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Tunable silver nano-ink for printable electronics and pen-on-paper-writing

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ABSTRACT

The article describes an efficient method for the preparation of silver nanoparticles ink for its application in printed electronics. The effective formulation using polyvinylpyrrolidone (PVP) and triethylamine leads to highly stable silver nano-ink. The spin-coated silver nanoparticulate films fabricated using the as-prepared nano-ink exhibit bulk-like conductivity at moderate annealing temperature of 60°C -100°C. Additionally; *pen-on-paper* type of conventional writing is successfully demonstrated with modifying the formulation of such nano-inks. The viscosity of as-prepared Ag nano-ink can be easily altered by varying the concentration of binders and solvents to suit its end applications. Such flexibility coupled with high conductivity and amphiphilic nature makes this silver nano-ink highly useful in various advanced printing techniques. Copyright © 2016 VBRI Press.

Keywords: Silver conductive ink; printable electronics; resistivity; pen-on-paper; AFM.

Introduction

The advancement in nanotechnology has brought new tools for electronic industry developed from utility of *in-situ* and *ex-situ* generated nano-films or particles from liquid phase handling. It is well known that nano-sized particles show unique and unusual physical and chemical properties due to their high surface to volume ratio drawing a lot of attention in electronic industry for the fabrication of low cost electronic devices [**1**]. In recent years, these unique properties are highly useful in printed electronics for the development of different applications such as RFID tags, flexible displays, antennas, transistors, sensors and photovoltaic's [**2-7**]. Printable electronics has opened up new avenues to many simple, low-cost and flexible products overcoming the limitations of conventional electronics. The printed electronics process is economically cheap, requires low working temperature, covers large area production, less time consuming, high speed processing, and most importantly, environment friendly [**8**]. Printed electronics also reduces the chemical waste produced during processing of equipments [**9**]. Generally, printed electronics is a technological advancement for hi-tech application that involves fabrication of electronic devices through printing techniques using nanoparticle (NP) ink on a flexible substrate. It is almost similar to the process used for printing ink on paper or foils [**10**]. The basic components of printed electronics are the materials used for the preparation of nano-ink and substrates required for printing. A lot of research has been conducted on the materials such as polymer, carbon and metals which show electric conductivity [**11**]. These conductive polymers are advantageous for making flexible devices but the ink prepared from conductive polymers and carbon materials exhibit low conductivity (10-100 S cm^{-1}) as compared to metallic NP inks. They are also chemically, thermally and electrically less stable than metallic nanoparticles [**12**]. Thus, extensive research is conducted globally to develop conductive nano-inks with highest conductivity by using different metal based NPs. Also, metallic nanoparticles compared to their bulk counterparts have the ability to be annealed at exceptionally low temperatures due to its high surface to volume ratio and thus reduction in melting points can be added as an advantage during sintering process. Low temperature annealing of nano-inks on flexible plastic substrates increases the commercial viability to manufacture flexible electronic devices [**13**].

Metallic nanoparticles such as gold (Au), silver (Ag) and copper (Cu) are the most investigated materials for formulating nano-ink due to their highest electrical conductivity [**14**]. Gold nanoparticles are highly conductive and enable low temperature annealing compared to bulk form. They are extensively used in electronic industry for fabricating electrodes and their application as conductive ink in making flexible devices due to its high conductivity, high thermal stability and anti-oxidation properties. However, gold NPs are very expensive for mass production and thus can be replaced by other metals like Ag and Cu [**14, 15**]. Copper NPs are also highly conductive and less expensive than gold and silver metals. Although copper is cheaper than gold and silver, it is highly prone to oxidation in ambient conditions which decreases its electrical conductivity. The use of organic capping prevents oxidation but this reduces the electrical conductivity. Thus, it is necessary to remove the organic protecting layer to get high electrical conductivity which requires sintering at high operating temperature (200 - 300 °C). Such high temperatures are not suitable for the use of certain plastic substrates which are necessary for flexible electronics. Indeed, the melting temperature of copper is also relatively higher than silver, which is not desirable for flexible electronics [**16**].

Owing to the limitations of various other metal nanoparticles, silver NPs are reported to be the best alternative for preparation of metal nano-ink compatible for printable electronics. Silver metal, due to its high electrical and thermal conductivity offers desired result for conductive ink [**13**]. The finely dispersed and highly stable Ag nanoparticles find its potential applications in transparent conductive coating in addition to other industrial applications such as nonlinear optical properties and antibacterial properties due to its chemical stability, optical transmittance, catalytic activity and excellent electrical conductivity [**17-19**]. Ag NPs are also resistant to oxidation even at ambient conditions which increases their compatibility for preparation of conductive silver nano-ink by various formulations. Synthesis of Ag NPs has been reported by various methods such as by electrolysis [**20**], by sono-electrochemical [**21**], by chemical reduction of silver salts [**22-24**], by gas evaporation [**25**] and by atomization [**26**]. It can also be formed by using organic solvents like ethanol and N, N-dimethylformaide (DMF) itself act as a reducing agent [**27**]. The preparation of silver NPs is also reported by polyol method in which ethylene glycol, propylene glycol, and diethylene glycol act as both reducing agents and solvent [**28**]. Comparing all these processes, chemical reduction method is most practiced because of its ease and simplicity. The stability of Ag nanoparticles (from oxidation) is important to realize its true potential for various applications. Along with the oxidation, aggregation and clustering of Ag colloids can alter its absorbance profile which originates from well-known surface plasmon resonance (SPR). Mishra *et.al* demonstrated excellent stability of Ag nanoparticles embedded in various matrices (C70 and polymers etc.) by studying the optical properties of these composites [**29-32**]. Similarly, the stability of nano-ink formulations is critical and can be improved at high metal loading by using optimum concentration of metal precursor, stabilizing agent, reducing agent and solvents without compromising the electrical conductivity of nano-ink [**33**]. Silver nano-ink can be prepared by two methods namely the *ex-situ* and *in-situ*. In *ex-situ method*, Ag nanoparticles are synthesized first followed by their dispersion in a medium of choice for ink preparation. However, *in-situ* method offers single step formulation of the nano-ink where the chemical reduction of metal precursor leads to the formation of silver nanoparticles directly in a pre-decided solvent or medium with proper reducing and capping agents.

In order to further simplify, we herein, report silver NPs based conductive nano-ink prepared by simple and convenient method. The viscosity of as-prepared Ag nano-ink can be easily altered by varying the concentration of binders and solvents. Additional binder in the form of triethylamine was used to achieve stability of the Ag nano-ink up to 2 months. Thin films from so-generated nano-inks were fabricated *via* spin-coating process and conventional writing on paper and plastic substrates was also demonstrated from the as-prepared nano-ink. The as-fabricated silver patterns show bulk-like conductivity at very moderate annealing temperature of 60 °C -100 °C. The effect of concentration of organics and silver content are also studied on the film morphology as well as its conductivity.

Experimental

Materials and characterisation

Silver nitrate ($AgNO_3$) was purchased from Alfa Aesar. polyvinylpyrrolidone (PVP) and polyvinylalcohol (PVA) were obtained from Loba Chemie, India. N, N-dimethylformamide (DMF) was purchased from Spectrochem, India. Triethylamine (TEA) was obtained from MERCK, India**.** The UV-visible spectra of silver nanoparticles in solution as well as films were recorded on Alalytikjena (Germany) UV-VIS spectrophotometer between 300-800 nm. The viscosity of silver ink was measured with Anton Paar MCR 101 rheometer. The measuring temperature was maintained at 25 °C and gap was set at 0.5 mm. The transmission electron microscopy (TEM) images of silver nanoparticles were obtained with G2 Tecnai transmission electron microscope operating at 300 kV. The contact angle was measured on glass substrate with Kruss DSA 100 (Germany). The X-ray diffraction (XRD) pattern of spin coated films and silver powder was obtained with D 8 Advance Bruker X-ray diffractometer with scanning rate of 4° min^{-1} from 10° to 90°. Fourier transform infrared spectra (FTIR) were recorded as KBr pellets in the range of 450-4000 cm^{-1} on a FTIR Perkin Elmer (Spectrum 2). An atomic force microscope (Asylum Research MFP3D) was used to measure the roughness of the AgNP film obtained on the glass substrate. Spin coating instrument (Spin NXG – P-1) was used to deposit thin films on the glass substrate at 2000 rpm for 60 sec to study surface roughness and conductivity. The resistance of film annealed at 100 °C was measured using a four-point probe method with Keithley Model 6220 DC. The resistivity of the film is defined as per the equation given below:

$$\rho = R\,\frac{w * t}{L}$$

where, ρ is the resistivity of film (ohm meter), R is the measured resistance of film (ohms), L is the length of film (meter), w is the width of the film (meter) and t is the thickness of film (meter).

Synthesis of silver nano-ink

Preparation of in-situ silver nano-ink without use of triethylamine

In three separate beakers, $AgNO_3$ (2.0 g) was pre-dissolved in 2 ml of distilled water and were labelled as A, B and C. Polyvinylpyrrolidone (PVP) was dissolved separately in N, N-dimethylformamide (DMF) (0.36 g /48 ml for A; 0.36 g /23 ml for B and 0.36 g /10.5 ml for C) and added to the three beakers to make 2.5 wt/v %, 5 wt/v %, and 10 wt/v % Ag content respectively. All the three reaction mixtures were kept at room temperature under constant stirring. The colorless solution gradually turned light yellow and eventually brown-black after a period of 5-6 hrs. The solutions of A, B and C were re-coded as APD 2.5, APD 5 and APD 10 representing 2.5 wt/v %, 5 wt/v %, and 10 wt/v %; Ag content respectively. These samples were directly used for characterization, spin-coating without any further modifications.

Preparation of in-situ silver nano-ink with use of triethylamine

In three separate beakers, $AgNO_3$ (2.0 g) was pre-dissolved in 2 ml of distilled water and were labelled as A, B and C. Polyvinylpyrrolidone (PVP) was dissolved separately in N, N-dimethylformamide (DMF) (0.36 g /48 ml for A; 0.36 g /23 ml for B and 0.36 g /10.5 ml for C) and added to the three beakers to make 2.5 wt./v %, 5 wt./v %, and 10 wt./v % Ag content respectively. All the three reaction mixtures were kept at room temperature under constant stirring for 10 min and then triethylamine (TEA) (0.254 ml) was added drop-wise in all three reaction mixtures. The color of the solutions was rapidly changed from light yellow to black. The solutions of A, B and C were re-coded as APDT 2.5, APDT 5 and APDT 10 representing 2.5 wt./v %, 5 wt./v %, and 10 wt./v % Ag content respectively. These samples were directly used for characterization, spin-coating without any further modifications.

Spin-coating of in-situ silver nano-ink and its annealing and metallization

A 2 × 2 cm glass substrate was cleaned with ethanol, distilled water and acetone to remove the particulate matter and organic impurity on the surface. Initially, a PVA solution was spin coated (1500 rpm, 60 sec) on the glass substrate to generate a PVA thin film on the substrate which was dried at 50 °C so as to create an optimized surface for better adhesion of silver nanoparticles. Three layers of silver nano-inks were then spin coated (2000 rpm, 60 sec) on the PVA coated glass substrate. Subsequently, the substrate was subjected to thermal treatment for 1 h at 100 °C resulting in the formation of silver thin films. The substrate was then naturally cooled in open atmosphere at room temperature.

Preparation of ex-situ Ag nano-ink for conventional writing

Typically, a mixture of hexane and ethanol (1:1) was added to the *in-situ* prepared Ag nano-ink samples to obtain sedimentation of sticky black precipitate at the bottom. All the filtrate was removed by decanting and the black precipitate was warmed at 50 °C for drying purposes. A desired amount of ethanol (vehicle) was added to this black precipitate to adjust its flow ability. This modified *ex-situ* Ag-ink was loaded in a simple fountain pen and desired patterns were written on either glass or paper substrate. A thin film was also spin-casted using such Ag nano-ink and resistivity measurements were conducted.

Results and discussion

For the single-step formulation of silver nano-inks, we have adopted simple method based on silver nitrate ($AgNO_3$) as a metal precursor, polyvinylpyrrolidone (PVP) as a capping agents and N, N-dimethylformaide (DMF) as a reducing agent as well as a solvent medium. Since, the nanoparticles have tendency to agglomerate, a suitable surfactant like PVP was used. However, it was noticed that the samples were less stable and sedimentation was observed after 2 weeks. In order to prevent agglomeration of silver NPs and increase the stability of the ink samples, triethylamine (TEA) was skilfully used. The addition of TEA as an additional slow reducing agent leads to full conversion of Ag^+ to Ag^0 with coordination of amine groups around the nanoparticles leading to enhanced stability. Overall, as-generated ink formulations can be prepared with varying concentration of Ag content with or without the combination of TEA. Another added advantage of choosing TEA was its boiling point (~89.5 °C) which will ensure that excess TEA will evaporate during the annealing stage. The tendency of sedimentation of Ag aggregates in *in-situ* nano-ink was found to be more with increase in silver concentration thus higher metal content could lead to lowering its shelf-life. The ink samples prepared with TEA were stable for more than 2 months as sedimentation was not observed visibly (**Fig. 1**).

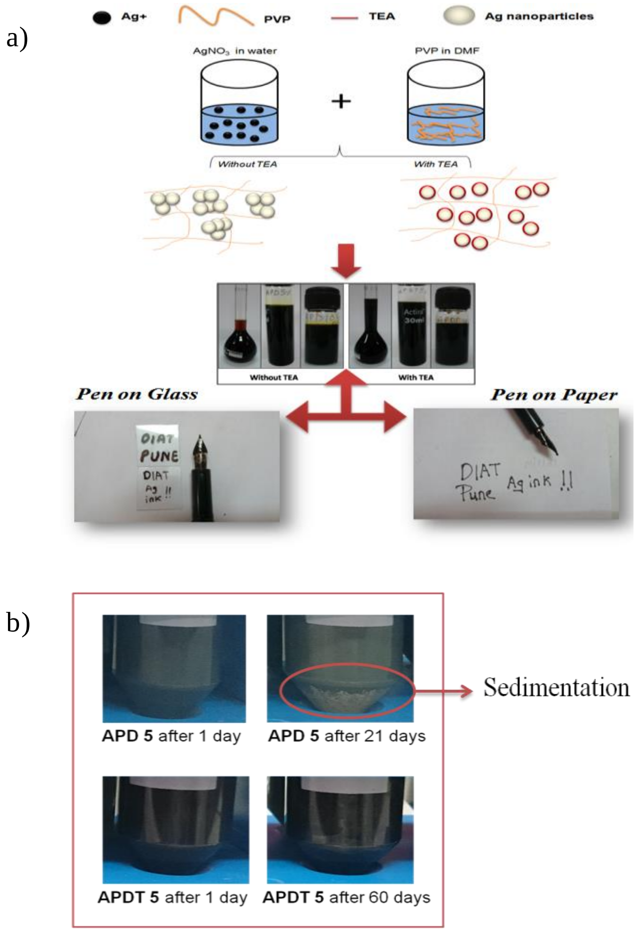

Fig. 1. (a) Schematic for preparation of Ag NPs ink and conventional writing with a fountain pen and b) Photographs of Ag nano-ink samples showing its stability. APD 5 samples represents 5 wt./v% Ag nano-ink samples prepared without the use of TEA and APDT 5 represents 5 wt./v % Ag nano-ink samples prepared using TEA.

For non-TEA samples the stability was about 2-3 weeks after which the sedimentation was clearly visible. However, the precipitation can be altered by sonication or mere shaking the sample for re-utilization. The variation in concentration of Ag in the ink enabled us to change the viscosity of the ink samples. This can be an advantage for the present ink formulation to find its use in various printing techniques where specific viscosity is required. The ink samples were dried by removal of solvent and converted back to an ink (*ex-situ*) suitable for conventional writing by adding ethanol as vehicle. The viscosity of such *ex-situ* Ag nano-ink can also be altered by controlling the vehicle concentration. The so-prepared *ex-situ* Ag nano-ink was loaded in a regular fountain pen for direct writing purposes. Both the *in-situ* Ag nano-ink and *ex-situ* Ag nano-ink samples were found to be suitable for glass and plastic surfaces for printing or writing purposes. In fact, we were successful in writing on regular paper with the *ex-situ* Ag nano-ink to demonstrate the *pen-on-paper* writing. The schematic representation of ink formulation and photographic images of conventional writing from the as-prepared samples is shown in **Fig. 1**.

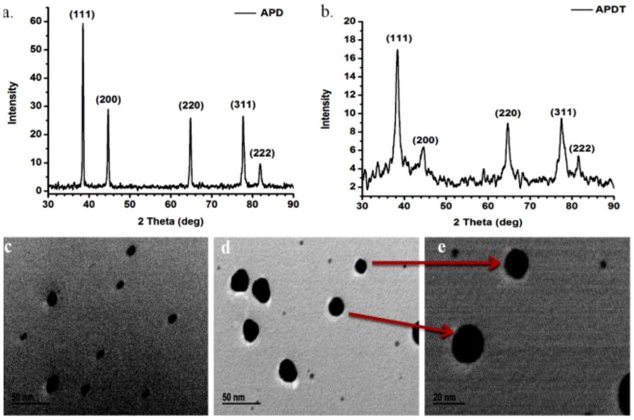

Fig. 2. XRD patterns of silver NPs (a) without TEA and (b) with TEA TEM images of as-prepared silver NPs with TEA c) APD 5 (5wt./v % Ag), (d) and e) APD 10 (10 wt./v % Ag).

The X-ray diffraction patterns generated from the dried ink confirmed the presence of silver NPs (**Fig. 2a**, **b**). The peaks well matched with the values for a face-centred cubic (FCC) crystal structure of silver. Five major peaks of silver NPs at 38.4º, 44.6º, 64.8º, 77.7º and 81.6º with TEA correspond to the (111), (200), (220), (311) and (222) crystal planes of silver NPs [**15**]. The diffraction peaks from any other impurities were not detected in the formulation without TEA however some minor peaks can be seen with TEA formulations that may be due to occurrence of etching of the nanoparticles thus leading to noise during recording. The crystallite size calculated by Scherer's equation was found to be 9 nm and 26 nm for sample with TEA and without TEA respectively. The increase in crystallite size for the sample without TEA reveals the efficient use of TEA as an additional capping agent which not only reduces the Ag-salt but also arrests the particle growth. It was also observed that samples prepared using TEA showed better remarkable stability (for months) as compared to non-TEA samples.

The TEM analysis was performed (**Fig. 2(c-e)**) for the as-prepared silver inks using TEA with APDT 5 (5wt. /v% Ag) and APDT 10 (10wt. /v% Ag). The TEM images demonstrated spherical Ag NPs with the particle size of 5-20 nm. The homogeneity of particles could be a result of extra TEA capping which controlled the particle growth. It was evident that APDT 5 has smaller particles than APDT 10.

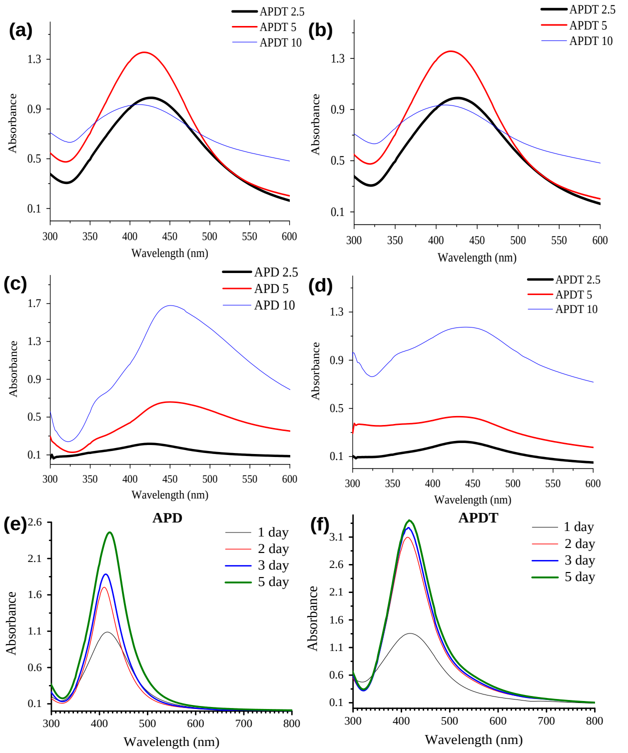

Fig. 3. UV-Vis absorption spectra of silver nano-ink (a) without TEA and (b) with TEA and without TEA and UV-vis absorption spectra of spin coated films c) without TEA and d) with TEA.

This could be due to higher nucleation occurring in the reaction medium as the Ag-salt concentration was increased. The *in-situ* Ag nano-ink was analysed by modern spectroscopic and analytical tools to understand the formation of Ag NPs in the ink and its stability with respect to time. In the first instance, absorption spectrum was measured during the formation of the ink and of the final product with varying silver concentration. The surface plasmon resonance (SPR) is unique feature of silver NPs and could serve as a tool to monitor the stability and distribution of Ag nanoparticles in a solution. The SPR for Ag nano-inks was obtained between 410-430 nm for different formulation with or without TEA (**Fig. 3a** and **3b**). The silver nano-ink formed without TEA showed narrow peak as compared to particles than sample with TEA. This could be due to higher nucleation occurring in the reaction medium as the Ag-salt concentration was increased. Also, the absorption increased with increase in Ag loading from 2.5 (APD2.5) to 10 wt./v % (APD10). The absorption peak with the maxima at about 430 nm, 418 nm and 422 nm without TEA and at about 426 nm, 418 nm and 412 nm with TEA for Ag NPs indicated marginal difference in terms of absorption energy (**Table 1**). Slight broadening in absorption pattern for TEA samples was probably due to wide-size particles distribution [**34-36**]. This may be a result of TEA acting as a reducing agent etching the surface and disturbing the homogeneity of the particles in solution. Another factor would be the concentration of TEA which was similar for all the three samples. Since, TEA also can act as a reducing agent; it might affect the Ag particle growth during the reaction. The UV-visible absorption spectrum was also recorded for silver nanoparticle films driven *via* spin coating on glass substrate using as-prepared nano-ink samples (**Fig. 3c** and **3d**). The films prepared from the formulations without TEA showed SPR at 424, 450 and 450 nm for APDT2.5, APD5 and APD10 samples, respectively. The films deposited with samples with TEA showed more stabilized SPR at about 432-440 nm and only marginally vary with silver metal content in the films. It was observed that with an increase in silver content, SPR has randomly shifted by about 10-25 nm when films were casted from ink where TEA was not employed (**Table 1**).

Table 1. SPR values of Ag nano-inks and spin casted films using Ag nano-ink.

	Ag nano-ink λ_{max} (nm)		Ag films λ_{max} (nm)	
Ag w/v	**APD**	**APDT**	**APD**	**APDT**
2.5 %	430	426	424	436
5 %	418	418	450	432
10 %	422	412	450	440

Table 2. Effect of time on SPR of Ag nano-ink.

Duration	APD		APDT	
	λ_{max} (nm)	FWHM	λ_{max} (nm)	FWHM
1 day	416	103	412	182
2 days	410	74	414	95
3 days	414	75	416	93
5 days	422	82	418	94

Such unconvincing observations in solution and films are probably obvious as during the stage when the ink was in solution form. The ionic reactants continue to interact with available neighbouring atoms and can cause disturbances to zero-valency of silver metal. This would not be the case for films as the final dry films after annealing will be highly stabilized and there is no possibility of ionic interaction thus leading to more stable SPR values. The change in refractive index of the surrounding would also affect the SPR band of silver NPs. Further, we studied effect of film thickness on SPR for sample (APD 5) as this provided the best SPR in solution as well as in film. It was observed that absorbance increased with increase in film thickness and SPR was marginally blue shifted and affected by about 5 nm only. The SPR with 3, 6 and 9 cycle spin coated films generated out of non-TEA based silver ink samples was systematically centred on at 450, 446 and 448 nm respectively (**Fig. S1**, supporting information). The trend indicates that although the SPR red shifted in comparison to the solution but it maintained its quality and consistency. Indeed, it has been reported that absorption spectrum of spherical silver NPs may show maxima between 410 nm and 450 nm with blue or red shift due to decrease or increase in particle size [**37-38**]. Additionally, the stability was studied by recording the absorbance of silver nanoparticles with respect to time and it was found that the intensity increased with time in both the formulations with and without TEA. **Fig. 4a** and **4b**, shows that as the silver concentration was increased from 2.5 to 10 wt./v %, its intensity increases with time due to qualitative maturity attained by the formulation over a period of time.

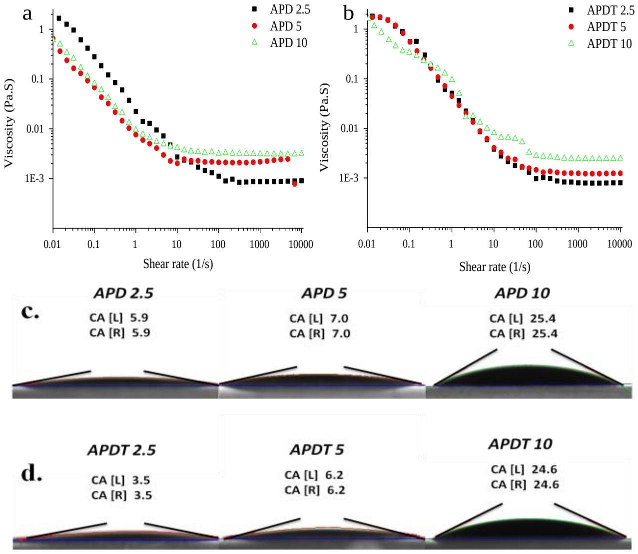

Fig. 4. Viscosity-shear rate graph of silver nano-ink at different silver concentration (a) without TEA and (b) with TEA, contact angle measurement of silver nano-ink on glass substrate (c) without TEA and (d) with TEA.

However, samples with TEA showed maximum intensity thus, it is believed that coordinating nature of TEA was suitably stabilizing the NPs up to only 5 w/v% (**Fig. S2**, supporting information). Indeed, the presence of TEA can improve the stability of silver nano-ink with acceptable variation in optical properties including particle size. It is likely that when the formulation was attaining its maturity with or without coordinating solvent, the shape and size of the nanoparticles were affected which eventually will affect the SPR phenomena in terms of either position or full width half maxima (FWHM). Typically, ink with 5% Ag content was adopted for FWHM study (**Table 2**). Since in the present case, the position almost remains same over 5-days period however, it indicated that the FWHM decreased after 5 days after remaining constant for 3 days.

Such observation hints towards wide size particle distribution in the sample due to constant ageing process (**Fig. S3** and **S2b**, supporting information). It is observed that the peak width has linearly decreased for the first two days and subsequently again linearly increased for the next three days (in a 5 days study) when sample did not contain TEA. However, sample with TEA showed constant peak width after three days despite irregular peak width in the first two days. Thus the presence of TEA can stabilize the ink formulation with very slow maturity. **Fig. 4** shows the rheological studies of the samples where viscosity of silver nano-ink at increasing shear rate upto 10000 s^{-1} was measured. It was observed that both the formulations with or without TEA exhibits shear thinning behaviour. In other words, the viscosity of silver nano-ink decreases with increases in shear rate. It is found that the viscosity of ink with or without TEA increases with increase in silver concentration from 2.5 % to 10 % which showed that silver loading was an important parameter to alter its viscosity. But, it should be noted that the increase in silver content may hamper the stability of the ink. It was also observed that ink without TEA showed slight increase in viscosity in comparison to ink with TEA. These as- prepared inks are stable for months when stored in a sealed containers and can be able to flow through fountain pens (~0.5µ tip). In addition, these inks can be written on both rigid and flexible substrates like paper and glass through fountain pens. Since, electronic printing is influenced by the interaction of ink with the substrates therefore it was only appropriate and important to understand spread ability and wettability of the ink. Contact angle measurement can provide information about the wetting properties [**10**]. **Fig. 4(c, d)** shows the contact angle of the silver nano-ink on glass substrate with or without TEA. The contact angle between ink droplet and substrate describes the wetting ability of ink with the surface. We found that the increase in concentration of silver leads to rise in the viscosity of the ink and therefore increase in contact angle. The silver nano-ink with 5 % Ag showed slight increase in contact angle whereas silver ink with 10 % Ag showed significant increase in contact angle. The contact angle of silver ink with the surface is below 90^o which indicates that spreading and wetting ability of as-prepared silver nano-ink was good and thus, revealed its potential for printing on the glass substrate. Also the wetting ability of silver nano-ink with or without TEA shows similar behaviour. We have found that the spreading ability of as-prepared silver nano-ink decreased with increase in silver loading. This indicated that higher silver content reduced the spreading ability of ink on the substrate and making it more suitable for end applications in electronics. The FTIR spectra confirmed presence of organics (PVA and TEA) in the dry powdered samples (**Fig. S4**, supporting information). The broad feature between 3500 and 2600 cm^{-1} belonged to the O-H stretch of the co-ordinated water. The band at 2781 cm^{-1} was attributed to the symmetric C-H stretching which was absent in ink containing TEA (APDT). The spectra also show peaks at 2427 and 2430 cm^{-1} attributed to C-N stretching. The intense peak at 1633 is clearly C=O stretch for the sample without TEA but this has considerably shifted to 1573 cm^{-1} in presence of TEA. The band at 1384 and 1412 cm^{-1} were derived from deformation of CH in plane. The C-O stretching was observed at 1015 and 1022 cm^{-1}[**39**].

Fig. 5 shows AFM images of the spin coated films deposited on glass substrates by the *in-situ* Ag nano-ink with TEA. The samples were sintered at 100 °C for 15 min after spin coating process. The AFM images of the samples with TEA showed smaller grain sizes as compared to the samples without TEA. It can be assumed that TEA forms an extra protecting layer on the surfaces of silver NPs as the amine group can coordinate with the surface Ag atoms of the silver NPs. The TEA layer would prevent the growth of particles and therefore reducing the grain size. On the other hand, the samples without TEA showed larger grain sizes which could be due to the PVP matrix holding large aggregates of silver NPs.

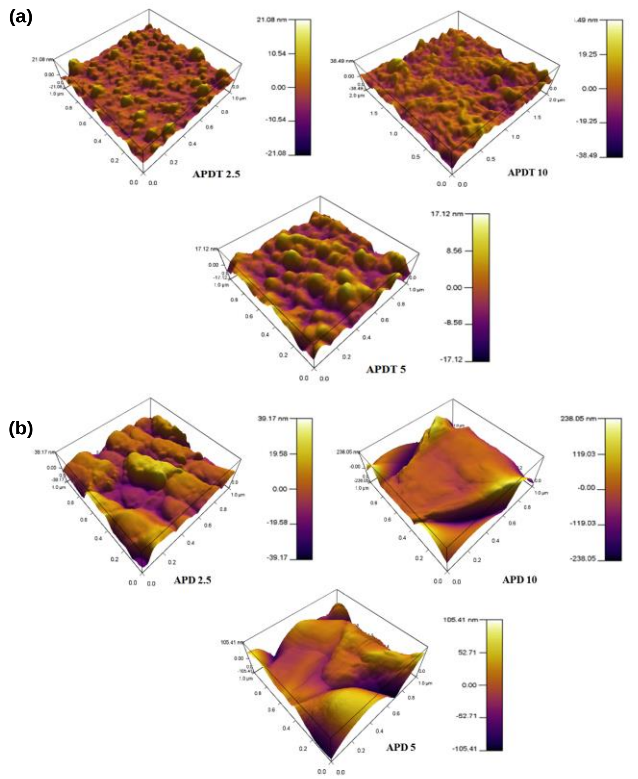

Fig. 5. AFM images of silver nanoparticulate thin films spin coated on glass substrates with Ag-nano-inks a) with TEA and b) without TEA.

The coalescence of Ag NPs will be very high in the films where TEA was not present as surface of the NPs would be naked. This coalescence will lead to growth in grain size even at low annealing temperatures (~100°C).

The variation of film thickness on glass substrate with increase in silver content was calculated from AFM and it is presented in **Fig. 5a** and **5b**. Even though the spin cycle (one) was same for the samples, the film thickness of the as-prepared film was found to be increasing with increase in silver content for both the formulation with or without TEA. Indeed, as the samples without TEA showed high aggregation, the as-deposited films are composed of larger grain sizes. We have seen that the viscosity of the ink increased with increase in silver content thus leads to increase in film thickness of the film. Also, it can be noted that the thickness of film containing TEA was very less than the film which does not contain TEA. It was evident from XRD analysis that the use of TEA reduces the particle size thus, very fine films are fabricated which can be considered as an advantage for flexible devices application. The thickness of film which does not contain TEA was higher due to presence of high Ag nano-aggregates which stacks over each other to form a thicker film. TEA mediated films have thickness of less than 100 nm however films without TEA shows thickness more than 100 nm which increased to about 870 nm with increasing Ag content. Hence, the AFM results confirm that the silver nano-ink with TEA was relatively better to cast thin nanometer scale films as compared to the samples without TEA. The effect of Ag loading on thickness and resistivity for the film deposited by spin coating method is presented in **Table 3**.

Table 3. Thickness and Electrical conductivity for the spin coated Ag film samples after annealing at 100 °C.

Concentration Ag w/v	**Electrical Resistivity (ohm cm) with TEA**	**without TEA**	**Thickness (nm) with TEA**	**without TEA**
2.5 %	1.88×10^{-5}	3.32×10^{-5}	65.82	115.66
5 %	1.93×10^{-5}	1.71×10^{-6}	71.02	608
10 %	1.59×10^{-5}	2.38×10^{-6}	76.98	868

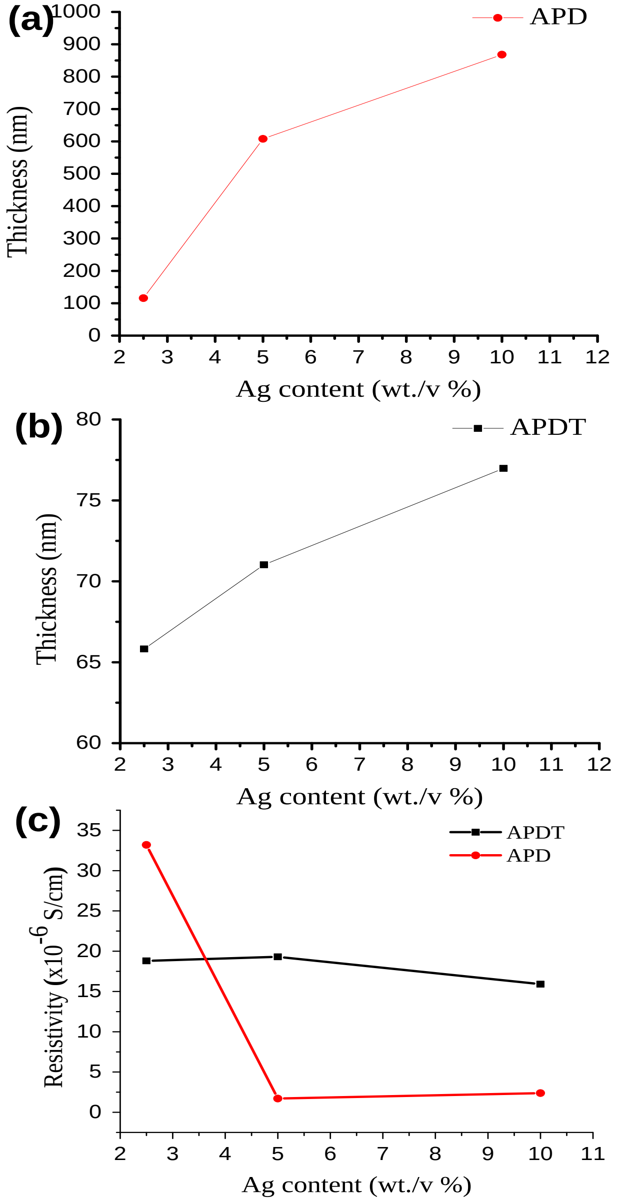

Fig. 6. Variation of thickness for spin coated Ag films by AFM (a) without TEA (APD), (b) with TEA (APDT) and (c) resistivity of spin coated Ag films after annealing at 100°C for 10 min.

Fig. 6. Variation of thickness for spin coated Ag films by AFM (a) without TEA (APD), (b) with TEA (APDT) and (c) resistivity of spin coated Ag films after annealing at 100 °C for 10 min.

The films fabricated from *in-situ* Ag nano-inks with TEA (APDT) showed slightly more resistivity as compared to the films fabricated from *in-situ* nano-inks without TEA (APD). This could be due to presence of additional organics in the form of trapped TEA in the films casted from APDT. The films fabricated from APD would contain less organics (only PVP) as compared to films fabricated from APDT (PVP and trapped TEA) resulting in lesser resistivity. It is well known that capping agents and surfactants hinder the charge transport and decreases the conductivity or increases the resistivity. The resistivity of spin coated film from *ex-situ* ink (5 wt./v %) which was used for conventional writing purpose was also measured. The calculated resistivity's (1.2×10^{-5} ohm cm) annealing was almost similar to their *in-situ* counterpart APDT when sintered at 60 °C for 15 min. Hence, the as-prepared films are highly conductive and show near bulk like resistivity of silver when sintered at relatively low temperatures (60 °C - 100 °C). In comparison with other literature reports, the patterns fabricated by similar type of Ag nanoparticle based ink (for *pen-on-paper* writing) attained bulk-like resistivity above 140 to 170 °C [**40-42**]. The only other report which as per our knowledge showed bulk-like resistivity at around 100 °C was for Ag-precursor based ink by Walker *et al.* [**10**]. In the present case, we have succeeded in lowering the annealing temperature to $\leq$100 °C with excellent bulk like resistivity for Ag (nanoparticulate) ink based films.

Conclusion

In this paper, we have studied an efficient method for the preparation of silver nanoparticles ink for its application in printed electronics. The characterisation of silver nano-inks confirmed average particle size of Ag was in the range of 5-15 nm. The silver ink formulations without TEA are stable for couple of weeks while with TEA are stable for a month as TEA act as the extra protecting agent and also a reducing agent. The resulting silver NPs showed high crystallinity and the viscosity of these inks can be altered by varying the silver concentration in the ink. Thin nanoparticulate films of Ag were successfully deposited on the glass substrates through spin coating method using the as-prepared Ag nano-inks. Additionally, these inks can be written on both rigid and flexible substrates like paper and glass through fountain pens. We have also succeeded in lowering the annealing temperature to $\leq$100 °C with excellent bulk like resistivity for Ag (nanoparticulate) ink based films. Thus, the ink formulated from the present method can be ideally used for the fabrication of flexible printable electronics as these inks are highly conductive in nature at low annealing temperatures. These inks can be used to fabricate electronic devices on low cost substrates such as paper, plastic and glass substrates due to their suitable wettability.

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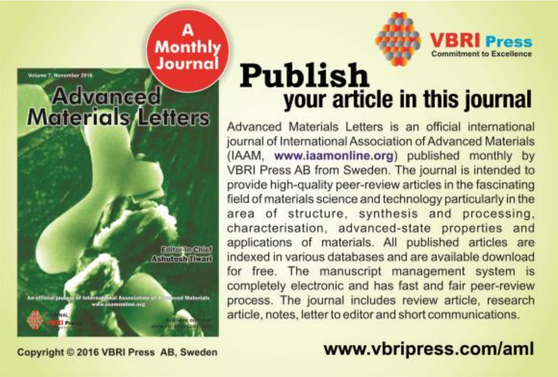

Supporting Information

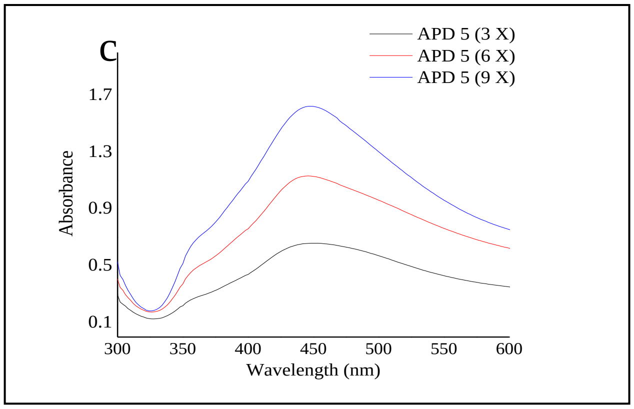

Fig. S1. UV-visible spectra of APD 5 spin coated film with variation in thickness; 3 X represents three spin cycles, 6 X represents six spin cycles and 9 X represents nine spin cycles. It was expected that with each cycle the thickness of film will be increased along with the concentration of Ag in the film.

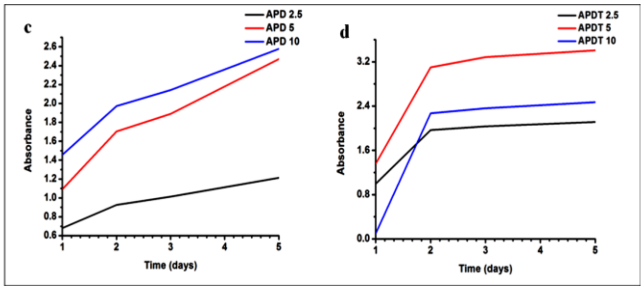

Fig. S2. Absorbance - time graphs for Ag nano-ink samples c) without TEA and d) with TEA.

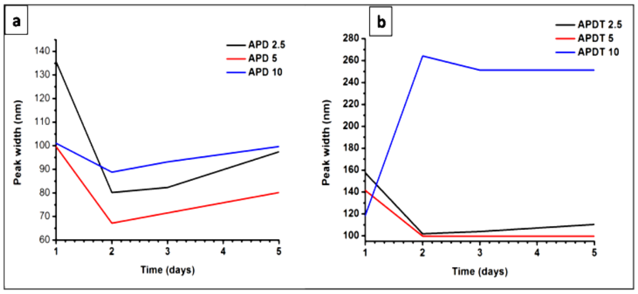

Fig. S3. Plot for peak width vs. time (at FWHM) for the Ag nano-inks samples (a) without and (b) with TEA.

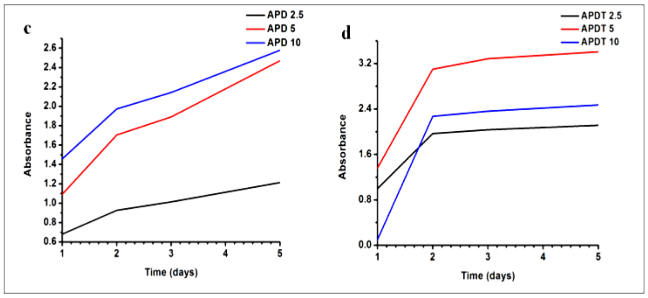

Fig. S4. FT-IR spectra silver NPs coated with PVP (a) without TEA (b) with TEA. The presence of TEA as well as PVP in the dried sample was confirmed from IR spectra.