Citrus sinensis peel waste assisted synthesis of AgNPs: effect of surfactant on the nucleation and morphology

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Abstract

Silver nanoparticles (AgNPs) were synthesized by using *Citrus sinensis* peel waste extract. Optical images and UV-visible spectroscopy reveals the appearance of yellow to brown-red color and surface plasmon resonance (SPR) band at 400–480 nm, respectively, due to the formation of AgNPs. The stable perfect transparent silver sols were formed in presence of cetyltrimethylammonium bromide (CTAB). The brownish precipitates appeared with sodium dodecyl sulphate (SDS) after 3 h. The nucleation, position of SPR band and intensity depends on the head group nature of cationic and anionic micelles of SDS and CTAB. The as-prepared AgNPs were characterized using conventional techniques such as Fourier-transform infra-red, energy dispersed X-ray detector, scanning electron microscope, transmission electron microscope, and X-ray diffractometer. Zeta potential of CTAB-AgNPs was calculated and found to be stable for ca. 1 week. Molar concentration (3.3×10^{-4} mol/L) and aggregation number (607,339.917) of DPE-AgNPs were calculated. Ascorbic acid, citric acid and total reducing sugars were estimated in dry and fresh peel extract. Gram positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* bacteria shows excellent antibacterial activities toward DPE-AgNPs.

Keywords *Citrus sinensis* · AgNPs · Surfactant · Morphology

1 Introduction

Use of different capping agent for the synthesis of metallic nanoparticles have received considerable attention in the past two decades, which exhibit different size, shape, optical, catalytic, water treatment, and sensing properties in the field of chemical, physical and medical sciences [1–4]. Due to presence of sharp SPR band, fabrication of AgNPs have been the research interest of various scientists in nanotechnology by using different chemical and physical methods [5, 6]. Most of these methods required the necessity of toxic non-biodegradable polymers, surfactants, ligands and organic solvents [7–10]. Yin et al. used chemical reduction method for the synthesis of AgNPs with Tollens' reagent (complex of silver ions with ammonia), sodium borohydride, sorbitol, and formaldehyde [11].

Yao et al. synthesized AgNPs by using grape seed and use as catalyst for the degradation of toxic dye [12]. Transition metal NPs have been fabricated from various parts of natural plants such as leaf [13, 14], fruit [15, 16], stem [17], roots [18], flower [19] and others sustainable low cost and eco-friendly natural materials [20, 21]. The bioorganic materials of natural resources acted as capping and reducing agent, which control aggregation and agglomerations of the NPs [22–24].

Citrus sinensis (orange) is one of the most popular fruit has been used around the world, the main world producers of orange fruit are Brazil, China and the USA [25]. As the result, there are millions of tons of orange peel waste have been throwaway. Orange peel contains soluble sugars, pectin, insoluble polysaccharides, polyphenols, amino acids, citric acid and ascorbic acid, and other biomolecules

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[26, 27]. Orange peel also contains large amount of moisture (80–90% w/w of water content). So, the investigators reused these wastes of orange to synthesis metal NPs which acted as reducing and stabilizing agents [28–32]. For example, Amanulla et al. used orange peel extract to the synthesis of TiO_2 NPs from titanium tetra chloride–redox reaction [28]. Omran et al. recycling the orange peel wastes for the eco-friendly and low cost preparation of AgNPs [30]. Kaviya and his coworkers reported the use of orange peel extract as a reducing agent for the synthesis of AgNPs and evaluated the antibacterial activity of against human pathogens [31]. Various investigators such as Barros et al. [33], Skiba et al. [34], and Awad et al. [35] used orange peel waste extract as reducing agent for the biogenic synthesis of AgNPs, and evaluated their antibacterial and catalytic activities against human pathogens and methylene blue under solar irradiation respectively. Soto and his co-workers utilized fruits peel for the preparation of AgNPs and determined their antimicrobial activities against foodborne pathogens [36]. Rangayasami et al. [37], Aswini et al. [38], Gavade et al. [39], and Gawade et al. [40] used Lindau leaf extract, Ledebouria Revoluta bulb extract, *Ziziphus jujuba* leaf extract, and *Calotropis procera* leaves for the fabrication of Ag and ZnNPs for various biological and photocatalytic applications, respectively.

Various stabilizers such as carbohydrates, lipids, organic solvents, proteins, polymers, polyphenols, and surfactant were used to control the morphology of metal NPs (from cubes, hollow structures, disks, multi-branched to multi-ponds) [1, 8, 15, 28, 41, 42]. Radhika et al. [43] and Kannan et al. [44] were prepared La–Sr–Co–Fe– δ , and Co-doped rare-earth-based ceria nanocomposites by using cetyltrimethylammonium bromide (CTAB) as a capping agent. Ceria based (Sm doped-CGO) nanocomposite was also synthesized by chemical precipitation method for electrolytic applications [45]. Out of these, CTAB surfactant has been considered as a best capping agent for the synthesis of advanced AgNPs having different morphology [46]. CTAB also tuned the plasmonic properties of AgNPs [47]. Kannangara et al. reported the synthesis of nano zeolite-A with using sodium dodecyl sulphate (SDS) for controlling the particle size and as a site directing agent and it gives a particle with phase with high degree of crystallinity [48]. Das et al. reported the effect of cationic CTAB surfactant on optical, dielectric and magnetic properties of cobalt ferrite NPs, and they also suggested that the CTAB reduces the particle size and enhanced the coactivity as well as remnant ratio of cobalt ferrite NPs [49]. Phuruangrat et al. used NaBH_4 as a reducing agent for the synthesis of $\text{Ag/Bi}_2\text{WO}_6$ nanoplates and $\text{Ag/Bi}_2\text{MoO}_6$ nanocomposites and determined their photocatalytic activities against rhodamine B toxic dye degradation [50, 51]. It has been established that the different kind of surfactant significantly reduce the

particle size without changing the shape. The size reducing ability is not same for all the surfactants, depending on the type of surfactant. However, the use of *C. sinensis* peel wastes as a reducing agent for the synthesis AgNPs has been ignored in presence of shape-controlling surfactants.

Therefore, the aim of this present study was to evaluate the role of surfactant on the morphology of *C. sinensis* peel wastes assisted synthesis of AgNPs. For this purpose, dry peel extract (DPE), and fresh peel extract (FPE) were prepared in water and used as a reducing agent with different concentrations for the preparation of AgNPs. CTAB and SDS were used as capping agent to determine the path of reduction of Ag^+ ions into metallic silver.

2 Experimental

2.1 Materials

Citrus sinensis (sweet orange) was collected from local grocery store, washed, and took out just the peel. For extract preparation, peel was dried for many days at room temperature. The 15 g powder of the dry orange peel was taken in a conical flask, add 250 mL deionized double distilled water, heated for 30 min under 60 °C, the solution could cool down to room temperature and filtered with Whatman filter paper No. 1. The resulting filtrate was stored in amber colored glass container in dark and labeled as DPE. The 15 g of fresh orange peel was also used for the preparation of extract under similar conditions and designated as FPE. Silver nitrate (molar mass = 169.87, 99.9%) solution (0.01 mol/L in 250 mL) was prepared in deionized double distilled water and stored in an amber glass container to prevent the photochemical reduction of Ag^+ ions. CTAB (molecular weight = 364.45 g per mol; Fluka, 99.9%) and SDS (molecular weight = 288.372 g per mol, 99.9% Sigma-Aldrich) solutions were prepared in deionized water and used as a stabilizer and/or capping agent.

2.2 *Citrus sinensis* peel extract assisted of AgNPs

DPE and FPE were used as a green reducing agent for the synthesis of AgNPs. The DPE (5.0 mL) was added into a series of conical flask containing different concentrations of AgNO_3 solution (ranging from 2.0 to 10.0 mL of 0.01 mol/L) and diluted with deionized water for fixed the volume constant. The total volume was maintained constant (50 mL) for all experiments. For the next experiments, the same concentration of AgNO_3 (1.0 mM) was added into the solution containing different amount of DPE (from 10 to 50%). The resulting reaction mixtures were stirred at room temperature with constant stirring. To determine the effects of stabilizers, the 5.0 mL of DPE was

mixed with AgNO_3 (1.0 mM) in different reaction vessel containing CTAB (from 4.0×10^{-4} to 10.0×10^{-4} mol/L) and SDS (4.0×10^{-3} to 10.0×10^{-3} mol/L) solutions. The colorless solutions became pale yellow, yellow to red orange red with increasing reaction time due to the formation of AgNPs [36]. The progress of reaction was monitored by recording SPR absorbance on a UV-visible spectroscopy (Shimadzu UV-visible multi Spec-1501). UV-Vis spectra were recorded at different time intervals in the wavelength ranging from 200 to 800 nm. The same experiments were performed with FPE with same concentrations of Ag^+ ions, CTAB and SDS at room temperature.

2.3 Characterization of NPs

UV-visible (UV-Vis, Shimadzu UV-visible multi Spec-1501) spectrophotometer was used for the measurement of spectra having 1 cm quartz cuvettes at different time intervals. Scanning electron microscope (SEM), transmission electron microscope (TEM, JEM 2100), equipped with energy dispersed X-ray detector (EDX), and Burker Tensor Fourier-transform infra-red (FTIR) instrument were used to determine the morphology of as-prepared AgNPs and capping action of surfactant with NPs. Rigaku X-ray diffractometer (XRD) operating at 40 kV with Ni filtered Cu K_α radiation ($\lambda = 1.54056$) were used to determine the crystalline nature of metallic silver. For TEM measurements, the one or two drop of silver sols was placed on the surface of carbon coated copper grid and the solvent was evaporated at room temperature before the experiment. The KBr disk was prepared by dropping resulting sols on the surface of pellet and dried in air before recording FTIR spectra. The aqueous suspensions of AgNPs were centrifuged for 30 min and solid AgNPs was washed with distilled water and dry at room temperature before the measurement of SEM. Fisher Scientific pH meter used to monitor the pH at the beginning as well as end of the reaction.

2.4 Estimation of biomolecules in *C. sinensis* peel extract

Water soluble constituents of *C. sinensis* peel extract were responsible to the reduction of colorless Ag^+ ions into dark yellow to red orange silver sols. Ascorbic acid, citric acid and water-soluble sugars were determined with standard methods in both DPE and FPE. Spectroscopic and titration methods were used to determine the concentration of ascorbic and citric acid in *C. sinensis* peel extract [52, 53]. Klein and Perry spectroscopic method was used for the quantitative estimation of ascorbic acid with slight modification [52]. In a typical experiment, the 5 g dry peel was mixed with required amount of metaphosphoric acid (5%, 20 mL), stirred for 30 min at room temperature and

filtered. The extract was treated with 2, 6-dichloroindophenol and the absorbance of resulting color was measured at 515 nm. A calibration curve (absorbance versus ascorbic acid concentration) was prepared for standard solution of authentic sample of ascorbic acid with 2, 6-dichloroindophenol and amount of ascorbic acid was calculated from the calibration graph. Titration methods were employed to determine the concentrations of ascorbic and citric acids in peel extract. For ascorbic acid estimation, the DPE was titrated with potassium periodate (KIO_4) in presence of starch as an indicator [54]. For citric acid, the extract was titrated against standard NaOH solution using phenolphthalein as an indicator. The results are given in μg of ascorbic and citric acid in per g of extract. Water soluble reducing sugars were estimated by using dinitrosalicylic acid color test method. Glucose was used as a standard for the construction of calibration curve by measuring the absorbance at 575 nm. The dissolved molecular oxygen gas was removed with bubbling pure nitrogen gas through the reaction test [54].

2.5 Calculation of molar concentration and number of silver atoms

The number of silver atoms NPs (N) and molar concentration (C) of NPs were calculated by using the following relations (Eqs. 1 and 2) for the 100% reduction of silver ions into metallic silver.

$$N = \frac{\pi \rho N_A}{6M} \times D^3 \quad (1)$$

$$C = \frac{N_T}{NVN_A} \quad (2)$$

where N, ρ , N_A , D and M are the aggregation number of AgNPs, density of metallic silver (10.5 g/cm^3), Avogadro's number (6.02×10^{23}), average diameter of AgNPs and atomic mass of silver (107.86 g), respectively. N_T and V, respectively, are the total silver atoms used as AgNO_3 and volume of the reaction mixture in liter (0.05 L).

2.6 Antibacterial activities of AgNPs

Antibacterial activities of DPE-AgNPs were determined by using turbidity kinetic method against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* [55]. In a typical experiment, the cultured bacterial cells were added into the separates reaction vessel containing the required amount of DPE-AgNPs (ranging from 10.0×10^{-5} to 40.0×10^{-5} mol/L). The progress of growth of bacterial (killing kinetics), was monitored by recording the decay of absorbance at 600 nm as a function of time.

The growth rate constants were calculated with first order rate-law ($\text{rate} = 2.303/t (\log(\text{OD}_a - \text{OD}_0 / \text{OD}_a - \text{OD}_t))$), where OD is the optical density at final, initial, and different time intervals at 600 nm). The gentamicin was used as standard inhibition control.

3 Results and discussion

3.1 Fresh peel extract assisted synthesis of AgNPs

Preliminary observations indicate that the yellow to dark red color was developed in a reaction mixture containing same amount of AgNO_3 (5.0 mL of 0.01 mol/L) and different amount of FPE. At higher extract concentration ($\geq 60\%$), dark yellow-red precipitate was formed instead of perfect transparent color. The resulting silver sols were unstable. To determine the stability of AgNPs, a series of experiments were performed with varying FPE concentration from (10% to 50%) at fixed concentration of AgNO_3 (5.0 mL of 0.01 mol/L = 1.0 mM) at 30 °C. The colorless reaction solution containing peel extract and AgNO_3 became pale yellow with reaction time, indicating the reduction of Ag^+ ions into metallic silver [46]. UV-visible spectra of resulting color were recorded as a function of time. Figure 1 shows the effect of FPE on the growth of AgNPs for different concentration. FPE shows an absorption peak at ca. 400 nm and spectra was featureless in the entire visible region (Fig. 1a, red line). A broad shoulder starts to develop at 450 nm, intensity increases with time and blue shifted from 450 to 465 nm, which might be due to the formation of AgNPs. The peak intensity of FPE was decreased with time at 400 nm, suggesting the role of water soluble chemical constituents (mainly ascorbic acid) of peel extract as reducing agent. Inspection of Fig. 1a–e clearly shows that the SPR intensity of broad shoulder at 450 nm increases with increasing concentration of FPE from 10 to 40% with a red shift and decreases for 50% FPE (Fig. 1e). At higher concentration, decrease in the SPR intensity might be due to the adsorption of FPE active constituents on the surface of AgNPs. Reaction-time profile (absorbance versus time) plots indicate that the all process (nucleation, growth, and stabilization) decreases with increasing the FPE concentration (Fig. 2).

3.2 Role of stabilizers

It is well known that the presence of a suitable stabilizer is essential to block the unlimited growth of metal NPs. To establish the role of stabilizers and to prepare stable silver sols at room temperature, two surfactants, CTAB and SDS were used as capping agent. UV-visible spectra of the mixture were recorded with different time intervals.

SPR intensity starts to develop in the visible region with increasing reaction time (Table 1). A broad shoulder was appeared at ca. 500 nm after 24 h. Inspection of Fig. 3a shows that the resulting silver sol exhibited a well-defined SPR band after 48 h and shape of the spectra depends on the reaction time. The same experiment was also performed with SDS (2.0 mL of 0.1 mol/L). Figure 3b shows the effect of reaction time on the formation of SDS-AgNPs. The resulting sols exhibited broad SPR shoulder in the entire visible region. The growth spectra of CTAB and SDS assisted AgNPs were different for both surfactants, which clearly explains the different stabilizing and/or capping action of surfactant [9]. Optical images of extract, CTAB and SDS-AgNPs indicate that the resulting sols are unstable in presence of SDS. The yellowish turbidity appeared within 120 min for SDS-AgNPs. Interestingly, CTAB-AgNPs (red orange color) was stable for ca. 24 h and no precipitate or turbidity was appeared (Scheme 1), which might be due to the capping action of CTAB micelles. CTAB stabilized the AgNPs and blocked the unlimited growth of NPs. As a result, perfect transparent of AgNPs were formed in presence of CTAB.

3.3 Dry peel extract assisted synthesis of AgNPs

To compare the reactivity of DPE with FPE towards AgNO_3 interaction, same experiments were performed with DPE and AgNO_3 with and without CTAB and SDS (Table 1). To determine the effect of DPE concentration on the stability of AgNPs formation, a series of kinetic experiments were performed fixed concentration of AgNO_3 and varying concentrations of DPE from 10 to 40%. At higher DPE concentration ($\geq 50\%$), the resulting silver sols were unstable and yellowish precipitate was formed due to the uncontrolled agglomeration process. UV-visible spectra were recorded as a function of time to the formation of silver NPs. Figure 4 shows the that the resulting silver sol exhibited a well-defined SPR band in the 400–500 nm within 5 min of reaction time. The reduction of Ag^+ into Ag^0 was fast and resulting sols show a SPR band at 468 nm after 5 min for extract stabilized AgNPs. The SPR intensity increased and decreased with time due to the uncontrolled capping action of extract but position of band remains constant for entire reaction time (Fig. 4a).

To determine the effect of surfactant, the lower DPE concentration (10%) was used for the entire studied. For CTAB-AgNPs ([CTAB] = 1.0 mM), a band was appeared at 418 nm (Fig. 4b). The resulting sol shows SPR band at 477 nm for SDS-AgNPs (Fig. 4c), which indicates the formation of larger size AgNPs. These results revealed that the SPR intensity, and band position depends on the reaction parameters such as reaction time, concentration of reducing and stabilizing agent. Inspection of these results

Fig. 1 Time resolved UV-visible spectra of AgNPs formation with varying concentration of DPE. Reaction conditions: $[Ag^+] = 1.0$ mM, $[DPE] = 10$ (a), 20 (b), 30 (c), 40 (d) and 50% (e), temperature = 30 °C

clearly indicates that the wavelength maxima of AgNPs depend on the nature of capping action of stabilizers (Table 1). The blue (from 468 to 418 nm) and red (from 468 to 477 nm) shift were observed for CTAB- and SDS-AgNPs, which might be due to the different capping and

stabilizing role of used surfactant during the nucleation step ($Ag^+ \rightarrow Ag^0$). It is well known that the fresh *C. sinensis* peel contained ca. 80–90% w/w of water, whereas dry peel has 20% water [56]. Ascorbic acid (=525 μ g/100 g extract), citric acid (=95 μ g/100 g extract) and reducing sugars

Fig. 2 Reaction-time profiles to the formation of AgNPs for Fig. 1 data

(=40 mg/100 g extract) were determined in DPE. Due to the high content of water, the same amount of fresh peel has the lower concentration of water soluble reducing agent than that of dried peel. On the other hand, FPE contained ascorbic acid = 50 µg/100 g extract. Ascorbic acid is a strong reducing agent than that of reducing sugars and citric acid. The different behaviors of both peel extract (fresh and dry) can be rationalized with the higher concentration of ascorbic acid DPE (Scheme 2), which clearly shows that the reduction of Ag^+ into Ag^0 was completed within ca. 10 min of the reaction time for the DPE.

3.4 Capping mechanism of stabilizers

The aqueous extract of orange peel contained water soluble polyphenols, sugars and organic acids [25, 26, 57, 58]. Out of these, ascorbic acid is the major constituents of peel extract in water at room temperature. CTAB and SDS were ionized in aqueous water and formed various aggregates (from monomer, dimer, and trimer to micelles). At critical micellar concentration, these aggregates are called as micelles, which incorporates the water soluble and water insoluble materials into its small volume via electrostatic, hydrophobic, hydrogen bonding and van der Waals forces [59]. The polar ionic head group has significant impact on the solubilization processes. Cationic and anionic head groups of CTAB and SDS micelles, respectively, repelled and attracted the Ag^+ ions due to electrostatic interactions. Ionized SDS formed complex with Ag^+ ions (Eqs. 3 and 4).

The reduction potential of Ag^+/Ag^0 (=0.799 V) was reduced to some extent after complex formation with ionized SDS [60]. This type of situation does not persist in CTAB due to repulsion between Ag^+ and positive head group ($-\text{N}(\text{CH}_3)_3^+$). Ascorbic acid transfers the electrons to the Ag^+ , which reduces to metallic Ag^0 (Eqs. 5 and 6).

Table 1 Effects of reaction parameters on the morphology of orange peel extract assisted synthesis of AgNPs

[FPE] (%)	[Ag^+] (mM)	CTAB/SDS	Observations
10	1.0	0.0	Pale yellow, λ_{max} = 450 nm, 120 min, stable
20	1.0	0.0	Pale yellow, λ_{max} = 455 nm, 120 min, stable
30	1.0	0.0	Pale yellow, λ_{max} = 460 nm, 120 min, stable
40	1.0	0.0	Pale yellow, λ_{max} = 460 nm, 120 min, stable
50	1.0	0.0	Pale yellow, λ_{max} = 465 nm, 120 min, stable
[DPE] (%)	[Ag^+] (mM)	CTAB/SDS	Observations
10	1.0	0.0	Yellow, λ_{max} = 468 nm, 5 min, stable
20	1.0	0.0	Yellow, λ_{max} = 468 nm, 5 min, stable
30	1.0	0.0	Yellow, λ_{max} = 468 nm, 5 min, stable
40	1.0	0.0	Yellow, λ_{max} = 468 nm, 5 min, stable
10	1.0	0.4 mM (CTAB)	Pale yellow, λ_{max} = 500 nm, 5 min, stable
10	1.0	1.0	Dark yellow, λ_{max} = 420 nm, 5 min, stable
10	1.0	5.0	Dark yellow, λ_{max} = 420 nm, 5 min, stable
10	3.0	1.0	Dark yellow, λ_{max} = 420 nm, 5 min, stable
10	5.0	1.0	Dark yellow, λ_{max} = 420 nm, 5 min, stable
10	7.0	1.0	Unstable, yellowish precipitate
10	1.0	2.0 (SDS)	Pale yellow, λ_{max} = 477 nm, 30 min, unstable
10	1.0	8.0	Unstable, yellowish precipitate

Fig. 3 Time resolved UV-visible spectra of CTAB-AgNPs (**a**) and SDS-AgNPs (**b**) formation with FPE. Reaction conditions: $[Ag^+] = 1.0$ mM, $[FPE] = 10\%$, temperature = 30°C

Scheme 1 Optical images of $AgNO_3$ and AgNPs formation with FPE in absence and presence of SDS and CTAB at different time

Metallic silver immediately converted to the stable species of colloidal silver after complexation and dimerization processes (Eqs. 7 and 8) [61].

On the other hand, the surface of silver NPs (Ag_4^{2+}) is positive [61], which also interacts with the negative head group of SDS micelles. Formation of $SD-Ag^+$ complex delayed the electron gaining tendency of silver ions from the reductant. The larger size silver NPs were formed for the slow redox reaction. As a result, yellowish turbidity was observed with SDS surfactant instead of perfect

transparent silver sols formation (Scheme 1). CTAB is a better stabilizing agent than that of SDS [9].

3.5 Characterization of AgNPs

Morphology of DPE-AgNPs and CTAB-AgNPs were determined by using TEM, SEM, EDX, FTIR, and XRD measurements. For DPE assisted synthesis of AgNPs, the reaction was completed within ca. 10 min of reaction time in presence of CTAB and resulting silver sols were stable. On the other hand, yellowish turbidity was appeared in presence of SDS. Therefore, samples of DPE-AgNPs and CTAB-AgNPs were prepared for the characterization. TEM images of DPE-AgNPs and CTAB-AgNPs are given in Fig. 4a and b, respectively, with UV-visible spectra. The NPs are spherical with size ranging from 11 to 35 nm for DPE (Fig. 4a). The NPs are aggregated in an unsymmetrical manner and leads to the formation of necklace-like metallic silver with CTAB having smaller size ranging from 8 to 22 nm (Fig. 4b). CTAB acted as a stabilizer and adsorbed on the surface of

Fig. 4 Time resolved UV-visible spectra and TEM images of DPE-AgNPs (a) and CTAB-AgNPs formation with DPE (b). Reaction conditions: $[Ag^+] = 1.0$ mM, $[DPE] = 10\%$, $[CTAB] = 1.0$ mM, temperature = 30°C

AgNPs. Particles are spherical in both cases. Minute black spots were also visualized on the surface of metallic silver, indicating the presence of orange peel biomolecules on the surface of NPs [21, 54]. The size distribution curves of DPE-AgNPs and CTAB-AgNPs are given in Fig. 5a and b, respectively.

Figure 6a and b shows the SEM and EDX of DPE-AgNPs and CTAB-AgNPs. These results reveal that the as-prepared AgNPs are spherical and aggregated to each other. Morphology (shape, size, and the size distribution) are different for CTAB-AgNPs than that of DPE-AgNPs. Inspection of EDX spectra clearly indicates that our sample did not contained N and Br, which might be removal of CTAB during the washing processes (Fig. 6). The presence of C and O might be due to the carbon coated Cu TEM grid and sample preparation at room temperature, respectively. EDX indicates that the NPs contained 100% pure silver content.

To determine the capping nature of CTAB, FTIR spectra were also recorded. Figure 7 shows the FTIR spectra of CTAB-AgNPs and DPE-AgNPs. The main peaks were

appeared at 2920 , 2880 , and 1420 cm^{-1} are assigned to asymmetric $\nu_{(as)}$ (CH_3), symmetric $\nu_{(s)}$ (CH_2), $\nu(\text{C}-\text{N})$ for pure CTAB. For CTAB-AgNPs, the peaks are red shifted and their intensity was also decreased. The peak at 3450 cm^{-1} for $\nu_{(as)}$ ($-\text{OH}$) might be due to the presence of polyphenols and ascorbic acid on the surface of AgNPs. The FTIR spectrum of DPE-AgNPs is depicted in Fig. 7, which shows the presence of two main absorption peaks at ca. 3450 and 1750 cm^{-1} , which assigned to the $\nu_{(as)}$ $-\text{OH}$ groups of ascorbic acid of orange peel constituents and carbonyl group as ester-like [62] (Fig. 7, inset).

XRD spectra of CTAB-AgNPs and DPE-AgNPs were recorded to determine the crystalline nature of NPs. XRD spectra of both AgNPs shows the presence of four Bragg peak at 2θ values of 38.2° (111), 44.3° (200), 64.5° (220), and 77.5° (311) (JCPDS file NO: 89-3722), which indicates that the NPs have face-centered-cubic metallic AgNPs. We did not observe any remarkable shift of all diffraction peaks of CTAB-AgNPs and DPE-AgNPs (Fig. 8). The average size of AgNPs was calculated using (Eq. 9).

Scheme 2 Effect of DPE and FPE on the nucleation and growth processes of AgNPs formation with CTAB

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (9)$$

where D , k ($=0.9$ constant), λ , β , and θ are the crystallite size of AgNPs, source of X-ray radiation ($=0.15406$ nm), full width at half maximum of the peak, and Bragg's angle, respectively. The average size of AgNPs was calculated using (Eq. 9). The calculated average particle is found to be 25 nm and 28 nm for CTAB-AgNPs and DPE-AgNPs, respectively, for the width of (111) Bragg's refraction.

Zeta potential provides significant information about the stability of NPs. To determine the stability of CTAB-AgNPs, zeta potential (ζ) was also calculated with Smoluchowski equation Eq. (10) [63].

$$\xi = \frac{4\eta\pi}{D} \times EM \quad (10)$$

where η = viscosity of the solvent, D = dielectric constant of the solvent, and EM = electrophoretic mobility. The NPs with zeta potential more negative than -30 mV and more positive than $+30$ mV are stable [24]. The zeta potentials were found to be -8 mV and -30 mV, respectively, for DPE- and CTAB-AgNPs. The lower value of zeta potential indicates that the DPE-AgNPs are unstable and yellowish turbidity was appeared after 24 h at room temperature. To determine the stability of CTAB-AgNPs, the zeta potential values were determined for 1 week (Fig. 9). We did not observe any significant change in the value of zeta potential, which shows that the stable AgNPs were formed with CTAB.

The N was calculated by substituting using the values of ρ , N_A , D , and M in Eq. (1). The average diameter of AgNPs was calculated by TEM (20 nm). The molar concentration of AgNPs were calculated with Eq. (2) by substituted the

Fig. 5 Size distribution curves of DPE-AgNPs and CTAB-AgNPs. Reaction conditions: $[Ag^+] = 1.0$ mM, $[CTAB] = 1.0$ mM, $[DPE] = 10\%$, temperature = 30°C

values of N_T , N , V and N_A . The calculated values of average diameter, N and C are summarized in Table 2. The values of N ($=607,339.917$) for DPE capped AgNPs is higher than that of N ($=179,952.568$) of CTAB-AgNPs, which might be due to the uncontrolled growth of AgNPs in absence of CTAB. Surfactant solubilized the reactants (Ag^+ and ascorbic acid) into its small volume, enhances the nucleation and controlled the growth processes [9, 23]. The DPE-AgNPs were unstable for long time storage, whereas CTAB-AgNPs are stable and can be used for the industrial and medicinal applications.

3.6 Antibacterial activities of DPE-AgNPs

It is well known that the metallic-silver and aqueous silver ions have been used to the treatment of human wounds and burns from the ancient time in the form of $AgNO_3$. The AgNPs shows potential antimicrobial activities against human pathogens [2, 8]. Therefore, antibacterial activities of AgNPs were determined against Gram-positive *S. aureus* and Gram-negative *E. coli* by using turbidity kinetic growth method [64]. The observed results are depicted graphically in Fig. 10 as absorbance-reaction time profiles. The reaction proceeds through an induction period (lag phase) followed by a growth as well as stationary phase, the nature of the kinetic curves depends on the concentration of AgNPs. The lag phase depends on the concentration of DPE-AgNPs. For *S. aureus* and *E. coli*, the rates were found to be $2.9, 2.5, 2.2, 1.6 \times 10^{-1} \text{ h}^{-1}$ and $3.7, 3.3, 3.1, 2.9 \times 10^{-1} \text{ h}^{-1}$ for $10.0, 20.0, 30.0$ and $40.0 \times 10^{-5} \text{ mol/L}$ DPE-AgNPs concentrations. The growth rates decrease with increasing the

NPs concentration. Our results are in good agreement to the observations of Sondi and Salopek-Sondi regarding to the effect of AgNPs on the growth of bacteria [64]. The growth rate killing of bacteria with gentamicin were found to be $3.6 \times 10^{-1} \text{ h}^{-1}$ and $4.4 \times 10^{-1} \text{ h}^{-1}$ for *S. aureus* and *E. coli*, respectively. The antibacterial activity of gentamicin is higher than that of DPE-AgNPs under our experimental conditions.

The role of metal ions in biological systems has been realized for a long time. Some metals are essential for the physiological activities of the cellular and subcellular functions [65]. Transition metals are the active constituents of various enzymes and proteins. Metal complex were used in tumor diagnosis and as anticancer agents. They are toxic at higher concentrations and disturbed the biological function of proteins and nucleic acids. Metal NPs were formed complex with protein cell wall bacteria, undergoes redox reaction, and released metal ions and reactive oxygen species inside the membrane cell wall. Cysteine formed complex with AgNPs, released Ag^+ ions and cysteine radical. Finally, cystine was formed after dimerization of generated radical, which changed the activities of protein cell wall. The decreases of growth rates with increasing AgNPs, can be rationalized due to the killing of bacterial cell activities.

4 Conclusion

We demonstrated the use of fresh and dry *C. sinensis* peel waste aqueous extract for the synthesis of AgNPs. UV-visible data revealed that the FPE and DPE have significant

Fig. 6 EDX and SEM images of DPE-AgNPs (a), and CTAB-AgNPs. Reaction conditions: $[Ag^+] = 1.0$ mM, $[DPE] = 10\%$, temperature = $30^\circ C$

Fig. 7 FTIR spectra of DPE-AgNPs and CTAB-AgNPs. Inset: FTIR spectrum of pure DPE. Reaction conditions: $[Ag^+] = 1.0$ mM, $[DPE] = 10\%$, temperature = $30^\circ C$

Fig. 9 Zeta potential of DPE-AgNPs and CTAB-AgNPs as a function of time. Particle charge was negative in both cases

Fig. 8 XRD spectra of DPE-AgNPs and CTAB-AgNPs. Reaction conditions: $[Ag^+] = 1.0$ mM, $[DPE] = 10\%$, temperature = $30^\circ C$

impacts on the nucleation and growth processes. The stability depends on the concentration of extract, silver

Table 2 The values average diameter, N, and C of DPE-AgNPs and CTAB-AgNPs

Parameters	DPE-AgNPs	CTAB-AgNPs
Average diameter(nm)	30	20
N	607,339.917	179,952.568
C (mol/L)	3.3×10^{-4}	1.11×10^{-7}

ions, CTAB and SDS. Nucleation was fast for DPE with and without externally added stabilizers. The as-prepared AgNPs shows SPR band position at 418, 468 and 477 nm for CTAB, DPE and SDS. TEM images shows that the AgNPs are spherical and poly dispersed. The zeta potential, aggregation number, molar concentration is -8 mV, 605,322.176, 3.3×10^{-4} mL/L and -30 mV, 179,952.568, 1.11×10^{-7} mol/L, respectively, for DPE-AgNPs and CTAB-AgNPs, respectively. Antibacterial activities of DPE-AgNPs against *S. aureus* and *E. coli* were evaluated by turbidity method. The bacterial growth rate were decreases with increasing concentration of DPE-AgNPs.

Fig. 10 The growth kinetic curves for the antibacterial activities of DPE-AgNPs against *S. aureus* (a) and *E. coli* (b) human pathogens as a function of AgNPs concentrations

Compliance with ethical standards

Conflict of interest None.

References

- Bakshi MS (2009) Room a simple method of superlattice formation: step-by-step evaluation of crystal growth of gold nanoparticles through seed-growth method. *Langmuir* 25:12697–12705
- Rai M, Yadav A, Gade A (2009) Silver nanoparticles as a new generation of antimicrobials. *Biotechnol Adv* 27:76–83
- Balwe S, Shinde V, Rokade A, Park S, Jeong Y (2017) Green synthesis and characterization of silver nanoparticles (AgNPs) from extract of plant *Radix Puerariae*: an efficient and recyclable catalyst for the construction of pyrimido[1,2-b]indazole derivatives under solvent-free conditions. *Catal Commun* 99:121–126
- Torres M, Gomez E, Fernandez M, Veglia A, Pacioni N (2019) Role of a cystine-based Gemini surfactant ligand in the synthesis of catalytic active silver nanoparticles. *J Mol Liq* 284:110–116
- Mehta SK, Chaudhary S, Gradzielski M (2010) Time dependence of nucleation and growth of silver nanoparticles generated by sugar reduction in micellar media. *J Colloid Interface Sci* 343:447–453
- Khabeeri OM, Al-Thabaiti SA, Khan Z (2020) Effects of ionic surfactants on the nucleation and growth of cyanidin 3,5-di-O-glucoside capped zerovalent iron nanoparticles. *Colloid Interface Sci Commun* 37:100272
- Hosseinzadeh R, Sabzi R, Ghasemlu K (2009) Effect of cetyltrimethyl ammonium bromide (CTAB) in determination of dopamine and ascorbic acid using carbon paste electrode modified with tin hexacyanoferrate. *Colloid Surf B Biointerfaces* 68:213–217
- Sharma VK, Yngard RA, Lin Y (2009) Silver nanoparticles: green synthesis and their antimicrobial activities. *Adv Colloid Interface Sci* 145:83–96
- Bakshi MS (2018) Engineered nanomaterials growth control by monomers and micelles: from surfactants to surface active polymers. *Adv Colloid Interface Sci* 256:101–110
- Pattanaik A, Venugopal R (2018) Investigation of adsorption mechanism of reagents (surfactants) system and its applicability in iron ore flotation—an overview. *Colloid Interface Sci Commun* 25:41–65
- Yin Y, Li Z-Y, Zhong Z, Gates B, Xia Y, Venkateswaran S (2002) Synthesis and characterization of stable aqueous dispersions of silver nanoparticles through the Tollens process. *J Mater Chem* 12:522–527
- Yao P, Zhang J, Xing T, Chen G, Tao R, Choo K (2018) Green synthesis of silver nanoparticles using grape seed extract and their application for reductive catalysis of Direct Orange 26. *J Ind Eng Chem* 58:74–79
- Zaheer Z, Rafiuddin (2013) Bio-conjugated silver nanoparticles: from *Ocimum sanctum* and role of cetyltrimethyl ammonium bromide. *Colloids Surf B Biointerfaces* 108:90–94
- Zaheer Z, Aazam ES, Kosa SA (2016) Effects of cationic and anionic micelles on the morphology of biogenic silver nanoparticles, and their catalytic activity for congo red. *J Mol Liq* 220:364–369
- Hussain S, Al-Thabaiti SA, Khan Z (2014) Surfactant-assisted bio-conjugated synthesis of silver nanoparticles (AgNPs). *Bioprocess Biosyst Eng* 37:1727–1735
- Zaheer Z (2018) Biogenic synthesis, optical, catalytic, and in vitro antimicrobial potential of Ag-nanoparticles prepared using Palm date fruit extract. *J Photochem Photobiol B Biol* 178:584–592
- Gopinath V, Ali DM, Priyadarshini S, Priyadarshini NM, Thajudhin N, Velusamy P (2012) Biosynthesis of silver nanoparticles from *Tribulus terrestris* and its antimicrobial activity: a novel biological approach. *Colloids Surf B Biointerfaces* 96:69–74
- Kosa SA, Zaheer Z (2019) Betanin assisted synthesis of betanin@silver nanoparticles and their enhanced adsorption and biological activities. *Food Chem* 298:125014
- Khan Z, Al-Thabaiti SA (2018) Green synthesis of zero-valent Fe-nanoparticles: catalytic degradation of rhodamine B, interactions with bovine serum albumin and their enhanced antimicrobial activities. *J Photochem Photobiol B Biol* 180:259–267
- Ranoszek-Soliwoda K, Tomaszewska E, Małek K, Celichowski G, Orlowski P, Krzyzowska M, Grobelny J (2019) The synthesis of

- monodisperse silver nanoparticles with plant extracts. *Colloids Surf B Biointerfaces* 177:19–24
21. Ahmad A, Mukherjee P, Mandal D, Senapati S, Khan MI, Kumar R, Sastry M (2002) Enzyme mediated extracellular synthesis of CdS nanoparticles by the fungus, *Fusarium oxysporum*. *J Am Chem Soc* 124:12108–12109
  22. Jayaprakash N, Vijaya JJ, Kaviyarasu K, Kombaiiah K, Kennedy LJ, Ramalingam R, Munusamy MA, Al-Lohedan H (2017) Green synthesis of Ag nanoparticles using tamarind fruit extract for the antibacterial studies. *J Photochem Photobiol B Biol* 169:178–185
  23. Bawazir WA, Alhogbi BG, Basaleh AS, Zaheer Z (2020) Capping action of ionic surfactants on the nucleation of lawsone-Ag⁺ redox system. *J Mol Liq* 309:113214
  24. Al-Ghamdi AD, Zaheer Z, Azam ES (2020) Sennoside A drug capped biogenic fabrication of silver nanoparticles and their antibacterial and antifungal activities. *Saudi Pharm J* 28:1035–1048
  25. Torre I, Martin-Dominguez V, Acedos M, Esteban J, Santos VE, Ladero M (2019) Utilisation/upgrading of orange peel waste from a biological biorefinery perspective. *Appl Microbiol Biotechnol* 103(15):5975–5991
  26. Prabasari I, Pettolino F, Liao M, Bacic A (2011) Pectic polysaccharides from mature orange (*Citrus sinensis*) fruit albedo cell walls: sequential extraction and chemical characterization. *Carbohydr Polym* 84:484–494
  27. Balu AM, Budarin V, Shuttleworth PS, Pfaltzgraff LA, Waldron K, Luque R, Clark JH (2012) Valorisation of orange peel residues: waste to biochemicals and nanoporous materials. *ChemSusChem* 5:1694–1697
  28. Amanulla A, Sundaram R (2019) Green synthesis of TiO₂ nanoparticles using orange peel extract for antibacterial, cytotoxicity and humidity sensor applications. *Mater Today Proc* 8:323–331
  29. Santos EB, Madalossi N, Sigoli FA, Mazali IO (2015) Silver nanoparticles: green synthesis, self-assembled nanostructures and their application as SERS substrates. *New J Chem* 39:2839–2846
  30. Omran BA, Nassar HN, Fatthallah NA, Hamdy A, El-Shatoury EH, El-Gendy NS (2017) Waste upcycling of *Citrus sinensis* peels as a green route for the synthesis of silver nanoparticles. *Energ Sources A* 40:227–236
  31. Kaviya S, Santhanalakshmi J, Viswanathan B, Muthumary J, Srinivasan K (2011) Biosynthesis of silver nanoparticles using *Citrus sinensis* peel extract and its antibacterial activity. *Spectrochim Acta A* 79:594–598
  32. Kahrilas GA, Wally LM, Fredrick SJ, Hiskey M, Prieto AL, Owens JE (2013) Microwave-assisted green synthesis of silver nanoparticles using orange peel extract. *ACS Sustain Chem Eng* 2:367–376
  33. Barros CHN, Cruz GCF, Mayrink W, Tasic L (2018) Bio-based synthesis of silver nanoparticles from orange waste: effects of distinct biomolecule coatings on size, morphology, and antimicrobial activity. *Nanotechnol Sci Appl* 11:1–14
  34. M. I. Skiba, V. I. Vorobyova (2019), Synthesis of silver nanoparticles using orange peel extract prepared by plasmochemical extraction method and degradation of methylene blue under solar irradiation, *Adv Mater Sci Eng*, 2019, 8306015, 8 pages
  35. Awad MA, Hendi AA, Ortashi KMO, Elradi DFA, Eisa NE, Al-Iahieb LA, Al-Otoby SM, Merghani NM, Awad AAG (2014) Silver nanoparticles biogenic synthesized using an orange peel extract and their use as an anti-bacterial agent. *Int J Phy Sci* 9:34–40
  36. Soto KM, Quezada-Cervantes CT, Hernández-Iturriaga M, Luna-Bárcenas G, Mendoza S (2019) Fruit peels waste for the green synthesis of silver nanoparticles with antimicrobial activity against foodborne pathogens. *LWT* 103:293–300
  37. Rangayasami A, Kannan K, Joshi S, Subban M (2020) Bioengineered silver nanoparticles using *Elytraria acaulis* (L.f.) Lindau leaf extract and its biological applications. *Biocatal Agric Biotechnol* 27:101690
  38. Aswini R, Meimozhi S, Tamilmozhi R, Kowsalya M, Murugesan S (2019) Green synthesis of silver nanoparticles using *Ledebouria Revoluta* bulb extract and its biological activity. In: Springer proceedings in materials. Proceedings of the international conference on nanomedicine (ICON-2019). Springer, Cham, pp 1–10
  39. Gavade NL, Kadam AN, Suwarnkar MB, Ghodake VP, Garadkar KM (2015) Biogenic synthesis of multi-applicative silver nanoparticles by using *Ziziphus jujuba* leaf extract. *Spectrochim Acta A* 136:953–960
  40. Gawade VV, Gavade NL, Shinde HM, Babar SB, Kadam AN, Garadkar KM (2017) Green synthesis of ZnO nanoparticles by using *Calotropis procera* leaves for the photodegradation of methyl orange. *J Mater Sci Mater Electron* 28:14033–14039
  41. Khullar P, Goshisht MK, Moudgil L, Singh G, Mandial D, Kumar H, Ahluwalia GK, Bakshi MS (2017) Mode of protein complexes on gold nanoparticles surface: synthesis and characterization of biomaterials for hemocompatibility and preferential DNA complexation. *ACS Sustain Chem Eng* 5:1082–1093
  42. Bakshi MS, Possmayer F, Petersen NO (2007) Role of different phospholipids in the synthesis of pearl-necklace-type gold–silver bimetallic nanoparticles as bioconjugate materials. *J Phys Chem C* 111:14113–14124
  43. Radhika D, Kannan K, Neseraj AS, Namitha R (2019) Facile low-temperature synthesis and application of La_{0.85}Sr_{0.15}Co_{0.85}Fe_{0.15}O_{3-δ} as superior cathode for LT-SOFCs using C-TAB as surfactant. *Mater Res Innov* 24(7):395–401. <https://doi.org/10.1080/14328917.2019.1686858>
  44. Kannan K, Radhika D, Neseraj AS, Ahmed MW, Namitha R (2019) Cost-effective method of Co-doped rare-earth-based ceria (Y-CGO) nanocomposite as electrolyte for LT-SOFCs using C-TAB as surfactant. *Mater Res Innov* 24(7):414–421. <https://doi.org/10.1080/14328917.2019.1706032>
  45. Kannan K, Radhika D, Neseraj AS, Revathi V, Sadasivuni KK (2020) A simple chemical precipitation of ceria based (Sm doped-CGO) nanocomposite: structural and electrolytic behaviour for LT-SOFCs. *SN Appl Sci* 2:1220
  46. Khan Z, Singh T, Hussain JI, Al-Thabaiti SA, El-Mossalamy EH, Obaid AY (2013) Starch-directed green synthesis, characterization and morphology of silver nanoparticles. *Colloids Surf B Biointerfaces* 102:578–584
  47. Albeladi AB, Al-Thabaiti SA, Khan Z (2020) Effect of CTAB on the surface resonance plasmon intensity of silver nanoparticles: stability and oxidative dissolution. *J Mol Liq* 302:112565
  48. Kannangara I, Jayawardhana Y, Munasinghe E, Rajapakse A, Bandara A, Weerasooriya R, Jayarathna L (2020) Synthesis and characterization of nano zeolite-A with aid of sodium dodecyl sulfate (SDS) as particle size-controlling agent. *Colloids Surf A Physicochem Eng Asp* 589:124–127
  49. Das S, Bououdina M, Manoharan C (2020) The influence of cationic surfactant CTAB on optical, dielectric and magnetic properties of cobalt ferrite nanoparticles. *J Ceramics Int B* 46:11705–11716
  50. Phuruangrat A, Keereesaensuk P-O, Thongtem S, Karthik K, Dumrongrojthanath P, Ekthammathat N, Thongtem T (2020) Synthesis and characterization Ag nanoparticles supported on Bi₂WO₆ nanoplates for enhanced visible-light-driven photocatalytic degradation of rhodamine B. *J Inorg Organomet Polym Mater* 30:1033–1040
  51. Phuruangrat A, Keereesaensuk P-O, Thongtem S, Ekthammathat N, Dumrongrojthanath P, Karthik K, Thongtem T (2020) Synthesis of Ag/Bi₂WO₆ nanocomposites using NaBH₄ as reducing agent for enhanced visible-light-driven photocatalysis of rhodamine B. *J Inorg Organomet Polym Mater* 30:322–329

52. Klein BP, Perry AK (1982) Ascorbic acid and vitamin A activity in selected vegetables from different geographical areas of the United States. *J Food Sci* 47:941–945
53. Sigmann SB, Wheeler DE (2004) Quantitative determination of citric and ascorbic acid in powdered drink mixes. *J Chem Educ* 81:1479–1481
54. Miller GL (1959) Use of dinitrosalicilic acid reagent for determination of reducing sugars. *Anal Chem* 31:426–428
55. Pal S, Tak YK, Song JM (2007) Does the antibacterial activity of silver nanoparticles depend on the shape of the nanoparticle? A study of the gram-negative bacterium *Escherichia coli*. *Appl Environ Microbiol* 73:1712–1720
56. Rezzadori K, Benedetti S, Amante ER (2012) Proposals for the residues recovery: orange waste as raw material for new products. *Food Bioprod Process* 90:606–614
57. Guimaraes R, Barros L, Barreira JCM, Sousa MJ, Carvalho AM, Ferreira ICFR (2010) Targeting excessive free radicals with peels and juices of citrus fruits: grapefruit, lemon, lime and orange. *Food Chem Toxicol* 48:99–106
58. Tabart J, Kevers C, Pincemailb J, Defraigne J-O, Dommes J (2010) Evaluation of spectrophotometric methods for antioxidant compound measurement in relation to total antioxidant capacity in beverages. *Food Chem* 120:607–614
59. Tascioglu S (1996) Micellar solutions as reaction media. *Tetrahedron* 52:11113–11152
60. Goia DV, Matijevic E (1998) Preparation of monodispersed metal particles. *New J Chem* 22:1203–1215
61. Henglein A (1993) Physicochemical properties of small metal particles in solution: “microelectrode” reactions, chemisorption, composite metal particles, and the atom-to metal transition. *J Phys Chem* 97:5457–5471
62. Zapata B, Balmaseda J, Fregoso-Israel E, Torres-Garcia E (2009) Thermo-kinetics study of orange peel in air. *J Therm Anal Calorim* 98:309–315
63. Melendrez MF, Cardenas G, Arbiol J (2010) Synthesis and characterization of gallium colloidal nanoparticles. *J Colloid Interface Sci* 346:279–287
64. SonDI I, Salopek-SonDI B (2004) Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria. *J Colloid Interface Sci* 275:177–182
65. Sigel H, Sigel A (eds) (2004) Metal complexes in tumor diagnosis and as anticancer agents. *Metal ions in biological systems*, vol 42. Marcel Dekker, Inc, New York

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