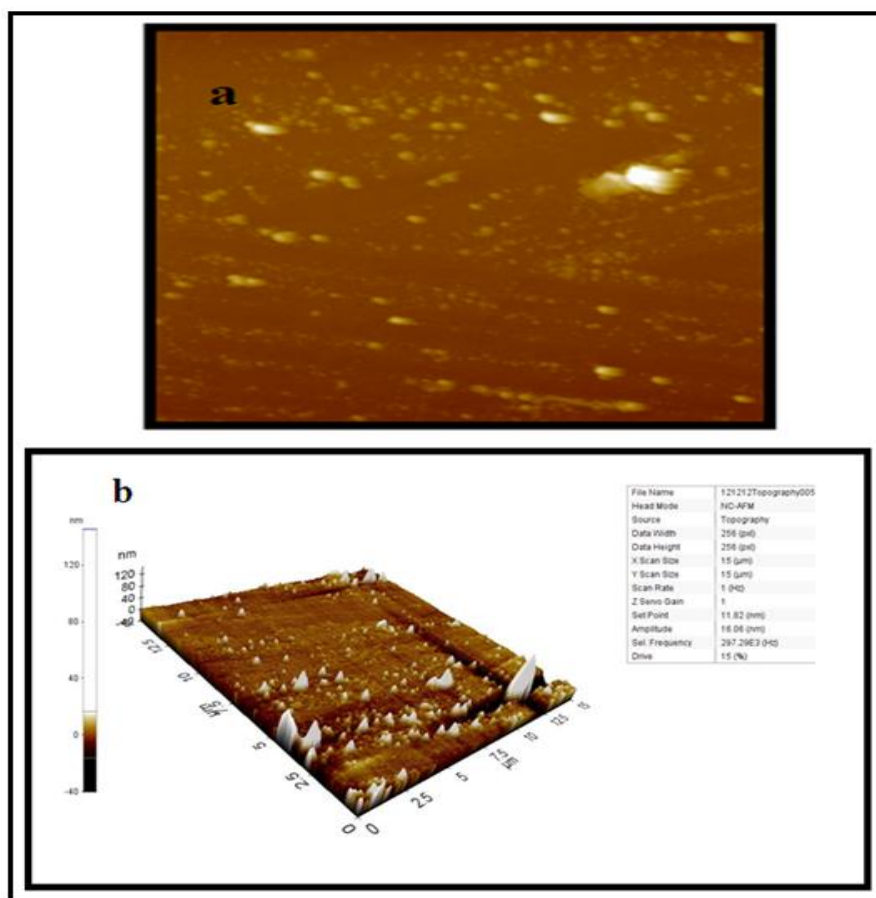


Fig.2 (a & b) AFM images of Au@SiO₂ core-shell NPs

3.3 High resolution transmission electron microscopy (HR-TEM)

The HR-TEM images of Au@SiO₂ are shown in Fig.3 (a & b) nearly well defined spherical morphology is observed. Its sizes distribute between nm with an average of about 20-30 nm. The shell thickness is found to be 7-10 nm. This image illustrates that each particle has a thin capping of SiO₂ shell. TEM studies reveal that the shells are completely covering the particles. There appears some non-uniformity in the shell thickness. The thickness of the silica shells could be changed by varying the amount of TEOS added. The density of the gold particles is higher than

for the SiO_2 therefore, in the TEM image the gold particles is much darker in comparison with the SiO_2 particles.

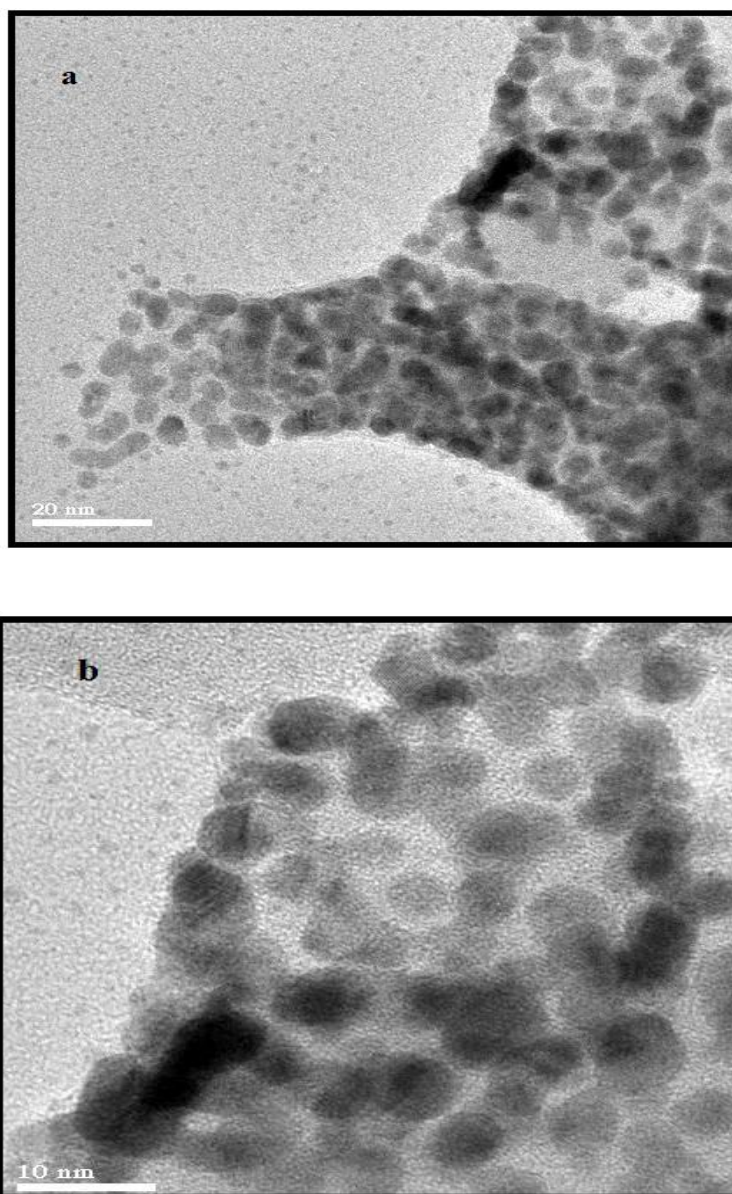


Fig.3 (a & b) HRTEM images of Au@SiO_2 core-shell NPs

3.4 DNA binding study

3.4.1 Electronic absorption titration

Absorption titration was carried out to monitor the interaction of a compound with DNA (Fig.4). The changes observed in the UV spectra of the complexes after mixing them with DNA (either increase or decrease in the intensity or shift in the wavelength) indicate the interaction of the nanoparticles with DNA. This bathochromism result might be due to the decrease in the energy of π - π^* transition, when the π -orbital of the base pairs of DNA coupled with the π - π^* orbital of the intercalated ligand. The nanoparticles with a fixed concentration in DMF-Tris-HCl buffer were titrated with the different concentration of CT-DNA. Addition of DNA to fixed concentration of nanoparticles, caused spectral changes. The observed strong hypochromicity (27.77 %) and bathochromic shift (20 nm) of the absorption maxima are an indication of the existence of an intercalative mode of binding between CT-DNA and the core-shell NPs, as expected for non-covalent interaction of nanoparticles with DNA. Such spectral changes have been often interpreted to arise from a strong interaction between the nanoparticles and base pairs of DNA. Intercalation involves the insertion of a planar molecule between DNA base pairs, which results in a decrease in the DNA helical twist and lengthening of the DNA [15].

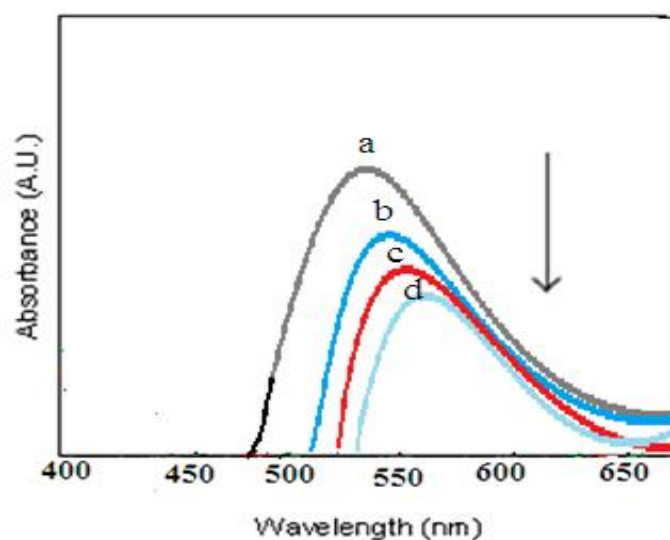


Fig.4. UV-Vis spectrum of Au@SiO₂ core-shell NPs (1×10^{-4} M) in 5mM Tris-HCl buffer with increasing amounts of DNA. a) Free NPs, b) NPs + 0.6×10^{-4} M DNA, c) NPs + 0.8×10^{-4} M DNA and d) NPs + 1×10^{-3} M DNA

The intrinsic binding constant (K_b) for Au@SiO₂core-shell NPs with DNA is found to be $4.289 \times 10^4 \text{M}^{-1}$. The binding constant values observed from the electronic spectral result (Fig.5) indicate the possibility of deep penetration of core-shell nanoparticles into the core of DNA.

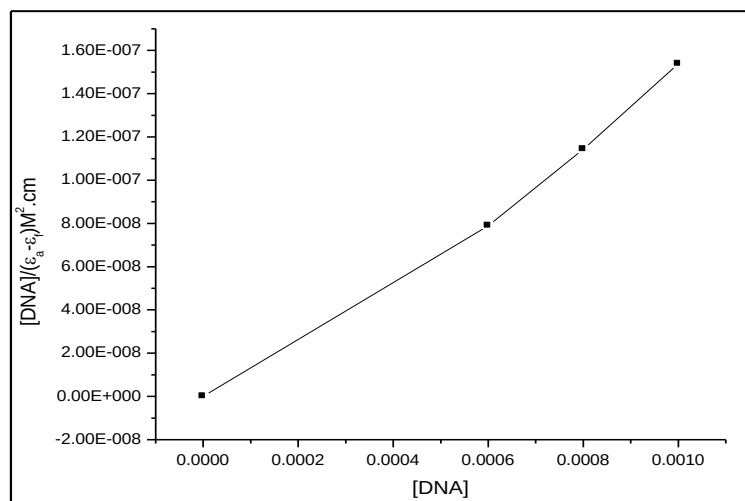


Fig.5 Plot for the determination of K_b

5. Conclusion

In the present study Au@SiO₂ core-shell nanoparticles were successfully prepared and their nanosize was confirmed using techniques such as FTIR, AFM and HRTEM techniques. The results of UV spectroscopy showed that the core-shell nanoparticles bind with DNA via interaction as well as intercalation with the base pairs of DNA. The observed spectral studies indicate that the nanoparticles were intercalated to the DNA due to their small size, which enhanced its solubility in aqueous medium. DNA intercalators have been used extensively as antitumor, antineoplastic, antimalarial, antibiotic and antifungal agents.

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