

# Role of Plasma-Induced Liquid Chemistry for the Reduction Mechanism of Silver Ions to form Silver Nanostructures

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**Abstract.** There exists a variety of reports on the synthesis of silver nanostructures by plasma-liquid interactions; however seldom are those that discuss the underlying reaction kinetics. The present study focuses in such direction where the role of plasma-induced chemistry has been analysed in detail with the reports on the influence of radicals on the formation of silver nanostructures. The silver nanostructures are synthesized from various precursor concentrations of silver and characterized by ultraviolet-visible spectroscopy and transmission electron microscopy analysis. Further, experiments have been carried out to clarify the role of reductants in silver nanostructures synthesis. It is found that hydrogen peroxide is unable to reduce the silver ions to silver atoms which is a necessary step to produce silver nanostructures. The addition of organic solvents such as methanol and ethanol has been found to enhance the production rate of silver nanostructures which indicates that methanol and ethanol are strong electron donors affecting the reduction process of silver ions. In order to probe the exact reaction mechanism for silver nanostructures synthesis, iodine has been used as hydrogen radical scavenger along with silver precursor solutions; however, it has been observed that addition of iodine ions generates a favourable condition for the reduction of silver ions. The ultraviolet-visible spectroscopy results indicate the existence of small clusters of silver ions and silver iodide and further transmission electron microscopy characterization suggests that a well-dispersed silver nanoparticles of less than 30 nm in size have been formed. The lattice spacing calculation from transmission electron microscopy images suggests the presence of crystallinity of the particles. Overall, it is found that there are two possible ways for the reduction mechanism of silver nanostructures: either via hydrated electrons or hydrogen radicals or both.

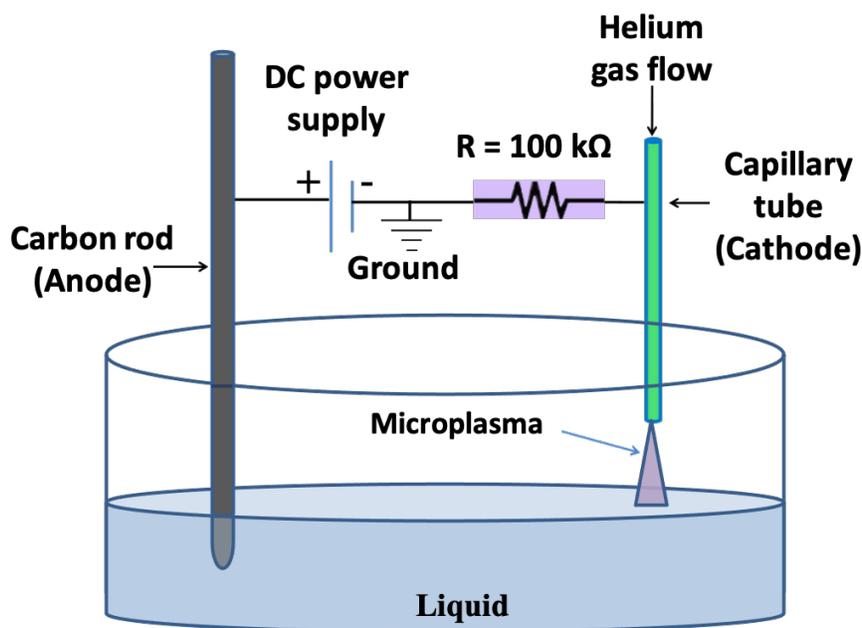
## Introduction

There exists a range of reports describing the synthesis of silver nanostructures (AgNSs) by means of plasma-based liquid process [1-5] due to their potential applications in various fields [6-9]. AgNSs are generally synthesized in solutions containing  $\text{Ag}^+$  ions where a reactive agents are used to form Ag atoms that nucleate and grow together in order to produce AgNSs. Depending on the nucleating seeds and the direction of the growth various sizes and shapes are AgNSs are synthesized. Often these chemical and physical methods require some reactive agents that are harmful and hazardous. The plasma-induced liquid chemistry (PiLC) is one of the ways that utilizes no such reactive agents for the synthesis process [10] and it can generate nanostructures (NSs) for ready-to-use purposes and applications.

One of the challenges faced in such PiLC studies is that the reactive species produced by plasma has a very complicated chemistry [11] and a multi-role to play in the synthesis process. Therefore,

the very basic need to such research area is to investigate the reaction mechanisms that clearly demonstrate the reduction process of ions to atoms with good experimental evidences. Peter Bruggeman and his colleagues presented a detailed review on such reaction analysis of plasma-liquid interactions. Although their focus was mostly on the reaction chemistry induced by plasma in liquids, but the analysis has helped various scientists in this field to correlate their experimental findings with the review and the observations made. The present study is such an attempt where AgNSs synthesized by PiLC are studied with a chemical analysis. We first discuss the synthesis process with the help of ultraviolet-visible (UV-Vis) spectroscopy and transmission electron microscopy (TEM) and then the impact of organic and iodine solutions on the reaction mechanisms are discussed in detail.

### Experimental Details



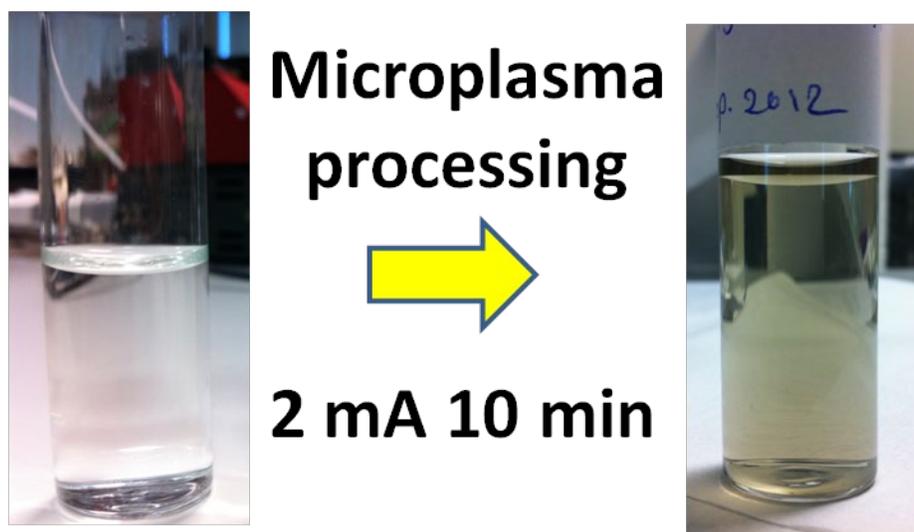
*Fig. 1. Plasma-induced liquid chemistry (PiLC) set-up.*

The PiLC set-up used for the synthesis is as shown in Fig. 1 where carbon rod is in contact with the liquid serving as the anode and the cylindrical stainless steel capillary tube (with inner diameter of 0.25 mm) acts as the cathode through which a helium gas is allowed to flow at fixed rate of 70 cubic centimetre per minute. A high DC power supply is used to generate microplasma between the capillary outlet and the surface layer of the liquid. The distance between the capillary outlet and the surface layer of the liquid is 0.7 mm.

A solid powder of silver nitrate ( $\text{AgNO}_3$ ) was obtained from Sigma Aldrich (UK) to prepare the aqueous solutions of different concentrations. Three different concentrations, 0.2 mM, 1 mM and 5 mM, were prepared by dissolving a proper amount of silver salt powder in distilled water. Each solution was treated by plasma at current of 2 mA for the period of 10 minutes. The synthesized samples were then characterized by UV-Vis spectroscopy and TEM analysis. In order to assess the reaction chemistry by plasma, experiments were performed with ethanol, methanol and iodine solutions obtained from Sigma Aldrich (UK).

## Results and Discussion

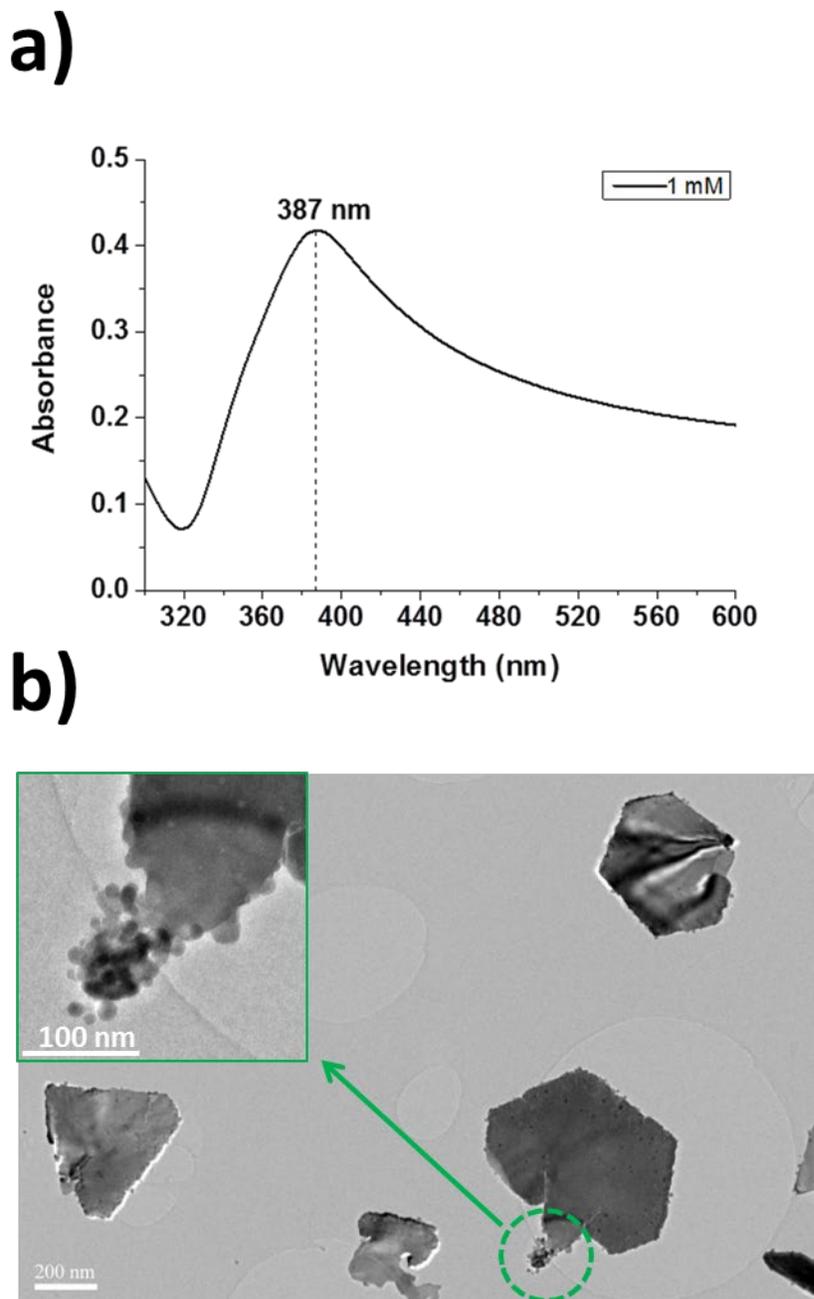
### Synthesis of AgNSs



*Fig. 2. Difference between the colour of 1 mM AgNO<sub>3</sub> solution before and after plasma treatment at current of 2 mA for the period of 10 minutes.*

The AgNO<sub>3</sub> solution with a molar concentration of 1 mM is treated by plasma with discharge current of 2 mA. As the plasma treatment continues, there is change in the colour of the solution (see Fig. 2). The solution turns into dark green-yellow after 10 minutes of treatment, which is in good agreement with the characteristic surface plasmon resonance (SPR) peak of AgNSs[12,13].

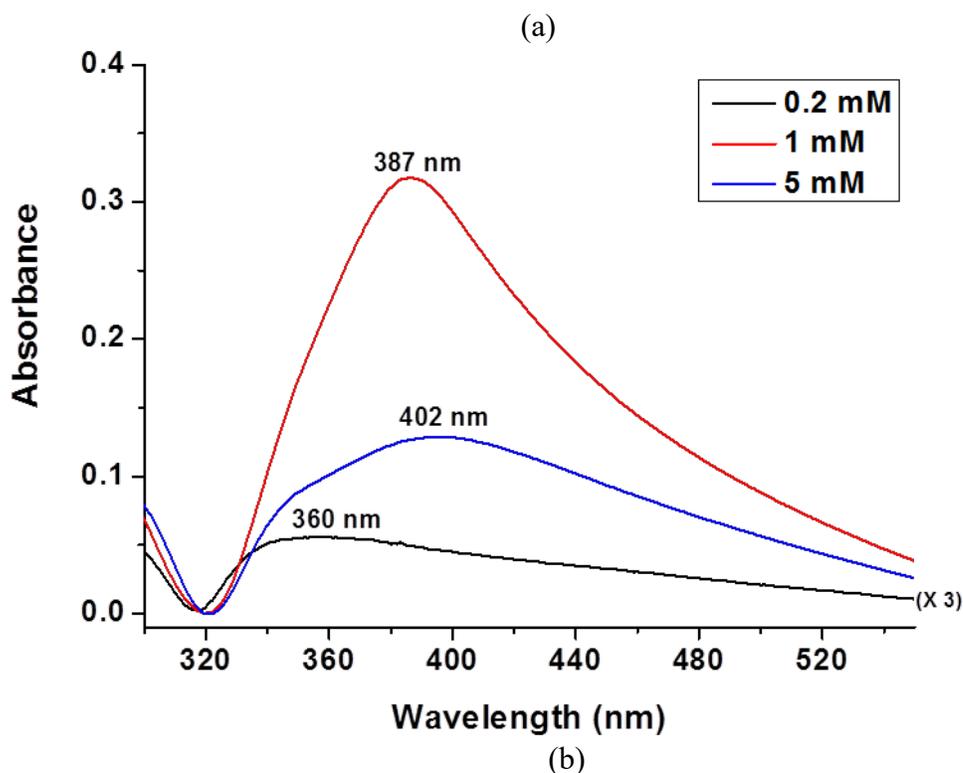
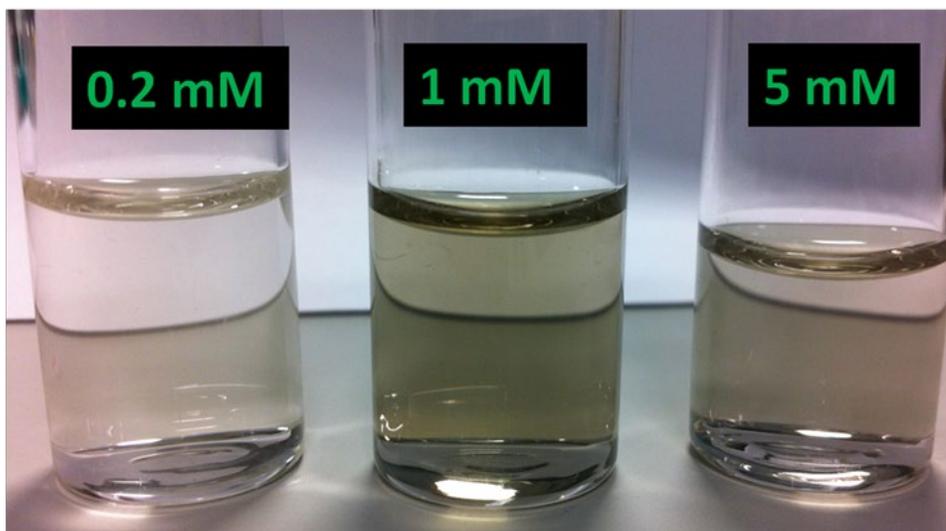
Fig. 3 shows the obtained UV-Vis and TEM results of the synthesized AgNSs. The absorption peak at 387 nm (as shown in figure 3a) can be compared from the literature [14-17]. The TEM analysis reveals that plasma processing treatment leads to small size of the particles varying in the range of 10 nm to 30 nm along with few different size structures. However, literature shows that the absorption peak of silver nanowires can be found around 380-390 nm [18-20]. Furthermore, a detailed study with another two different concentrations of silver precursors, 0.2 mM and 5 mM AgNO<sub>3</sub> are performed by plasma treatment procedure same as above.



**Fig. 3.** Plasma treatment of 1 mM AgNO<sub>3</sub> solutions produces silver nanostructures (a) UV-Vis spectra and (b) transmission electron microscopy (TEM) image.

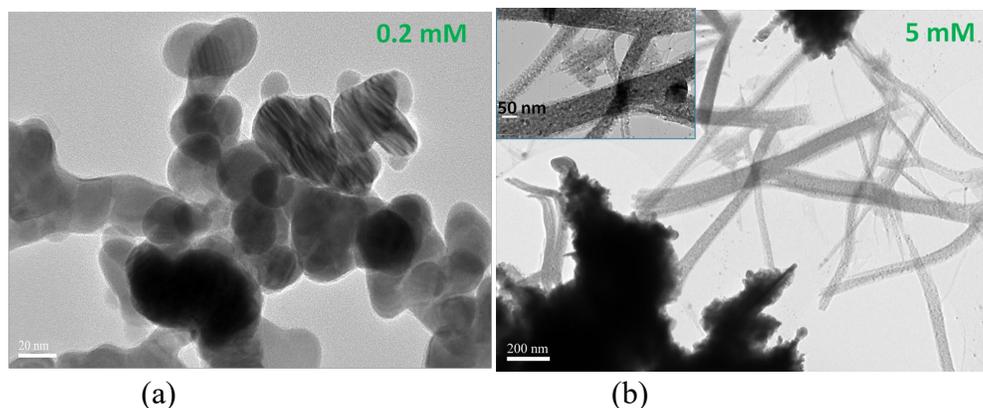
Fig. 4a shows a comparative image of the silver nanostructure colloids with different concentrations. Fig. 4b shows a comparative graph of UV-Vis. spectroscopy, which indicates that 5 mM AgNO<sub>3</sub> has a peak shifted from 387 nm to 402 nm while 0.2 mM AgNO<sub>3</sub> did not exhibit sharp peak but has a broad absorption band observed around 360 nm. The broadening of the peak for 5 mM AgNO<sub>3</sub> is much stronger than 1 mM AgNO<sub>3</sub> precursors, which indicates that the full width at half maximum (FWHM) for 1 mM AgNO<sub>3</sub> (103 nm) is less compared to 5 mM

precursors(149 nm). It can also be observed that the intensity of absorption for 0.2 mM is quite lower as compared to 0.1 mM and 5 mM samples. On the other hand, intensity of absorption for 5mM precursors is less compared to 1 mM because of variation in size and change in the morphology in case of 5mM sample.



**Fig. 4.** (a) Photographs of AgNSs samples prepared from different concentrations 0.2 mM, 1 mM and 5 mM. (b) Comparison of UV-Vis absorption spectra of the samples obtained from 0.2 mM, 1 mM and 5 mM AgNO<sub>3</sub> concentrations (Note that 0.2 mM sample has the intensity of the absorption that is multiplied here by a factor of 3 for clarity)

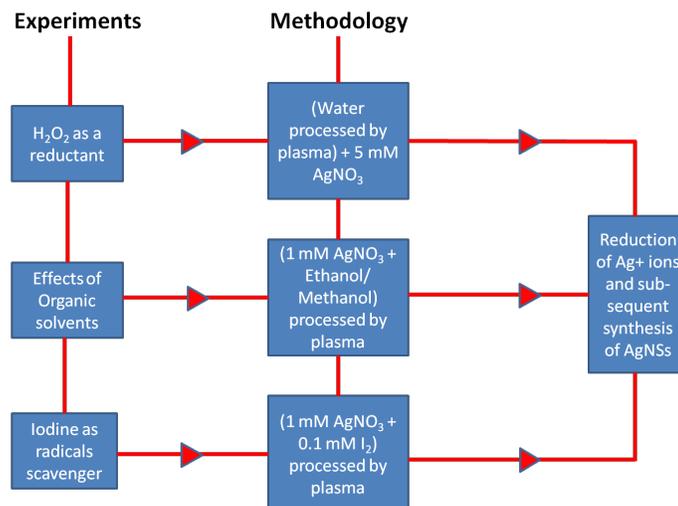
In order to assess the effect of silver precursor concentration on the optical and morphological properties of the synthesized silver nanostructures, another two different concentrations of silver precursors namely 0.2 mM and 5 mM  $\text{AgNO}_3$  are processed by plasma with same plasma processing conditions as above and characterized by UV-Vis and TEM (see Fig. 4). Fig. 4a compares the photographs of the AgNSs of different concentration 0.2 mM, 1 mM and 5 mM. UV-Vis results demonstrates that increasing the  $\text{AgNO}_3$  concentration to 5 mM shifts the absorption peak from 387 nm to 402 nm (see Fig. 4b). However, the 0.2 mM  $\text{AgNO}_3$  concentration does not exhibit any sharp absorption peak, but instead a broad absorption band around 360 nm can be observed. It can also be noted that broadening of the absorption peak for the sample with 5 mM is much stronger than the sample with 1 mM; i.e. the full width at half maximum (FWHM) for 1 mM (103 nm) is less than that for 5 mM (149 nm). The reduction in the intensity of absorption for the 0.2 mM sample is quite apparent because of the lower  $\text{AgNO}_3$  concentration used. On the other hand, the intensity of absorption for 5 mM is less than that of 1 mM and the reason could be the existence of different morphological structures or smaller particles in 5 mM.



**Fig. 5.** TEM images of the synthesized AgNSs with (a) 0.2 mM and (b) 5 mM  $\text{AgNO}_3$  concentrations.

Fig. 5 shows TEM analysis of 0.2 mM and 5 mM concentration of silver precursors. It can be observed that 0.2 mM silver precursors produces nanoparticles having size varied from 20 nm to 30 nm with nearly spherical shape. Fig. 5a also shows agglomerated nanoparticles which means nanoparticles stick together during the growth of the silver nanostructures. These results indicate the absence of the stabilizer indicating they are not electrostatically stabilized. The nanostructures are also non-uniform in size and shape which is also well reported in Huang *et al.* article [21]. As shown in figure 5b, 5mM silver precursors exhibits some nanowires having diameter varied from 50-70 nm. The inset image of Fig. 5b reveals interesting features in case of 5 mM silver nanostructures. It shows small nanoparticles are attached to the surface of the nanowires which may be due to the coulomb attractive force.

## Analysis of reaction mechanisms for the synthesis of AgNSs



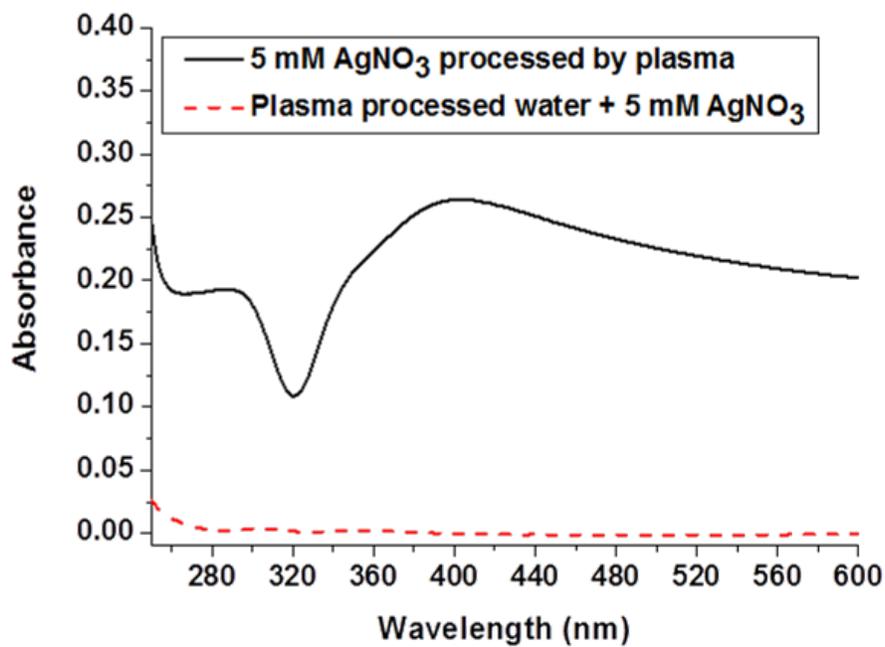
**Fig. 6.** Diagrammatic view of the experiments and corresponding strategies utilised to understand silver nanostructures (AgNSs) synthesis mechanism. Experiments are performed to clarify the better look in the possible role of  $H_2O_2$  as a reducing agent, on the impact of organic solvents and on the probability of using iodine ( $I_2$ ) as a radical scavenger.

The synthesis of silver nanostructures by plasma-liquid interactions has been reported previously by a number of researchers; however a small fraction of them discusses the preparation without any surfactant and their respective liquid-chemistry. [4, 21-33]. In this part of discussion, we propose different mechanisms leading to the reduced form of silver ions. In the present work, silver nanostructures are formed with no help from any additional surfactants. The plasma-liquid interface shows up the change in the colour of the solution and hence the much needed liquid-chemistry for the synthesis should occur at the plasma-liquid interface that is responsible for the conversion of  $Ag^+$  cations to  $Ag^0$  atoms. The reduced  $Ag^0$  atoms then nucleate and grow together to produce AgNSs. A set of experimental strategies is designed to clarify the role of reduction mechanism for AgNSs formation. Fig. 6 indicates the diagrammatic view of the experiments conducted to probe the reaction chemistry involved. The experiments are conducted to clarify the proper insights in the probable reductive role of hydrogen peroxide, in the impact of ethanol and methanol solutions, and on the probability of employing iodine ( $I_2$ ) as a radical scavenger.

### $H_2O_2$ as a possible reducing agent

There are different possible pathways for the reduction mechanism of silver nanostructures, for instance through hydrogen radicals ( $H^\bullet$ ) inside the liquid [25, 27, 34-36], aqueous (hydrated) electrons ( $e^-_{aq}$ ) [33, 34, 37, 38] and hydrogen peroxide ( $H_2O_2$ ) [25]. It has been observed previously that the silver nanoparticles actually decompose the hydrogen peroxide [39] and that is why the two reactions, i.e. silver nanoparticles decomposing the hydrogen peroxide and the reduction of  $Ag^+$  cations by hydrogen peroxide, are competing with each other. Therefore, this contradiction state that hydrogen peroxide reducing the  $Ag^+$  cations cannot be expected. So, to clarify the role of hydrogen peroxide, the experiment is carried with plasma processed water. It has been found that distilled water treatment by plasma generates the hydrogen peroxide which does not decomposes in water for at least four hours [11]. When the plasma processed water at 2 mA is added to silver

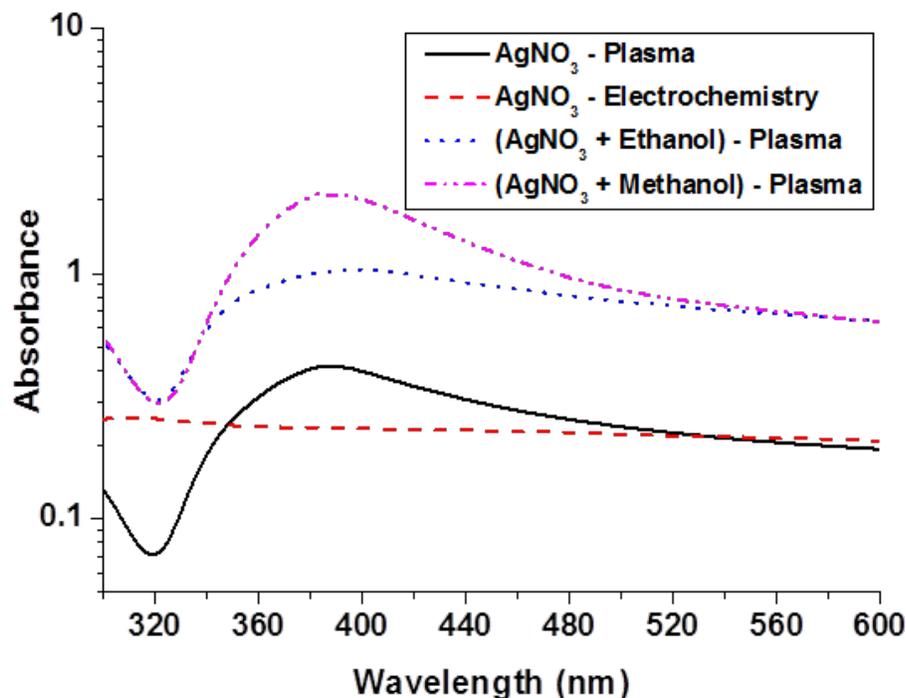
nitrate solution, it is found that the colour of the solution does not change. The results are shown in Fig. 7 where the absorption spectrum of the plasma processed water added with silver nitrate is compared with that of the plasma processed silver nitrate solution (i.e. 5 mM AgNSs). There is no clear evident surface plasmon resonance peak as compared to the 5 mM AgNSs sample which sufficiently demonstrates inability of hydrogen peroxide to reduce  $\text{Ag}^+$  cations.



**Fig. 7.** Absorption spectra of plasma treated water sample mixed with 5 mM  $\text{AgNO}_3$  (red line) and absorption results 5 mM  $\text{AgNO}_3$  solution treated by plasma are also shown for comparison (black line).

#### Influence of ethanol and methanol solvents

The literature review suggests that the presence of the organic solutions influences the reductive scheme of  $\text{Ag}^+$  cations to synthesize silver nanoparticles. For instance, the reports on the synthesis of AgNSs by photochemical techniques and pulse radiolysis methods indicate that the proper ratio of ethanol and silver precursor solutions helps to affect the reduction rate of  $\text{Ag}^+$  to form  $\text{Ag}^0$  atoms [24,40,41]. In other words, the ethanol added in the silver precursor act as a reducing agent. In order to scavenge the hydroxyl radicals and hydrated electrons one can also utilize tert-butyl alcohol or methanol or 2-propanol in order to achieve the reductive situations [40-42]. For instance, Kamat et al. have clearly reported that the presence of tert-butyl alcohol to the silver precursor solutions would help to achieve the scavenging of hydroxyl radicals and therefore the remaining reactive radicals (i.e. hydrated electrons) would act as reductants for  $\text{Ag}^+$  cations [42]. In this section, we present the results of the addition of ethanol and methanol in silver nitrate solutions for plasma processing. 1 mL of ethanol and 1 mL of methanol is mixed with 10 mL of silver nitrate solution of treated by plasma at current of 2 mA individually one by one and the absorption results are shown in Fig. 8. The Fig. 8 also includes in the absorption results gained by direct electrochemistry; the two electrodes carbon rod and the capillary tube both are immersed in the liquid and the current of 2 mA is applied.



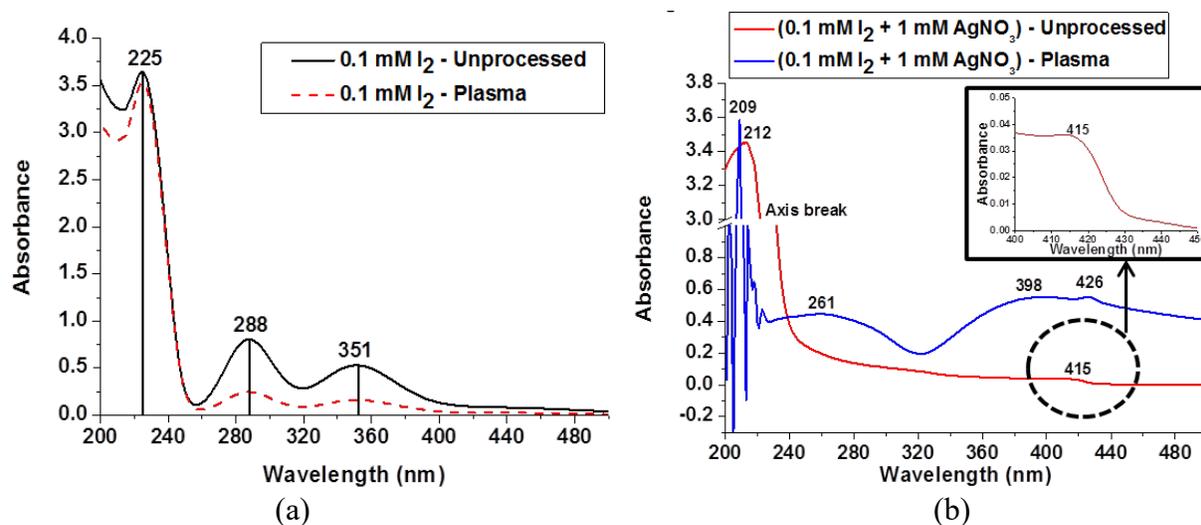
**Fig. 8.** Absorption spectrum of 1 mM AgNO<sub>3</sub> solutions treated by plasma and direct electrochemistry. The impact of ethanol and methanol on the synthesis of AgNSs is shown in graph. The ethanol and methanol are mixed with 1 mM AgNO<sub>3</sub> solutions and treated by plasma. In all the cases, the plasma is operated at current of 2 mA for the period of 10 minutes.

The results as shown in Fig. 8 suggest that silver nanostructures are not formed by direct electrochemistry indicating that a different reaction mechanism is at play that must be induced by plasma-activated chemistry. The experiments with the ethanol and methanol clearly enhances the intensity peak of the synthesized silver nanostructures which is in well agreement with previously reported articles [24]. Therefore, the experiments conducted with organic solvents reflect that methanol and ethanol have a strong capacity to act as a donor of electrons. In other words the negative redox potentials of both the organic solvents appear to be high and therefore it affects the reduction of silver cations[43].

#### Iodine as a radical scavenger

As per the literature survey[1,4,21,32,34,41] and also the experimental findings received in this work so far, we have two probabilities for the reduction of Ag<sup>+</sup> cations: either it may get reduced via hydrogen radicals or via hydrated electrons (or both). In a similar plasma-based system but with slightly different configuration, it has been found that AgNSs could not be formed where plasma was generated at the anode part [44]. Hence, the reduction of Ag<sup>+</sup> cations may take place through electrons [45]. In this section we describe the results of experiments conducted with iodine solutions along with the silver precursor concentrations. The iodine molecules interact with the hydrogen radicals through the reactions [46],





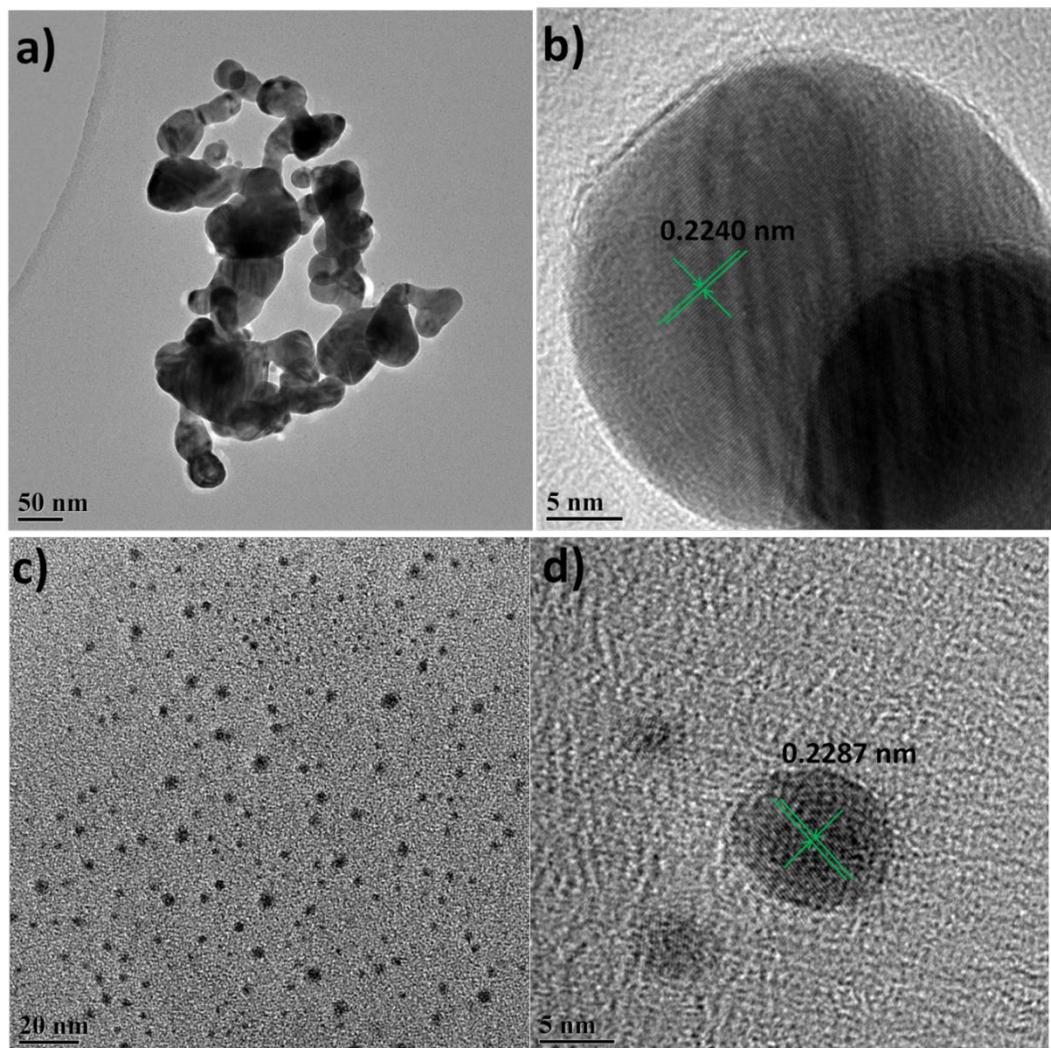
**Fig. 9.** (a) The UV-Vis spectrum measurements of unprocessed and plasma treated 0.1 mM I<sub>2</sub> solution. (b) The UV-Vis spectrum measurements of plasma treatment of 0.1 mM I<sub>2</sub> solution mixed with 1 mM AgNO<sub>3</sub> solutions. The graph compares the absorption peaks before and after plasma treatment. In all the cases, the plasma is operated at current of 2 mA for the period of 10 minutes.

The purpose of using the iodine is to scavenge the H<sup>•</sup> radicals generated by plasma-water reactions and therefore they would not be able to reduce the Ag<sup>+</sup> cations which leaves only the hydrated electrons as a pathway to the silver reduction. In order to observe the effects of plasma treatment on the iodine solution, 0.1 mM I<sub>2</sub> solution is processed by plasma at current of 2 mA and the absorption measurement is compared with the same obtained from the unprocessed I<sub>2</sub> solution. As shown in Fig. 9, there three different absorption peaks exhibited by the unprocessed I<sub>2</sub> solution: 225 nm is relevant to the solvated I<sup>-</sup> ions [46-48] and other two peaks at 288 nm and 351 nm are associated with the I<sub>3</sub><sup>-</sup> ion [46,48]. It is also important to note the reaction of iodine with water molecules via reaction [49,50]



It can be observed from Fig. 9a the plasma treatment of I<sub>2</sub> solution reduces the intensity corresponding to the presence of I<sub>3</sub><sup>-</sup> ions to 30% and the presence of I<sup>-</sup> ions reduces to 92% of their initial unprocessed values. So, it can be concluded that the forward rate of the reaction (3) is reduced. The plasma processing of water generates a huge amount of H<sup>+</sup> ions that can react with I<sup>-</sup> ions and hence the presence of 225 nm peak corresponding to I<sup>-</sup> ions in plasma processed I<sub>2</sub> solution confirms. As indicated by the red dotted graph in Fig. 9a, the plasma processing does not scavenge the I<sup>-</sup> ions. The aqueous 0.1 mM iodine solution is mixed with the 1 mM silver nitrate with a volume ratio of 1:10 and plasma treatment at current of 2 mA is performed. The results of absorption spectrum are shown in Fig. 9b. A new absorption band with a center-peak at 415 nm appears which correspond to silver iodide (AgI) [51-53] appearing due to the reaction with [54]

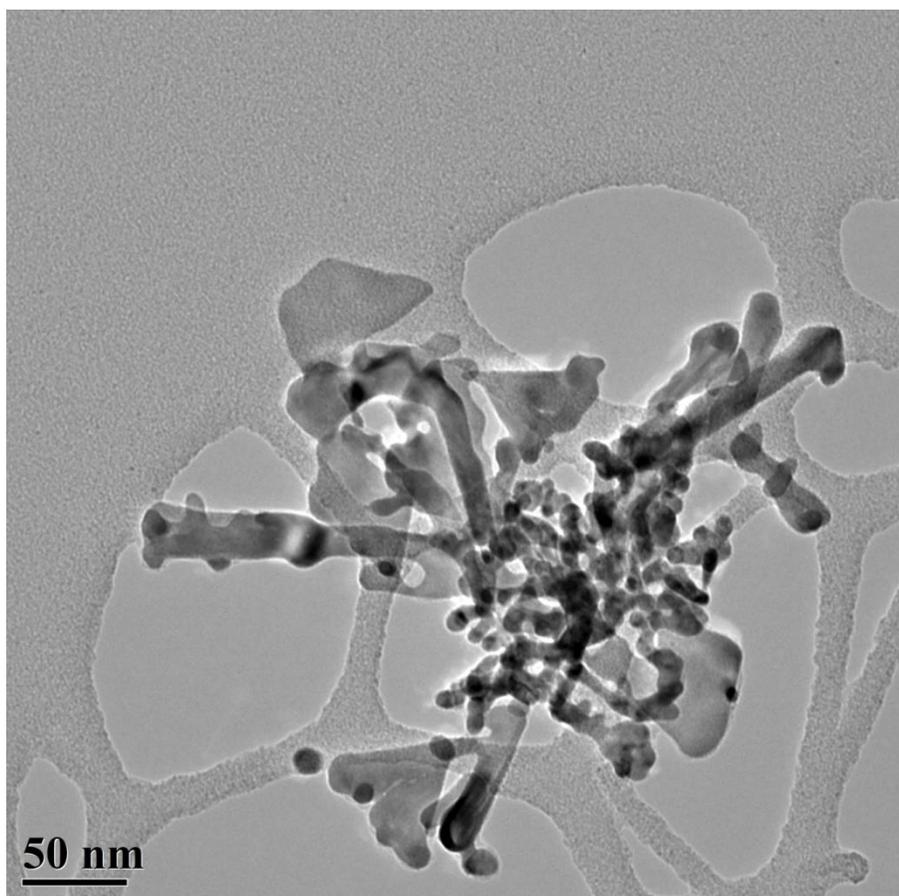




**Fig. 10.** (a)-(b) TEM images of AgNSs of 25 nm to 30 nm in size and (c)-(d) TEM images of the AgNSs of 2 nm to 5 nm in size. The AgNSs samples are prepared from plasma treatment of 0.1 mM  $I_2$  solution mixed with 1 mM  $AgNO_3$  solutions at current of 2 mA for the period of 10 minutes.

Due to the presence of the silver ions, the absorption peaks at 351 nm, 288 nm and 225 nm are not observed here and a peak at 212 nm is found that corresponds to highly dispersed  $Ag^+$  ions [51,55,56]. We also observe the presence of absorption region centered at 415 nm corresponding to silver iodide [51,57,58]. There also exists a characteristic SPR peak at 398 nm indicating the presence of AgNSs. However, the intensity of absorption is enhanced and the peak is having a red-shift of 11 nm as compared to the results of AgNSs obtained from 1 mM silver precursor solutions (refer to Fig. 2a). The absorption maximum at 415 nm is still there after plasma processing, however it has a red-shift of 11 nm. This means that there is still the presence of silver iodide. The peak at 261 nm correspond to the presence of silver ion clusters  $Ag_m^{\delta+}$  [34,38,42,59,60]; where  $\delta$  = different ionic states of  $Ag^+$  ions and  $m$  = number of Ag atoms. The existence of nanostructures is also confirmed by the TEM images (see Fig. 10). The nanostructures are in the range of 2 nm to 5 nm (group-A) and 25 nm to 30 nm (group-B) in size. There also appears the presence of the

larger nanostructures agglomerated as shown in Fig. 11. As evident from the TEM images, the lattice spacing from Fig. 10b and Fig.10d is 0.224 nm and 0.229 nm for the groups A and B respectively. The lattice spacing at 0.229 nm can be attributed to the (111) plane of the silver crystals [61,62] and the spacing of 0.224 nm could arise due to the possible compression of the (111) plane caused by the strain on the surface. The presence of I<sub>2</sub> solution in the silver precursor helps to form silver iodide and the left-over silver ions undergo the reduction mechanisms via plasma-induced cascaded chemistry i.e. either via H<sup>•</sup> radicals or/and e<sup>-</sup><sub>aq</sub>. Therefore, two possible reactions can be of the form:



**Fig. 11.** Nanostructures produced by plasmatreatment of 0.1 mM I<sub>2</sub> solution mixed with 1 mM AgNO<sub>3</sub> solutions at current of 2 mA for the period of 10 minutes.

### Conclusions

In conclusion, it has been observed that hydrogen peroxide is not playing a role of reductant for Ag<sup>+</sup> cations. The hydrated electrons or/and hydrogen radicals are two possible reactive species serving as a reducing agent for Ag<sup>+</sup> cations and related synthesis of AgNSs. The presence of ethanol and methanol in the silver nitrate solution seems to accelerate the synthesis mechanism of AgNSs. The experiments conducted with the iodine solutions reflect that fact that the addition of I<sup>-</sup> ions enhances the process of reduction of Ag<sup>+</sup> cations and therefore there seems an increment in the density of AgNSs. The analysis from the TEM data suggests that iodine ions generates the

comfortable conditions for the synthesis of small NPs i.e. less than 10 nm. However, the complications of iodine solutions with silver nitrate can be more clarified if there are some quantified interpretations available in terms of solution chemistry. Further analysis can offer a pathway to explore the plasma-induced chemistry for a better control at the reaction kinetics.

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