Synthesis Luminescent Plasmonic Silver Nanoparticles and The Chemical Affinity towards sulphur atom in Sulphide and Thiourea molecules: Ab-Initio DFT Study

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Research Article

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Synthesis Luminescent Plasmonic Silver Nanoparticles and The Chemical Affinity towards sulphur atom in Sulphide and Thiourea molecules: Ab-Initio DFT Study

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Abstract

Three different luminescent silver nanoparticles(AgNPs) were synthesized by simple reduction method with the different mole ratios of L-ascorbic/citrate solution and stabilized with CTAB. The prepared three AgNPs were characterized by UV, fluorescence, FTIR, dynamic light scattering measurements and Scanning Electron Microscopy. The plasmon bands of AgNPs-reddish-brown (RB), green (G) and reddish-green (RG) were centered at 565, 587 and 592 nm, respectively. The highly luminescence emission was observed for AgNPs(G). The size diameters of the prepared AgNPs-G, RG and (RB) were measured by dynamic light scattering (DLS) method at 24.3 nm, 66.28 nm and 103.46 nm, respectively. The electrochemical properties of AgNPs-RG was recorded the oxidative part of AgNPs into Ag^{+} at +0.23 V and the reduction part of Ag+ into Ag0 was recorded at -0.49 V vs. Ag/AgCl). Cetyl trimethylammonium bromide (CTAB) was stabilized AgNPs(RG) which recorded in infrared and scanning electron microscope measurements. The concentration of thiourea, sodium sulphide was detected by the electrochemical sensitivity of AgNPs(RG)-CTAB. A calibration curve between electrochemical sensitivity of AgNPs-CTAB vs concentration of sulphur molecule. The limit of detection (LOD) was founded 2.10 and 1.90 µmole L^{-1} of sodium sulphide and thiourea, respectively (R^2=0.94, n=3). The computational calculations are used to illustrated the chemical affinity of sulphur atom in sodium sulphide or thiourea towards AgNPs(RG).

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Keywords: Luminescent Ag NPs; CTAB capping; Chemosensor; Sulphur molecules; Chemical affinity.

1 Introduction

Silver nanoparticles AgNPs, have a unique properties like optical electronic properties and magnetic widely used in various fields such as catalytic and biological applications[1]. Silver nanoparticles (AgNPs) have prominent significance as analytical and bioanalytical sensors. The plasmonic fluorescence has significant importance due to widely used in a large number of scenarios ranging from biomedical research to optoelectronic devices. The fluorescence emission of plasmonic nanoparticles can be enhanced, quenched or spectrally shaped by controlling the near field interaction of sulphur molecules and silver nanoparticles. Generally, the fluorescence emission would be rapidly quenched when the sulphur molecules directly come into contact with plasmonic nano-silver due to the non-radiative energy transfer process[2] or dissociation of AgNPs into Ag^{+}. [3]The SPR phenomena of AgNPs is associated with the coupled oscillation of free electrons on the conduction band accompanying enhanced local electromagnetic field, which is intensely sensitive to surrounding medium conditions. When a nanoparticle is exposed to an electromagnetic wave, the electrons in the particle oscillate at the same frequency as the incident wave. silver nanoparticles exhibit various spectral characteristics, these are strongly dependent on their size, shape, interparticle spacing and environment[4]. The chemical reduction of silver salt into AgNPs using tris-sodium citrate as reducing agent was simple and famous method[5]. The shape and size diameter of AgNPs solution were dependent on pH values of medium. The size diameter of AgNPs was decreased by increasing pH value.[6]. Sui and et al studied the stability of AgNPs in the presence cetyl trimethylammonium bromide(CTAB) as a capping agent where CTAB molecules strongly bind to AgNPs with formation bilayer shell.[7]. Thiol and di-sulphide molecules can be quenched with change the redox cycle of AgNPs. Several research articles are interested to determinate the concentration of sulphus containing molecules such as thiourea, sodium sulphide and total sulphur contents in vegetables. Thiourea(TU) is common compound containing sulphur atoms and known as toxic and hazardous. It can lead to a disturbance of carbohydrate metabolism as well as chronic goitrogenic and other glandular problems in humans. Therefore, the determination of TU is of great importance.[8]. The silver nanoparticles sensor used in colorometric method to detect thiourea (TU) amounts based on the changing of the absorption spectra of AgNPs plasmon band by adding different thiourea amounts[9]. The present method will introduce a simple and sensitive electrochemical method to determine the sulphur compounds based on the changes of redox peak of AgNPs(RG)-CTAB with addition of different amounts of sulphur molecules.

The present work will be introduced a simple reduction method for preparation of luminescent AgNPs with different mole ratio between citrate/L-ascorbic acid. The prepared AgNPs- reddish-brown (RB), green (G) and reddish-green (RG) are characterized with advanced UV-VIS, fluorescence, electroanalysis and dynamic light scattering (DLS) measurements,Scanning electron microscopy (SEM),. The factors affecting on the plasmon bands of the prepared AgNPs were studied by s solvent polarity, pH values and the influences of cetyl trimethylammonium bromide(CTAB) as capping agent. The CTAB-stabilized AgNPs(RG) was used to determine the concentration of molecules containing sulphur atom such as sodium sulphide, thiourea (TU) and the total Sulphur present in vegetables. Density function theory (DFT) of optimized structure of thiourea and sodium sulphide was done. The computational calculations were used to expect the chemical affinity of sodium sulphide and thiourea to coordinate with AgNPs(RG). The analytical validation of the present method was applied.

2 Materials and Methods

Silver nitrate ($AgNO_3$), trisodium citrate ($Na_3C_6H_5O_7$), -Lascorbic acid ($C_6H_8O_6$), cetyl trimethylammonium bromide

(CTAB) sodium sulphide andthiourea were used in the experiment. All chemicals and solvents were recived Sigma Aldrich (USA).

2.1 General Procedure for Synthesis of Silver Nanoparticles

The experimental technique, with slight modification to the existing method reported by Dads[10], has been applied for this study. In detail, 80 mL of 0.9 mmol L^{-1} $AgNO_3$ and 20 ml mixture of 0.8 mmol L^{-1} tris-sodium citrate and 1.0 mmol L^{-1} ascorbic acid was heated with stirring till reach 60°C separately. Then added 20 ml of a solution to the 80 ml of $AgNO_3$ with vigorous stirring by maintaining 60°C for 20 minutes. After that, stopped heating, and the solution cooled to room temperature with continuous stirring. The color of colloidal solution was dependent on the molar ratio between ascorbic acid and citrate. The molar ratio between ascorbic / citrate was 10: 8, 8: 8, and 8:10 that gave AgNPs colors a reddish-green, Green and reddish-brown, respectively.

UV Shimadzu spectrophotometer and 4000-USBFL spectrofluorometer (Ocean Optics, Oceanview software, USA),was usedto record the absorption and fluorescence spectra of AgNPs . Electrochemical analyses were performed using a Gamry 5000 potentiostat in a three-electrode system with a standard Ag/AgCl reference electrode (prepared in saturated KCl solution), Pt-wire as counter electrode, and gold working electrode (size diameter, 2 mm). The size diameter of AgNP colloidal solutions e was measured by the dynamic light scatter (DLS) instrument model Nano DS, SN 161.The interaction and stabilization of AgNPs(RG)-CTAB was confirmed by the Fourier-transform infrared spectroscopy (FTIR)Alpha backer (OPUS software, USA) and Scanning electron microscopy (SEM) image of AgNPs(RG)-CTAB was obtained from Phillips CM201C microscope at 80 kV (Phillips, The Netherlands).

2.3 Computational Details

All DFT calculations of the chemical affinity of sodium sulphide and thiourea towards AgNPs were performed using the Gaussian G09W program. Geometry optimizations were conducted using density functional theory (DFT) with Becker s three parameter exchange functional [11], the Lee-Yang-Parr correlation functional)(B3LYP) and the 6.31G(d) split-valence double zeta basis set was used[12]. After completing optimization, the theoretical properties of the studied compound such as Electron affinity (EA), Ionization energy (IE), hardness and softness and the HOMO, LUMO are recorded.

3. Results and Discussion

3.1 Characterization of AgNPs

The three different types of AgNPs were synthesized via slightly modified of Dados method by using citrate-ascorbic acid ratio [10]. The color of colloidal solutions of Ag NPs were observed as greenish(G), reddish green (RG) and reddish brown (RB). The absorbance spectra of the AgNPs-RB, AgNPs-G and AgNPs-RG shown a strong plasmon bands were centered at 565, 587 and 592 nm, respectively (see **Figure. 1(a)**). The bandwidth and band position of surface plasmon resonance(SPR) of AgNPs was dependent on the size diameter and the symmetrical shape of SPR band that indicates the AgNPs is spherical shape. [13, 14]. The surface plasmon band of AgNPs was affected by the changing of solvent polarity where the plasmon band was shifted to longer wavelength is called positive solvato-chrmosium in polar solvents such as water, methanol and ethanol, while, the blue-shift was observed in less polar solvent (dimethylformamide) is called negative solvato-chrmosium. The shift in peak position of AgNPs plasmon band was observed in polar solvents due to the agglomeration AgNPs with the change in the size diameter of AgNPs [15]. The origin of luminescence spectra of AgNPs(G), AgNPs (RG) and AgNPs(RB) were centered at 592, 587 and 565 nm, respectively. The strong luminescence intensity was observed of AgNPs(G) greater than AgNPs(RB) and AgNPs(RG) is attributed to the varied of energy gap (see **Figure. 1(b)**) [16] and fast recombination between e-LUMO

and hole-HOMO of AgNPs[17]. Approximation of Mie-Drude theory[18] can calculate the size diameter of the AgNPs, The energy gaps of AgNPs(G), AgNPs(RB) and AgNPs(RB) were 2.48, 2.30 and 2.10 eV respectively, according to Tauc relation plot[19].

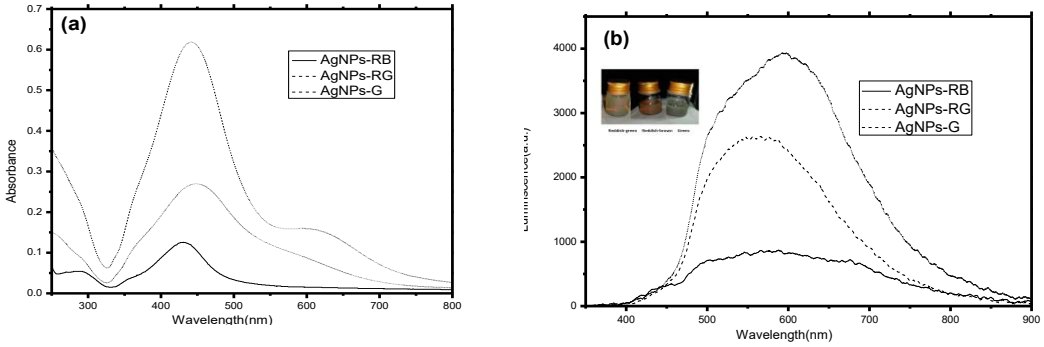


Figure 1. The UV-VIS (a) and luminescence spectra(b) of dispersed colloidal of AgNPs(RB), AgNPs (RG) and AgNPs(G) in ethanolic solution.

The Dynamic light scattering technique was used to measure the size diameter of the prepared AgNPs, especially in the range of 2–500 nm[20]. The size diameters of AgNPs(G), AgNPs(RG) and AgNPs(RB) were recorded as 24.3 nm, 66.28 nm and 103.46 nm, respectively, Due to the influence of Brownian motion ,the size obtained from DLS is usually larger than TEM[21]. The size and shape of AgNPs were dependent on the energy gap where the size of AgNPs is inversible proportional to the size diameter[22]. The plasmon resonance shape of AgNPs was confirmed that AgNPs-G, AgNPs-RG are monodispersed and AgNPs-RB is polydisperse due to the bright luminescence and weak luminescence of AgNPs accordingly[23].

The electrochemical properties of AgNPs(RG) on the surface of electrode was recorded the oxidative part of AgNPs into Ag+ at +0.23 V and the reduction part of Ag+ into Ag^0 was recorded at -0.49 V vs. Ag/AgCl) (see **Figure. 2**). The voltammogram cycle of AgNPs was shown only one oxidative part in cycle of AgNPs is attributed to the high size diameter of AgNPs[24].

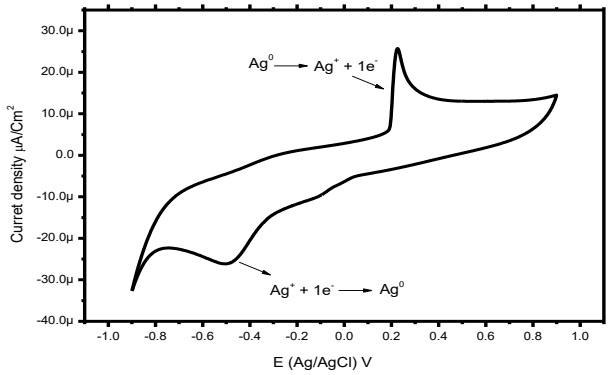


Figure. 2. shows typical cyclic voltammograms scan of the AgNPs(RG) evaluated in 10μM HCl as well as a bare glassy carbon electrode at scan rate 100mV/s.

The absorption spectra of AgNPs-RB at pH values in the range 02.50-10.00 was studied. The narrow and blue-shift of the plasmon peak AgNPs-RB was recorded by raising the pH value where the changing of plasmon peak position of AgNPs that indicates the size diameter was decreased, we conclude that raising the pH of the solution results in the formation of nanoparticles with smaller size and vice versa. On the other hand, the broadening of the surface plasmon resonance peak indicates the existence of a wider range of sizes in the solution [6].

3.2.The stabilization of the prepared AgNPs (RG)with CTAB

The absorption and luminescence spectra of AgNPs-RG are measured at different concentrations of CTAB in the range 0.1-0.9 mmol L^{-1} (see **Figure 3(a)**). Without addition of [CTAB], the SPR band of citrate negative- AgNPs appeared at around 416 nm. The pre-micellar effect can be brought in fact that small aggregates of CTAB exist below the critical micellar concentration (CMC; 0.90 mmol L^{-1}). The red shift of about 6 nm was observed by adding [CTAB] (from 0.1-0.9 mmol L^{-1}), the shape of the AgNPs spectrum has been changed entirely (see **Figure 3(a)**). The decrease in the SPR band intensity with addition [CTAB] may be due to the sub, post and dilution-micellar effects. Finally, the CTAB interacts with AgNPs and protected from agglomeration effect [25]. The Photoluminescence of AgNPs was increased by adding more concentration of CTAB is attributed to the CTAB micelles interacted physically with the AgNPs and AgNPs incorporated into the micelles of CTAB and protect the AgNPs(RG)-luminescent form the quenching[7]. The electrochemical properties such as electroactivity of AgNPs(RG) was increased by adding initial concentration of CTAB due to the formation of small micelles of CTAB surrounded by AgNPs(RG) molecules. While in the higher concentration of CTAB, the inhibition of the electroactivity of AgNPs(RG) was observed due to the growth of CTAB large micelles around AgNPs(RG) and high frequency which leads to slowdown motion of AgNPs(RG) from bulk to surface of electrode(see **Figure 3(b)**)[26]

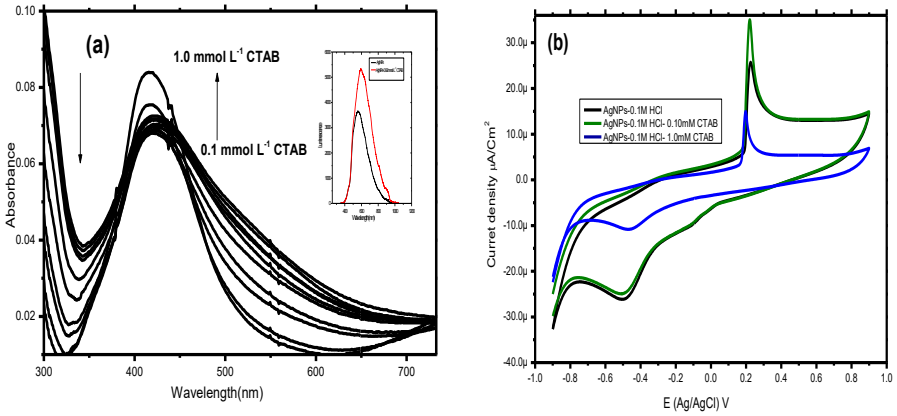


Figure. 3. The absorption spectra (a) and the voltammograms scan(b) of the AgNPs-RG in 10µM HCl upon addition of CTAB at scan rate 100mV/s.

The interaction and stabilization between AgNPs(RG) with CTAB as capping agent was confirmed. The IR spectrum of CTAB possesses a strong and broad band at 3335.50 cm^{-1} that can be attributed to the stretching vibrations of the ammonium group in CTAB. Peaks at 2923.93 cm^{-1} and 2853.64 cm^{-1} are attributed to two different C−H band vibrations of the $-CH_2$ group in CTAB. The band at 1635.71 cm^{-1} followed by the band at 1472.94 cm^{-1} corresponds to the asymmetric and symmetric stretching vibration of N^+-CH_3, respectively. [27] As for the CTAB-AgNPs, the broad absorption band at 3256.43 cm^{-1} arose from the stretching vibration of the O−H bond of the water environment. The packing density in CTAB-capped Ag NPs is not so sufficient to produce any change in CH_2 stretching modes. The bandwidth change, however, reflects some changes from the structural order of the methylene chain groups in aggregate structure. Narrower bandwidths have been found to be resulted from a more ordered structure of the alkyl chains for bound CTAB molecules, which implies that CTAB molecules are arranged in some order on NPs surface.[28]

Scanning electron microscope images shown the AgNPs(RG) on the presence of CTAB in microscale diameter[29] The CTAB was stabilized the AgNPs via formation of micelles to protect it from agglomeration. The silver nanoparticles grown over the large particle size of CTAB (see Figure 4(b))

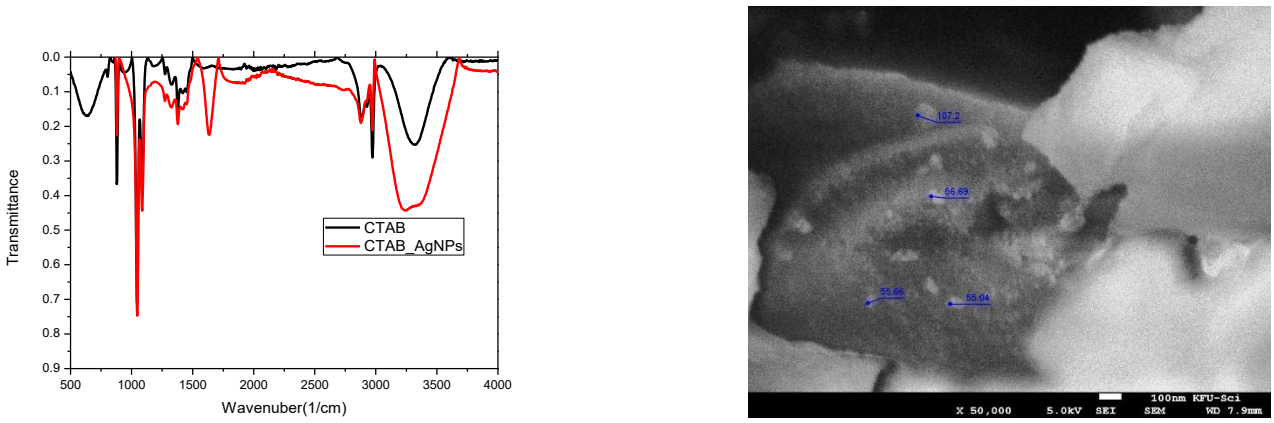
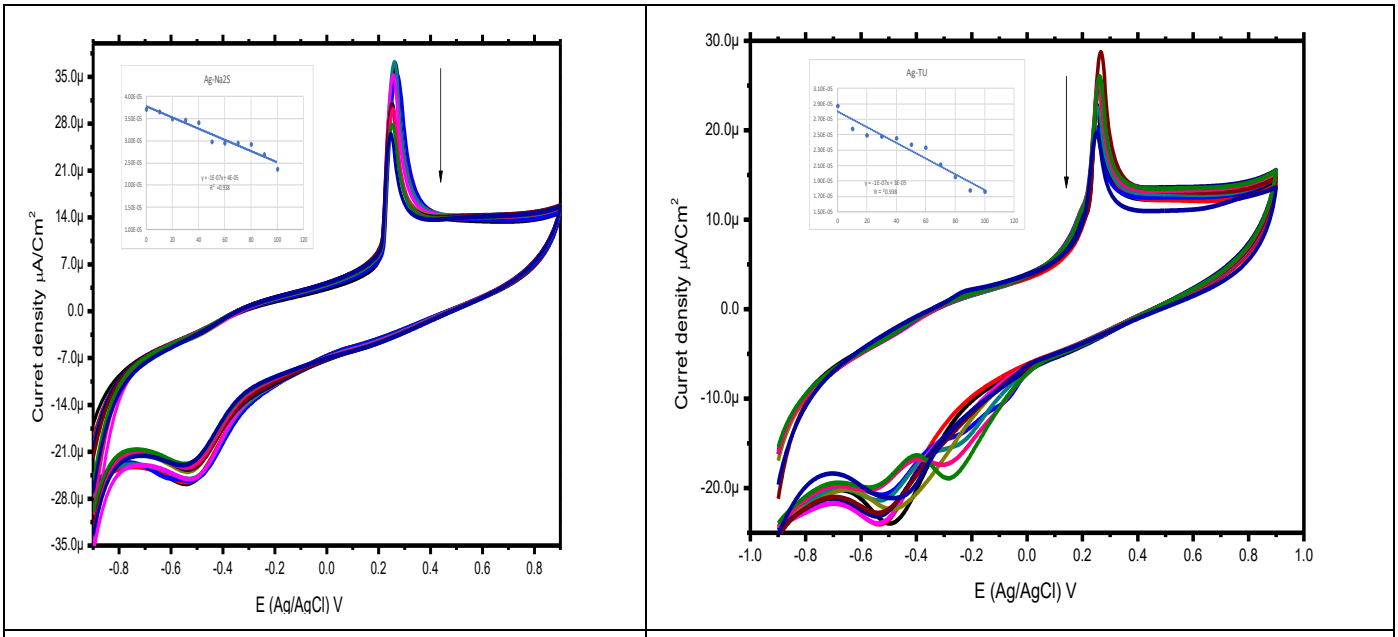


Figure. 4. The IR spectrum (a) and SEM image(b) of AgNPs(RG)-CTAB system

3.3 The Chemical Affinity of AgNPs(RG)-CTAB Towards Sulphide and Thiourea

The plasmon peak of CTAB-stabilized AgNPs was centered at 446 nm. The position and width of plasmon peak of AgNPs was changing after addition of (sodium sulphide) S^{2-} in the concentration range 10-100 µmmol l^{-1}. that means the size of AgNPs increased .The color of dispersed AgNPs was changed bright reddish green into red this attributed to a highly aggregated AgNPs with formation of Ag_2S, so can be used this behavior to detect the S^{2-} using luminescent AgNPs[30]. The luminesce of AgNPs was increased by increasing the S^{2-} concentration due to aggregation of AgNPs[31]. In cyclic voltammetry, the reversible cycle of anodic and cathodic peaks was observed. while the intensity of anodic peak increased by increasing the concentration of S^{2-} analyte due to the charge of AgNPs became more negative.[32] The plasmon band of CTAB-stabilized AgNPs was slightly decreased with increasing the thiourea concentration range 10-100µmmol l^{-1}, the color of colloidal solution AgNPs was turned into red color due to Thu was replaced the citrate anions around CTAB- AgNPs and the Thu can adsorb on the AgNPs via the S atom due to the strong affinity of AgNPs towards S more than O in thiourea molecule[33].The calibration curve was plotted between current of redox peak of AgNPs-CTAB vs the concentration of sulphur molecules(thiourea or sodium sulphide) in µmole L^{-1} . The limit of detection (LOD) was founded 2.10 and 1.90 µmole L^{-1} of sodium sulphide and thiourea, respectively(R^2=0.94) with replicate times n=3. (see Figure 5 and Table 1.)



(a) (b)

Figure 5. Represented the CVs scan of the AgNPs-RG/CTAB in 10µM HCl upon addition of 10-100 µmol l^{-1} of Na2S (a) and TU(b) (insert calibration cureve at oxidation peak of AgNPs-RG/CTAB upon addition of 10-100 µmol l^{-1} of Na2S (a) and TU(b))

Table 1. The analytical validation parameters of sodium sulphide and thiourea.

Sulphur molecules (µg L^{-1}), n=3	*LOD	*LOQ	Correlation coefficient (R^2)	R.S.D % <02.00%
Sodium sulphide	2.10	4.40	0.94	0.20
Thiourea	1.90	5.70	0.94	0.18

The Energy of the HOMO is directly related to the ionization potential and LUMO Energy is directly related to the electron affinity. Stability of the structures can be determined by the energy difference between HOMO and LUMO orbitals which is known as energy gap. The energy gap is used in determining molecular electrical transport properties. In addition, according to Koopmans' theorem the energy gap, E gap, defined as the difference between HOMO and LUMO energy(see equation (1)) [34].

$$E_g = (E_{HOMO} - E_{LUMO}) \cong IP - EA \quad (1)$$

The charge values are played important role to detect the chemical affinity of this sulphur molecules towards reaction with AgNPs. HOMO and LUMO energy values are useful to estimate Ionization potential (I) and Electron affinity (A) by the following **equation (1) and (2).** The data of HOMO, LUMO gap, ionization potential, and electron affinity are given in **Table 2** and **equations (2) and (3)**.

$$IP = -E_{HOMO} \quad (2)$$

$$EA = -E_{LUMO} \quad (3)$$

The HOMO and LUMO energies are used for the determination of global reactivity descriptors. It is important that, hardness (η) and softness (S) (see **equations (4) and (5)**)be put into a molecular orbital's framework[35]. We focus on the HOMO and LUMO energies in order to determine the interesting molecular/atomic properties and chemical quantities. These are calculated as following equations given in **Table 2.**

$$(\eta) = \frac{I-A}{2} \quad (4)$$

$$(S) = -\frac{1}{\eta} \quad (5)$$

Table 2. The chemical reactivity parameter such as electron affinity and softness of sulphide and thiourea.

Sulphur molecules	EHOMO (eV)	ELUMO (eV)	Eg (eV)	η (Hardness)	S (softness)
Na_2S	-4.5	-1.2	-3.3	3.91	0.26
TU1	-6.8	0.4	-7.2	7.04	0.14
TU2	-5.8	-1.7	-4.1	4.96	0.20

The higher values of softness(S) of sulphur molecules were observed in sodium sulphide. The reason is chemical affinity in sodium sulphide due to the formation of Ag_2S-moleules[30]

Conclusion

The chemical reduction method was used to prepare silver nanoparticles AgNPs, the ascorbic acid was used as a reducing agent and sodium citrate as a stabilizing agent. The ratio between ascorbic acid /sodium tris-citrate played important role to give three different colored AgNPs (reddish green, reddish brown and green). The absorbance spectra

of the AgNPs(RB), AgNPs(G) and AgNPs(RG) are shown a strong plasmon bands were centered at 565, 587 and 592 nm, respectively, this is the evidence for the formation of three different silver nanoparticles. The pH values were affected on the size diameter of the AgNPs by observing the shift of plasmon band, where the pH value increases, the surface plasmon peak shifts to left indicating a decrease in the size of the prepared nanoparticles. The CTAB was stabilized the AgNPs via formation of micelles to protect it from agglomeration. The plasmon behavior was shown the chemical affinity AgNPs(RG)-CTAB towards the small and bigger sulphur molecules. The highly softness(S) was observed in sulphide molecule to coordinatewith AgNPs-CTAB. The sensitivity of AgNPs(RG)-CTAB chemosensor achieved in the present work for de termination of the total sulfur compounds in vegetables.

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Conflicts of interest: “There are no conflicts to declare”.

Availability of data and material: "All data is provided in full in the results section of this paper.".

Declarations: Not applicable.

Code availability: Gaussian G09W program

Author Contributions: Conceptualization was done by all authors, Esam Mohamed Bakir and Ranjith Kumar Karnati; methodology, Esam Mohamed Bakir and Ranjith Kumar Karnati; software, Esam Mohamed Bakir; validation, Esam Mohamed Bakir; formal analysis, Esam Mohamed Bakir; investigation, Esam Mohamed Bakir.; resources, Esam Mohamed Bakir and Ranjith Kumar Karnati.; data curation, Esam Mohamed Bakir and Ranjith Kumar Karnati; writing—original draft preparation, Esam Mohamed Bakir, writing—review and editing, Esam Mohamed Bakir and Ranjith Kumar Karnati; visualization, Esam Mohamed Bakir; supervision, Esam Mohamed Bakir; project administration, Esam Mohamed Bakir and Ranjith Kumar Karnati; funding acquisition, Esam Mohamed Bakir.

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