



Carnosine induced formation of silver nanochains: A radiolytic study



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HIGHLIGHTS

- Effect of carnosine on Ag clusters.
- Effect of carnosine on the size of Ag nanoparticles.
- Carnosine is an effective stabilizer for Ag nanoparticles.
- Effect of pH on the morphology of the Ag nanoparticles.

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ABSTRACT

Interaction of carnosine with silver clusters and its nanoparticles is studied at pH 8.2 and 9.2. Using time resolved kinetic measurements we show that carnosine interacts with the charged silver clusters. Using ionizing radiation silver particles are also produced in aqueous solution. In the presence of carnosine distinct differences in the surface plasmon absorption band of Ag nanoparticles is observed with change in pH. The results suggest that silver nanochains get formed through dipole–dipole interaction due to weak interaction with carnosine. UV–Vis spectrophotometry and transmission electron microscopy are used to characterize the nanoparticles.

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1. Introduction

Carnosine (beta-alanyl-L-histidine) is a dipeptide of beta-alanine and L-histidine amino acids. It is highly concentrated in muscle and brain tissues of mammals (1–20 mM). It is also a source of β -alanine in human body (Crush, 1970; Kohen et al., 1988). Carnosine is perceived to have numerous biological roles such as pH buffering, regulation of enzyme activity, and inhibition of oxidative reactions (Kiss et al., 2013). Carnosine has multifunctional antioxidant properties viz. it inactivates reactive oxygen species, scavenge free radicals (Aruoma et al., 1989; Boldyrev, 1990; Kohen et al., 1988) and chelate pro-oxidative metal ions (Baran, 2000; Decker and Faraji, 1990; Sundberg and Martin, 1974).

It is known that transition metals act as catalysts in the formation of reactive oxygen species (Stoys and Bagchi, 1995; Liu et al., 2010; Beer et al., 2012). It is suggested that the ability of carnosine to chelate metal ions can prevent metal induced

damage (Tamba and Torreggiani, 1998, 1999). In most of the reported approaches the reduction and stabilization of the Ag nanoparticles occur by adsorption of reducing agents such as borohydride (Lee and Meisel, 1982) and citrate (Turkevich et al., 1951). Silver nanoparticles have bactericidal properties and their biocompatibility is being explored for various bio-analytical applications (Shkilnyy et al., 2009). Thus, attempts were made to use small organic molecules having biological significance to form and stabilize Ag nanoparticles (Jacob et al., 2008, 2011a, 2011b). To realize fully the utility of Ag nanoparticles they must be modified using proteins, peptides, etc. Taken together the above mentioned reports, it will of interest to study the binding of carnosine with metal having bactericidal properties as this may have a significant biological relevance. Hence, in order to obtain a wider insight, in this study free radical reactions were studied with Ag^+ ions in the presence of carnosine. Finally a protocol for synthesis and stabilization of Ag nanoparticles in the presence of carnosine was proposed. The formed particles were characterized using UV–Vis spectrophotometry and transmission electron microscopy (TEM).

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2. Experimental details

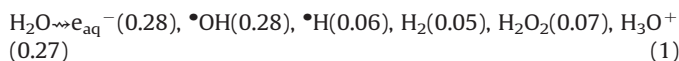
2.1. Materials

Silver perchlorate (Aldrich), L-carnosine (Aldrich) tert-butyl alcohol (Sisco, India), Na_2HPO_4 (BDH) and KH_2PO_4 (BDH) were used as received. Solutions were prepared in Millipore water (conductivity $0.06 \mu\text{S cm}^{-1}$). The solutions were purged with IOLAR grade high purity N_2 ($> 99.99\%$) prior to irradiation. All experiments were carried out at ambient temperature close to 23°C .

2.2. Methods

The 7 MeV pulse radiolysis kinetic spectrophotometric detection set up used in this study and the data analysis protocols have been discussed in detail before (Kapoor and Varshney, 1997). Briefly, samples were irradiated in a $1 \text{ cm} \times 1 \text{ cm}$ suprasil quartz cuvette kept at a distance of approximately 12 cm from the electron beam window, where the beam diameter is approximately 1 cm. Electron pulses of either 500 ns or $2 \mu\text{s}$ were used. An aerated 10^{-2} M KSCN solution was used for dosimetry, and the $(\text{SCN})_2^{\bullet-}$ radical was monitored at 475 nm. The absorbed dose per pulse was calculated (Buxton and Stuart, 1995) assuming $G[(\text{SCN})_2^{\bullet-}] = 2.6 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$ at 475 nm. Absorbed doses per pulse were of the order of 14 Gy.

The radiolysis of water produces reactive free radicals, hydrated electrons, OH radicals and H atoms, and molecular products H_2O_2 and H_2 , according to the stoichiometry (Buxton et al., 1988; Spinks and Woods, 1990) shown in reaction (1)



where the numbers in parentheses represent the radiolytic yields, G-values, the quantity of species formed per Joule of energy deposited at pH 7 in $\mu\text{mol J}^{-1}$. For studying the e_{aq}^- reaction, $\cdot\text{OH}$ radicals were scavenged by adding tert-butanol (reaction 2)



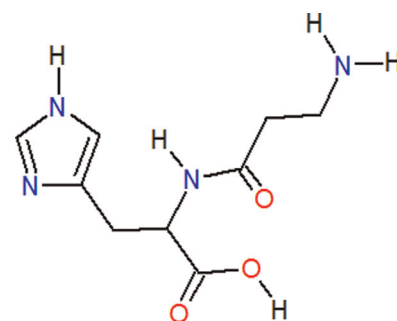
2.3. Characterization

Absorption measurements were taken on Jasco V-560 spectrophotometer. The UV–Vis absorption spectra were recorded at room temperature using a 1 cm quartz cuvette. TEM characterization was carried out using a JEOL JEM-2000FX electron microscope. Particle sizes were measured from the TEM micrographs. The particle size was calculated by taking average of at least 100 particles. Zeta potentials were determined by Nanosizer Z (Malvern Instruments).

3. Results and discussion

The structure of carnosine is shown in Scheme 1. The pK_a of the carboxyl group in carnosine molecule is around 2.5, the first of imidazole ring is 6.8 and pK_a of the second ionization is larger than 12 (Tamba and Torreggiani, 1999). The reactivity of carnosine towards e_{aq}^- was found to be low at pH 9.2. The results are similar to that reported for histidine and alanine at somewhat similar pH (Buxton et al., 1988). Therefore, the pulse radiolysis experiments are carried out at pH 9.2.

Fig. 1 shows optical absorption spectra of transient obtained after 500 ns electron pulse irradiation due to the reaction of e_{aq}^-



Scheme 1. Structure of carnosine.

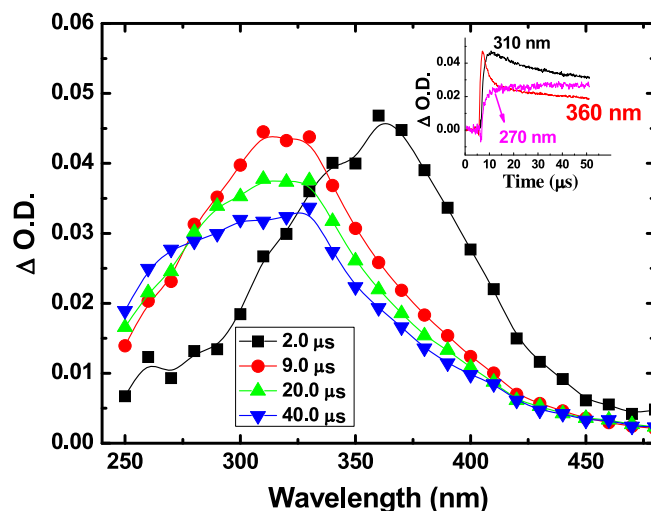


Fig. 1. Time resolved transient absorption spectra of silver clusters obtained after electron pulse irradiation of an aqueous solution containing $1 \times 10^{-4} \text{ M}$ AgClO_4 , $5 \times 10^{-4} \text{ M}$ carnosine, 0.1 M tert-butanol at pH 9.2. Inset: time profile traces at different wavelengths.

with Ag^+ ions in the presence of carnosine at pH 9.2. The molar ratio of Ag^+ and carnosine was 1:5. The transient spectra showed bands for silver atom (Ag^0 , 360 nm, reaction 3) and its clusters: Ag_2^+ at 310 nm (reaction 4) and Ag_3^{2+} at 270 nm. The observed bands are similar to that reported in the literature (Belloni, 1998; Henglein, 1993; Janata et al., 1994). It is pertinent to mention here that the formation of trimer silver cluster, Ag_3^{2+} , as an intermediate in the formation of bigger silver cluster formation has been shown and described in detail earlier (Janata et al., 1994). On comparing the transient optical spectra of silver clusters with that obtained in the absence of carnosine (Fig. S1) it can be noted that the absorbance of the ionic clusters decreased in presence of carnosine. This could be due to the change in molar absorptivity (Janata et al., 1994) and/or the environment effect. Thus, it can be inferred that ionic silver clusters interact with carnosine.



It is known that interaction of Ag^+ ions and its clusters with ligands depends on the charge of the ligand (Rémita et al., 1996; Belloni, 1998; Kapoor, 1999). The binding of Ag clusters and/or nanoparticles with carnosine may get affected by the protonation of the imidazole ring. Thus, to study the effect of pH an attempt was made to study the above mentioned reactions at $\text{pH} < 9$. It was noticed that the reactivity of e_{aq}^- with carnosine increased at pH closer to pK_a of the imidazole ring. The results corroborate the

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