Pak. J. Engg. & Appl. Sci. Vol. 21 July, 2017 (p. 1–11)

Insitu Photosynthesis and Stabilization of Copper Nanoparticles

Rabia Nazar[*1]

1. *Polymer and Process department, University of engineering and technology Lahore, Pakistan*

***** **Correponding Author:** E-mail: rabianazar1@gmail.com , rabia.nazar@uet.edu.pk

Abstract

A facile method to prepare copper nanoparticles by UV-irradiating a sample containing a radical photoinitiator and a copper-amine coordination compound of copper chloride is reported. In the absence of any inert gas protection, the copper-amine coordination compound was reduced directly to copper particles by UV-irradiation. Poly vinylpyrrolidone (PVP) and pyrrole both were used as capping agents. Sodium ascorbate plays a role as an antioxidant for colloidal copper, due to its ability to scavenge free radicals and reactive oxygen molecules, and therefore helps in stabilizing the copper nanoparticles for few minutes in open air. Dynamic light scattering (DLS) results showed that copper nanoparticles formed in the presence of (PVP) were narrower, along with the narrowing of size distribution as compared to those in the presence of other stabilizers. Evaluation of the irradiation process was conducted by UV–vis spectroscopy using model systems for copper particles obtained in a solvent and also when the solvent was substituted by acrylic monomer. Presence of stabilizers tends to increase the resistance of copper nanoparticles formed in acrylic monomer against oxidation in an open atmosphere.

Key Words: UV-Irradiation, Copper Nanoparticles, Sodium Ascorbate, No inert gas protection, PVP

1. Introduction

Copper nanoparticles synthesis has drawn more attention as compared to other available noble metal nanoparticles. It is an inexpensive metal[1] but like other noble metals, it possess electronic[2], catalytic[3], antimicrobial[4] and optical properties[5]. Apart from its useful properties: the main challenge to use them in practical applications lies in their inherent tendency to oxidize when exposed to air[6-7], and aggregation of nanoparticles which may give rise to unwanted properties of the particles[8]. The formation of oxides on the surface of the nanoparticles gives rise to a major problem i.e. the reduction in electrical conductivity and therefore restricts their use in conductive printing applications[9-10].

There are different approaches to protect the noble metal particles by hindering the oxygen penetration to the surface of these particles, and to prevent agglomeration and coagulation processes. A protective thin layer of silica can be used to avoid the interaction of oxygen molecules with the nanoparticle surface and to prevent the nanoparticles from aggregating and contacting each other. A lot of work has been done to protect the gold and silver metal particles by coating their surfaces with silica layer[11-12]. However, Kobayashi *et al.*[13] prepared Cu nanoparticles in aqueous solution and reported their stability for atleast one month with the help of silica coating. A more commonly employed technique to stabilize the metal particles is with the help of surfactants, they may avoid the aggregation of the particles by binding themselves to their surface. Size and shape of the Cu NPs may be controlled by using different surfactants like oleic acid[7], alkanthiols[14], sodium dodecyl sulphate[15], CTAB[6] etc.

Another promising approach to stabilize the Cu NPs is to use polymers as capping agents. Among these polymers, poly vinylpyrrolidone (PVP) has been widely used as a capping agent for the stabilization of nanoparticles[8,16-17]. Jeong *et al.*[18] demonstrated the effect of the weight of PVP on the size of the Cu NPs, and thereby confirmed that there is a direct relation between the mol. wt. of PVP and the particle size of NPs, which in turn determines the electrical conductivity of the film formed. Kobayashi *et al.*[1] employed a conductive polymer i.e. polypyrrole to chemically stabilize copper nanoparticles, and hence those particles coated with polypyrrole proved to be chemically stable even in the air.

There are different techniques reported since the 1990s to synthesize copper nanoparticles; including chemical reduction in solution by using hydrazine[5],sodium citrate[19],polyol[20] and sodium borohydride[21]. Apart from this, different other techniques like metal vaporization[22], electrochemical deposition[23], photochemical reduction[16,24-25] have been in use . The simplest and more economical among all the above mentioned techniques is the use of UV-irradiation to reduce metal salts in the presence of any suitable photoinitiator. Only a limited data is available on this technique.

Kapoor et al.[16] reported for the first time the photochemical fabrication of copper nanoparticles by using PVP as a capping agent.

In this study, we report the formation of copper nanoparticles by using benzophenone as a photoinitiator in ethanol by UV-irradiation. In order to stabilize the copper particles, surfactants like Poly vinylpyrrolidone (PVP) and pyrrole were used as capping agents, and the effect of these stabilizers on the size and size distribution of obtained copper particles was observed. It was aimed to synthesize and store the Cu particles in the absence of inert gas.

2. Materials and Methods

Poly ethylene glycol di acrylate (PEGDA) having an average molecular weight of 700 was purchased from Aldrich. Copper chloride dihydrate ($CuCl_2.2H_2O$) was used as copper precursor, Diethanol amine (DEA), ethanol and Pyrrole (C_4H_5N, 98%) were purchased from Aldrich Sigma. Benzophenone (BP) and Darocur 1173 were supplied by BASF. Poly-vinyl Pyrrolidone (PVP) (Mw=40,000 g/mol) was purchased from fluka. All these chemicals were used as received without any further purification.

2.1 Sample Preparation

In order to prepare ethanol solution of copper salt, 0.01M $CuCl_2$ was dissolved in 10ml ethanol in the presence of 0.02M photoinitiator(benzophenone) and mixed them for 5 minutes in the ultrasonication bath. To prepare copper amine coordination complex 0.04M diethanol amine was added in the above mentioned solution. This solution will be called as copper-amine coordination complex in the rest of the text. The resultant solution was diluted as per requirement and deaerated in UV cuvette by bubbling nitrogen for ten minutes and then sealed that cuvette to inhibit the entrance of oxygen. The solution was irradiated for different intervals of time (1min,3min,5min,10min) under UV light at a radiation intensity of 45mW/cm^2.

Inorder to stabilize the particles, two capping agents (i.e. PVP and pyrrole) were selected. PVP was added 0.5(w/v)% in the copper-amine coordination complex and mixed with the help of ultraturax for 5 minutes. Also, pyrrole 0.2(w/v)% was added in the copper-amine coordination complex. Prior to irradiation, both the solutions were diluted as per requirement and deaerated in UV cuvette by bubbling nitrogen for ten minutes and then sealed that cuvette to inhibit the entrance of oxygen. Both these solutions were irradiated for different intervals of time (1min,3min,5min,10min) under UV light at a radiation intensity of 45mW/cm^2.

In order to check the effect of an anti-oxidant i.e. Sodium ascorbate: copper-amine coordination complex was prepared by dissolving 0.01M $CuCl_2$ in 10 ml H_2O and after this 0.02M photoinitiator(Darocur 1173) and 0.04M diethanol amine (DEA) was added. To this, $CuCl_2$-amine coordination complex 0.02M sodium ascorbate was added followed by adding 0.5(w/v)% PVP and mixed them in an ultrasonication bath for 3-5mins. The obtained solution was diluted to obtain the UV-vis spectra in a desired range. We do not use rubber capped air tight cuvettes which were used in all the formulations made till now. The solutions were irradiated for different times under in a nitrogen atmosphere at an intensity of 45mW.cm^{-2}.

In order to characterize the polymeric films containing copper salt: formulations were prepared by adding different concentrations of copper chloride i.e.1wt% and 0.5wt% while keeping the diethanol amine constant at 2wt%, and PI (benzophenone) was added at a higher concentration i.e. 5wt% in order to guarantee the curing.

0.2(w/w)%Pyrrole was added in the polymeric formulation(as mentioned above), and mixed with the help of ultraturax for 5 minutes.

0.5(w/w)%PVP was added in the polymeric formulation(as mentioned above), and mixed with the help of ultraturax for 5 minutes.

The films of these three formulations of 100 µm were subjected to UV-irradiation under nitrogen at an intensity of 45mW.cm^{-2} for the necessary time to get cured.

2.2 Characterization

UV-vis spectra of the samples was obtained by using double beam UNICAM UV2 (ATI Unicam, Cambridge, UK) spectrophotometer with variable lit width in a spectral range of 190–1100nm. The particles size distribution was measured by using DLS Zetasizer Nanoseries ZS90 instrument purchased from Malvern Instrument (UK). This can measure the size of particles in the range from 2 nm to 3 µm. Before measurement, all samples were diluted 1:100 (to optimize the measurement) in ethanol. Each measurement was repeated three times. The conversion of the photopolymerization reaction was monitored by Fourier Transform-Infra Red (FT-IR) analysis. FT-IR scans were performed using a FT-IR spectrometer(Thermo-Nicolet 5700 instrument) Conversion was calculated monitoring the decrease of the area of the absorption band of the reactive functionality (acrylate C=C peak at 1632 cm^{-1}) with time. The area was normalized by a constant signal in the spectra (C=O peak at 1725 cm^{-1}).

3. Results

3.1 Optical Characterization of $CuCl_2$-Ethanol Solution

The $CuCl_2$-ethanol solution was UV-irradiated for different irradiation times (1min, 3min, 5min, 10min) at a radiation intensity of $45mW.cm^{-2}$. A clear change in color with the increase in irradiation time is manifested. The color of the $CuCl_2$ ethanol solution changes from green to transparent after 3 minutes of UV-irradiation, the solution turns light black after 5 minutes of irradiation and after the maximum irradiation time i.e. 10 minutes black precipitates formed on the wall of the cuvette (shown in Figure 1). The results of time dependent UV-vis spectra are (shown in Figure 2) where clear visible changes in the spectra can be observed with the change in time of irradiation. Prior to irradiation, the absorption band of $CuCl_2$-ethanol solution appears to be in the range of 650-900 nm. According to literature[26], the visible band is attributed to the UV-vis absorption spectra of $CuCl_2$.

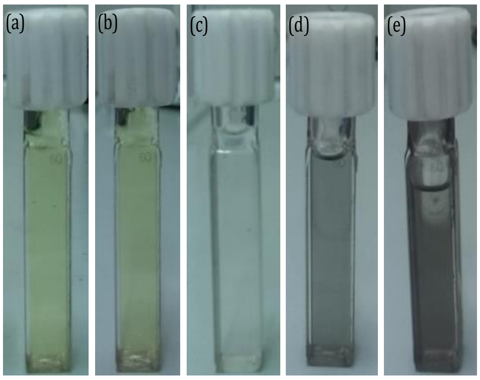

Figure 1: Color change observation of $CuCl_2$-ethanol solution a) before UV, (b) 1mins, (c)3mins, (d)5mins, (e)after 10mins of UV-irradiation.

While the band below 400 nm corresponds to the absorption of photoinitiator. The UV-vis spectra after 1 min of UV-irradiation is identical to the one before irradiation, accordingly there was no color change recorded after 1 min of irradiation. However, with the further increase in the irradiation time to 3 mins, the $CuCl_2$-ethanol solution became nearly colorless (shown in Figure 1) subsequently the absorption peak in the range of 650-900 nm completely disappears, which shows the conversion of Cu^{2+} state to Cu^{+}. After 5 minutes of UV-irradiation an absorption band appears in the range 560-630 nm, centered at around 600 nm. The absorption increases with the further increase in irradiation time to 10 mins and the absorption band became more wide ranging from 560-720 nm.

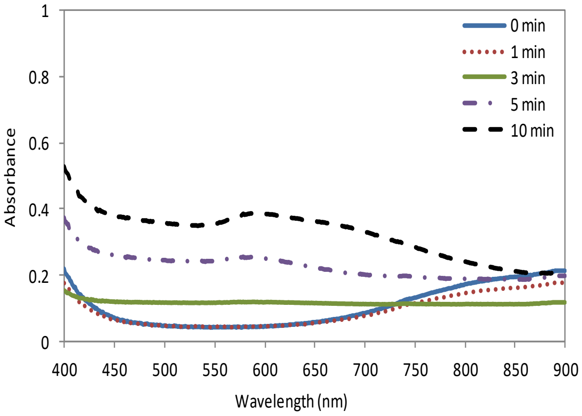

Figure 2: UV-vis spectra of $CuCl_2$ ethanol solution under different irradiation times

3.1.1 Optical characterization of $CuCl_2$-Amine Coordination Complex

The change in color upon adding diethanol amine to $CuCl_2$-ethanol solution demonstrates the formation of a complex between copper chloride and diethanol amine (DEA) shown in Figure 3. UV-vis spectra analysis shown in Figure 4 was carried out to confirm the formation of $CuCl_2$-amine coordination complex and to investigate the effect of different intervals of UV-irradiation time.

The UV-vis absorption spectra of $CuCl_2$-amine complex prior to irradiation show a net absorption peak at around 700 nm. According to the literature,[255] this peak is assigned to the copper-diethanol amine coordination complex. The change in color and the absorption spectra appeared to be quite different than those observed in the photoreduction of the $CuCl_2$-ethanol solution *(shown in Figure 1 and 2)*. The absorption peak at 700nm completely disappeared after 1 min UV-irradiation, since the color of the solution turns from blue to completely colorless. This phenomenon shows the photoreduction of Cu^{2+} to Cu^{+} state. With the further increase in irradiation time i.e. to 3 and 5 mins, the solution changes its color from transparent to red and the absorption spectra shows an absorption peak at around 590 nm which is due to the formation of Cu NPs, along with an additional absorption at around 750-800nm, which is the identification of presence of CuO on the surface of the obtained particles. However, with the maximum UV-irradiation time i.e. 10 mins, the solution turned into deep red color(Figure 3-c), a very sharp absorption peak appears at around 590nm: which confirms the formation of copper particles[27-28]. The absorbance peak as shown in Figure 4 obtained after 10 mins of irradiation corresponds to the formation of Cu^0 from Cu^{+} state; diethanol amine makes it possible as it serves to solubilize the Cu^{+} ion in an ethanol solution, and avoids the precipitation of cuprous compound, as observed for the systems which do not contain the complexing agent.

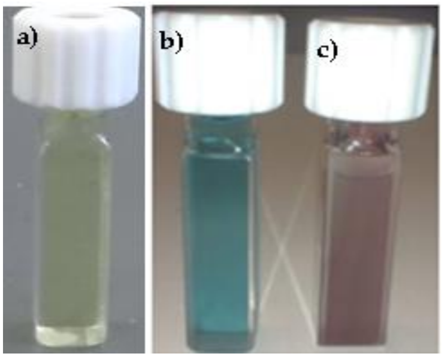

Figure 3: Color change observation: a) $CuCl_2$-ethanol solution, b) $CuCl_2$-amine co-ordination complex, c)$CuCl_2$-amine coordination complex after 10 mins UV-irradiation.

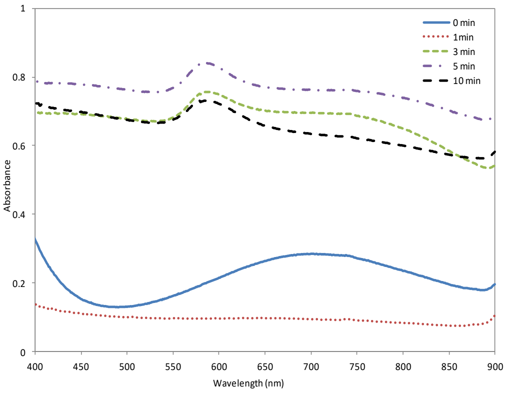

Figure 4: UV-visible spectra of copper chloride-amine coordination complex under UV-irradiation at different times

Nevertheless, the intensity of absorption decreases after 10mins of UV-irradiation. The decrease in absorbance observed after the maximum UV-irradiation time is due to the aggregation and precipitation of the particles. A film of copper colloids was also clearly observed on the wall of the quartz cuvette.

Based on the UV-vis results, shown above: it is clear that diethanol amine helps in photoreducing the copper salt to copper particles.

3.2 Stabilization of Cu NPs in Solution

We report the stabilization of copper nanoparticles against oxidation and aggregation by photoreducing $CuCl_2$-amine coordination complex in the presence of two capping agents i.e. pyrrole and PVP and an anti-oxidant i.e. sodium ascorbate

3.2.1 Effect of Pyrrole as a Stabilizer on Cu-NPs

UV-vis spectra of $CuCl_2$-amine coordination complex in the presence of 0.2(w/v)% pyrrole was recorded after different intervals of irradiation time (1min, 3min, 5min, 10min) is shown in Figure 5. The change in color of $CuCl_2$-amine coordination complex in the presence of pyrrole after different intervals of time is noticed to be the same as it was observed for the $CuCl_2$-amine coordination complex without the presence of pyrrole (*Figure 3*). The UV-vis spectra after irradiating this solution for 5 mins, a characteristic peak appears at around 580nm which confirmed the formation of Cu nanoparticles[1].

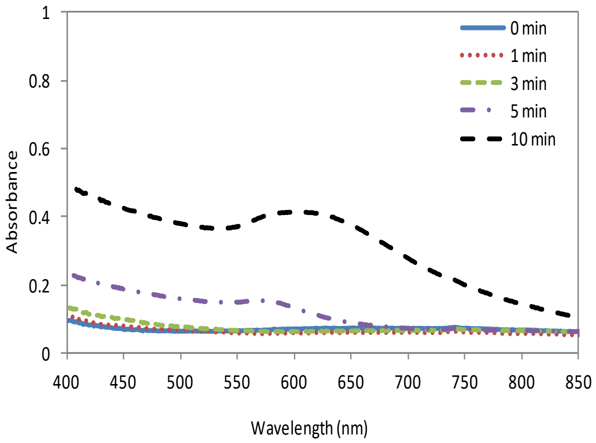

Figure 5: UV-visible spectra of $CuCl_2$-amine coordination complex in the presence of 0.2(w/v)% pyrrole under UV-irradiation at different times of irradiation.

Absorption increases with the further increase in irradiation time to 10mins, and the absorption peak at 580 nm shifts to a larger wavelength (580nm to 610nm). As per literature[29], this shift in the absorption wavelength shows an increment in size of the prepared copper nanoparticles.

3.2.2 Effect of PVP as a Stabilizer on Cu-NPs

The absorbance spectra of $CuCl_2$-amine coordination complex in the presence of 0.5(w/v)%PVP is shown in Figure 6. A deep red colored solution was observed after irradiating $CuCl_2$-amine coordination complex in the presence of 0.5(w/v)% PVP for 10 mins. After 5mins UV-irradiation a characteristic plasmon band appears at about 575nm which is the same absorbance band observed for copper nanoparticles in literature[30]. Absorbance increases with the increase in irradiation time to 10 mins, a very sharp peak is observed after the maximum irradiation time and no shift change is observed in this case.The stable position of absorbance peak observed in Figure 6 with the increase in irradiation time indicates that there is no aggregation of the particles.

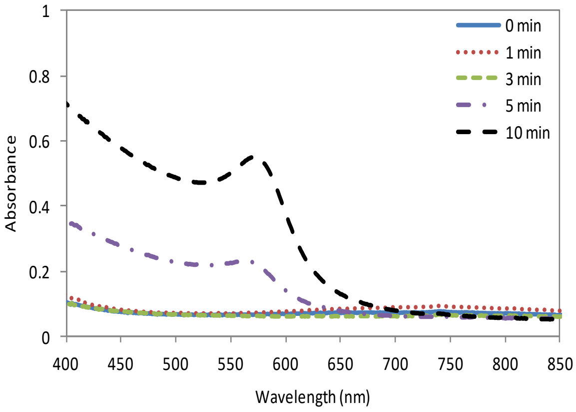

Figure 6: UV-visible spectra of $CuCl_2$-amine coordination complex in the presence of 0.5 (w/v)% PVP under UV-irradiation at different times of irradiation

3.2.3 Effect of Sodium Ascorbate as a Stabilizer on Cu-NPs

The UV-vis absorption spectra of copper nanoparticles in the presence of sodium ascorbate before and after irradiation are shown in Figure 8. As is clear from the spectra, a sharp peak at around 575 nm is observed after maximum irradiation time which confirms the formation of Cu-NPs. As seen in Figure 7, a color change is evident of the irradiated complex with the increase in irradiation time starting from 1min to 10 mins.

It is to be noticed that the solutions were not stored in air-tight cuvettes. As is clear from the spectra, a sharp peak at around 575 nm is observed after maximum irradiation time. which confirms the formation of Cu-NPs. Hence, the Cu-amine coordination complex in the presence of Sodium ascorbate and PVP when UV-irradiated for 10 mins become oxidative stabilized in an open air atmosphere sustained for almost 20 mins. And the spectra measured after 20 mins of opening the container, shows a peak at around 576 nm (no shift in wavelength) with the decreased intensity as measured earlier for the same solution before coming into contact with air.

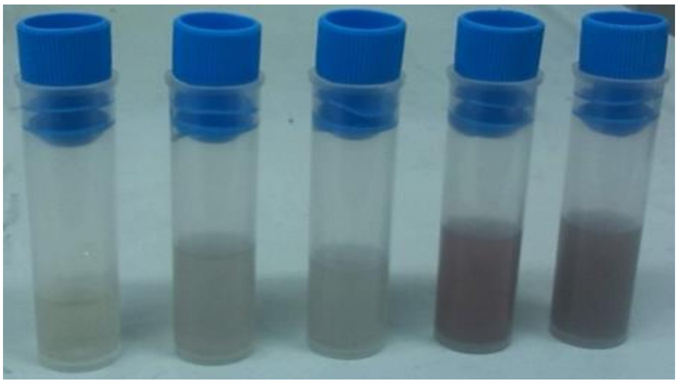

Figure 7 Color change observed after different times of UV-irradiation

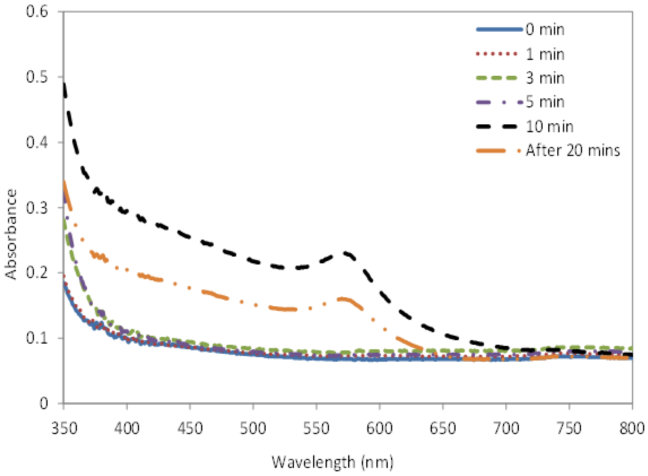

Figure 8: UV-vis spectra of $CuCl_2$-diethanol amine coordination complex in the presence of 0.02M Sodium ascorbate and 0.5(w/v)% PVP

3.3 DLS Analysis

Particle size distribution was measured with the help of DLS technique. DLS analysis was performed on the copper-amine coordination complex, and also on the copper-amine coordination complex stabilized with pyrrole, PVP and sodium ascorbate to check the effect on the size distribution of the particles obtained after subjected to UV-irradiation for 10 mins.

It can be observed by looking at Figure 9 that when there is no stabilizer added: particle size has a broad distribution ranging from almost 340 to 800 nm, and the mean particle size is calculated to be 516nm. Also in the presence of pyrrole, there is no profound change observed in the particle size distribution, it ranges from almost 255 to 800 nm. The mean particle size in this case is found to be 435 nm. However, one can observe a drastic change in the particles size distribution of the particles which ranges from almost 70 to 200 nm with the addition of PVP. And the mean particles size of the Cu particles obtained is about 120 nm. And the particle size distribution of the Cu-amine complex in the presence of sodium ascorbate and PVP ranges from 70-530 nm, having mean particle size 230nm.

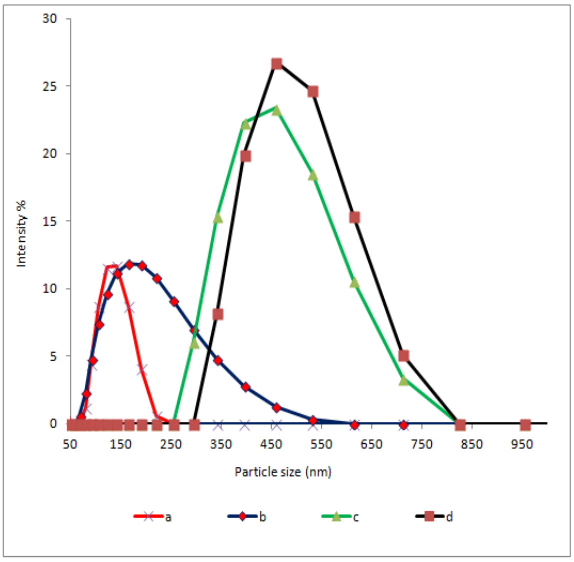

Figure 9: Particle size distribution from DLS (a) Cu-amine solution in presence of 0.5(w/v)%PVP. (b) Cu-amine solution in presence of 0.5(w/v)%PVP and 0.02M Na-ascorbate (c)Cu-amine coordination complex in presence of 0.2wt%Py. (d) Cu-amine coordination complex

It can be easily observed from the Figure above that copper nanoparticles photosynthesized in the presence of PVP shows the narrowest particle size and size distribution.

4. Photopolymerization of Acrylic Oligomers in the Presence of $CuCl_2$ and Diethanol Amine

After studying the irradiation of the copper salt in the solution form, the next step was the investigation of the contemporary acrylic resin crosslinking reaction and in-situ formation of copper metal particles. The films of 100 µ thickness (formed as prescribed in section 2.1) were subjected to UV-irradiation under nitrogen at an intensity of 45mW.cm^{-2} respectively; the resulting UV-crosslinked films obtained were red in color.

FT-IR analyses conducted to monitor the acrylic double bond conversion during curing showed that after 30 s of UV-irradiation one reaches the complete conversion of the PEGDA acrylic double bond, with a complete disappearance of the C=C band centered at 1620 cm^{-1} as reported in Fig 10. This is in agreement with previous investigations[31] and attributable to the high reactivity of PEGDA acrylic resin[32]. When copper salt, pyrrole and PVP were added to the monomer, no significant detrimental effect was evidenced on the final acrylic double bond conversion.

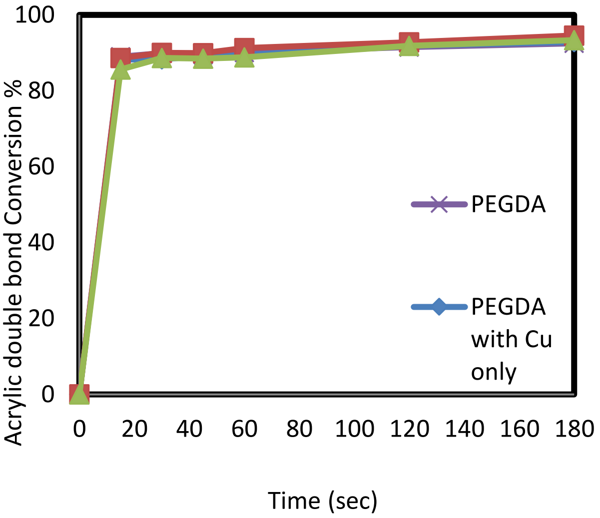

Figure 10: PEGDA double bond conversion as a function of irradiation time

Irradiation was continued for 10 minutes to assure photoreduction of the silver salt and the UV-crosslinked films were subjected to UV-Vis spectroscopy analyses.

The crosslinked films in the presence of higher amount of $CuCl_2$ have deep red color as compared to the one having lesser percentage 0.5% $CuCl_2$ as shown in Figure 11.

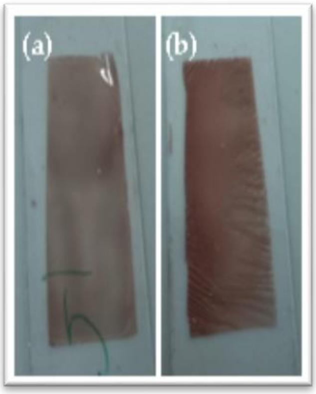

Figure 11: Color change observed in a freshly prepared film containing a) 0.5wt%$CuCl_2$, b) 1wt%$CuCl_2$

The absorption spectra of UV-cross linked films in the presence of 1 wt% and 0.5 wt% $CuCl_2$ measured immediately after their preparation is shown in Figure 12. A clear and strong absorption band centered at around 574nm was observed in the presence of 1 wt% $CuCl_2$, and absorption spectra of very low intensity and at about 576nm is observed for 0.5wt% $CuCl_2$ respectively. It is clear from the Figure 12, the intensity of the surface plasmon absorbance increases with the increase in the concentration of copper salt in the photocurable formulation. The strong absorption peak at 574 nm can be attributed to the formation of copper particles, as previously recorded for the UV-irradiation of ethanol solution containing the copper precursor.

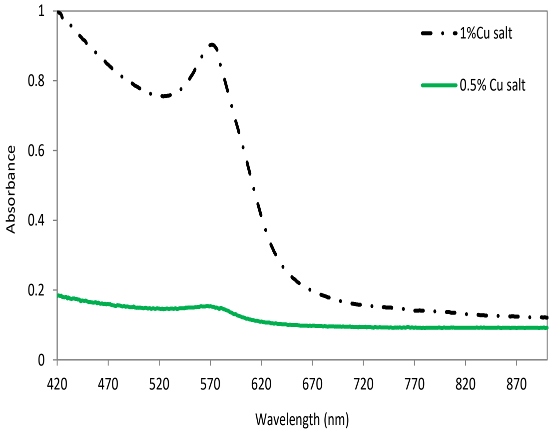

Figure 12: UV-Vis absorption spectra of the crosslinked film freshly prepared containing 0.5wt% and 1wt%$CuCl_2$, 5wt%PI, 2wt%DEA

The UV-cross linked polymeric films were exposed to an ambient atmosphere and the red color of the film starts tarnishing as soon as exposed to air. The change in color observed in the films after two hours is shown in Figure 13, where we can observe that the film containing 0.5wt% $CuCl_2$ becomes almost transparent and the film containing 1wt% $CuCl_2$ still has some redness on its one side. However, the UV-vis spectra of the same films after being exposed for 2 hours to the open atmosphere is shown in Figure 14.

A decrease in the intensity of the absorption spectra is quite obvious. A shift towards higher wavelength for the peak containing 0.5wt% Cu salt content leads to the fact that the copper particles starts to aggregate and starts oxidizing back to copper oxide state when added to a very low concentration. Although the intensity of the absorbance spectra decreases for the peak containing 1wt% of $CuCl_2$ salt concentration, but no such shift in wavelength is observed.

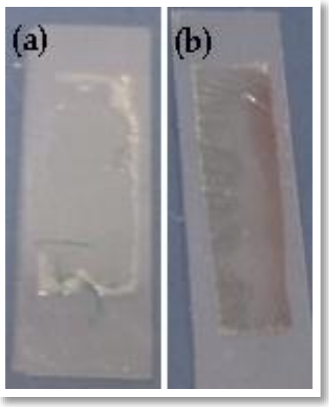

Figure 13: Color change observed in a film after 2 hr containing a) 1wt%$CuCl_2$, b) 0.5wt%$CuCl_2$

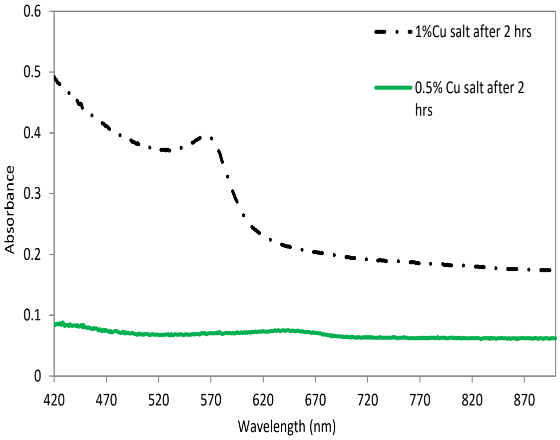

Figure 14: UV-Vis absorption spectra of the crosslinked film containing 1%$CuCl_2$ and 0.5wt% $CuCl_2$, 5%PI, 2%DEA after 2 hrs in an open atmosphere

4.1 Stabilization of UV-cross Linked Films against Oxidation

In this work, 0.5(w/w)% PVP and 0.2(w/w)%pyrrole were used as the polymeric capping agents and added to the polymeric formulation containing 1wt% $CuCl_2$, 5wt% benzophenone and 2wt% diethanol amine. We investigated the effect of the presence of pyrrole and PVP on the photochemical formation of copper particles, their stability against oxidation with the help of UV-vis spectra

4.1.1 Effect of Pyrrole

The crosslinked film containing 0.2(w/w)% pyrrole obtained after UV-irradiation was red in color as shown in Figure 15. The deep red color of the film can be attributed to the formation of copper particles, as previously observed for the UV-irradiation $CuCl_2$-amine coordination complex.

However, for the confirmation of the formation of copper nanoparticles, UV-crosslinked films were subjected to the UV-vis spectra. Spectra in Figure 16 show a single absorption peak at around 575 nm.

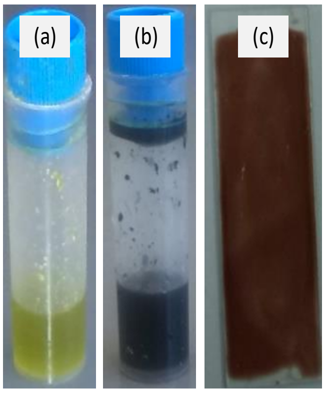

Figure 15: Change in color observed (a) $CuCl_2$-amine coordination complex in PEGDA, (b) in the presence of 0.2%(w/w) pyrrole, (c) Freshly prepared crosslinked film in the presence of 0.2%(w/w) pyrrole

To monitor the stability of copper particles in air, we measured the absorption of the cross-linked film after regular intervals of time. The UV-vis spectra of freshly prepared film and after exposing it to ambient atmosphere for different intervals of time are shown in Figure16. The decrease in intensity can be easily observed with the increase in time of exposure to the open atmosphere. A red shift in wavelength was observed from 575 nm for the freshly prepared film to 578 nm after exposure in air for 1 hr. After being exposed to air for 2 and 3 hrs absorption spectra was shifted towards 579 nm. Usually with the increase in particle size, absorption peak shifts towards higher wavelength.

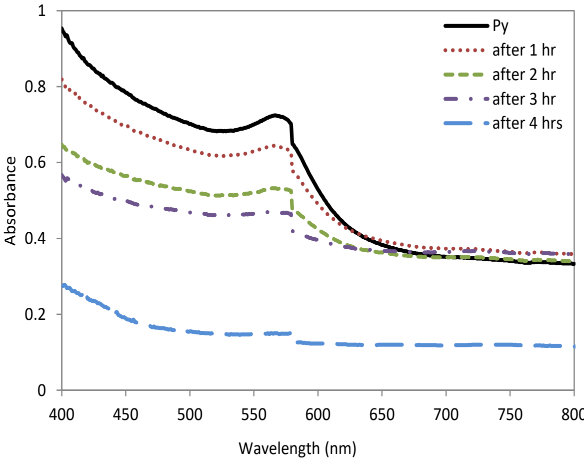

Figure 16: UV-vis spectra of the cross linked films containing 1wt%$CuCl_2$, 5wt%PI, 2wt%DEA in the presence of 0.2(w/w)%pyrrole after regular intervals of time

4.1.2 Effect of PVP

Investigation of the contemporary acrylic resin crosslinking reaction and in-situ preparation of copper particles was carried out in the presence of PVP as a polymer capping agent The films of 100 µ were subjected to UV irradiation under nitrogen at an intensity of 45mW.cm^{-2}. A deep red colored film was obtained after irradiating the sample for 10mins (shown in Figure 17). In a similar way, stability of copper particles obtained in the presence of 0.5(w/w)% PVP was measured after regular intervals of time. The UV-vis spectra in Figure 18 clearly show a strong absorption band at around 575 nm for the freshly prepared film, which confirms the formation of copper particles. However, the intensity of absorption band decreases with the increase in time of contact with air. The UV-cross linked film containing PVP as a stabilizer show a stable position of absorbance peak at around 575 nm even after 2 hrs of exposure. However, a red shift to 576 nm and 578 nm was observed after exposing for 3 hrs and 4 hrs respectively.

After being exposed to air for 6 hrs no absorption spectra was recorded. This straight line observed in all the UV-spectrum after few hours of exposure to air could be due to the oxidation of copper particles to copper oxide (I) nanoparticles since the similar optical behavior of copper oxide (I) nanoparticles have been reported by Halin et al.[33]

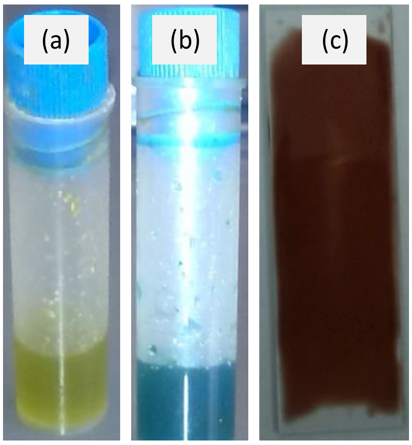

Figure 17: Change in color observed (a) $CuCl_2$-amine coordination complex in PEGDA, (b) in the presence of 0.5%(w/w) PVP, (c) Crosslinked film in the presence of 0.5%(w/w) PVP

The results show that copper nanoparticles can be successfully prepared and stabilized against oxidation by photoreducing copper precursor in an acrylic resin in the presence of stabilizers by one step photochemical method. Although Cu particles obtained in the presence of 0.2wt%pyrrole and 0.5wt% PVP persisted against oxidation, but for only few hours in an open air atmosphere.

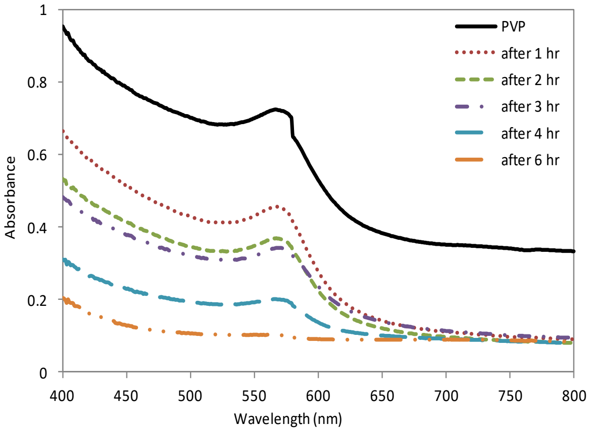

Figure 18: UV-vis spectra of the cross linked films containing 1%$CuCl_2$, 5%PI, 2%DEA in the presence of 0.5% PVP after regular intervals of time.

Conclusions

The experimental results show that copper nanoparticles can be formed by photoreducing $CuCl_2$ salt in the presence of a radical photoinitiator and using diethanol amine as a ligand. The experimental results show that copper nanoparticles are smaller and more uniform when PVP is added to the solution. It can be also effectively employed in the preparation of acrylic nanocomposites by simultaneous photoreduction of copper chloride to Cu nanoparticles and photocrosslinking of a difuctional acrylate. Sodium ascorbate helps in stabilization of the prepared Cu NPs in solution form against oxidation. In the future work, the idea is to use Sodium ascorbate to stabilize the Cu particles embedded in polymeric films in order to use them in practical applications.

Acknowledgments

The author would like to acknowledge the DISAT department of politecnico di torino to provide all the support to carry out this research. And also is grateful to the HEC (Higher Education Commission) of Pakistan for financing the PhD scholarship of the author.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

[1] Kobayashi, Y., Ishida, S., Ihara, K., Yasuda, Y., Morita, T., & Yamada, S. (2009). Synthesis of metallic copper nanoparticles coated with polypyrrole. Colloid and Polymer Science, 287(7), 877-880.

[2] Kim, H. S., Dhage, S. R., Shim, D. E., & Hahn, H. T. (2009). Intense pulsed light sintering of copper nanoink for printed electronics. Applied Physics A: Materials Science & Processing, 97(4), 791-798.

[3] Huang, Z., Cui, F., Kang, H., Chen, J., Zhang, X., & Xia, C. (2008). Highly dispersed silica-supported copper nanoparticles prepared by precipitation− gel method: a simple but efficient and stable catalyst for glycerol hydrogenolysis. Chemistry of Materials, 20(15), 5090-5099

[4] Cioffi, N., Torsi, L., Ditaranto, N., Tantillo, G., Ghibelli, L., Sabbatini, L., & Traversa, E. (2005). Copper nanoparticle/polymer composites with antifungal and bacteriostat-

ic properties. Chemistry of Materials, 17(21), 5255-5262.

[5] Huang, H. H., Yan, F. Q., Kek, Y. M., Chew, C. H., Xu, G. Q., Ji, W., ... & Tang, S. H. (1997). Synthesis, characterization, and nonlinear optical properties of copper nanoparticles. Langmuir, 13(2), 172-175.

[6] Wu, S. H., & Chen, D. H. (2004). Synthesis of high-concentration Cu nanoparticles in aqueous CTAB solutions. Journal of colloid and interface science, 273(1), 165-169.

[7] Mott, D., Galkowski, J., Wang, L., Luo, J., & Zhong, C. J. (2007). Synthesis of size-controlled and shaped copper nanoparticles. Langmuir, 23(10), 5740-5745.

[8] Giuffrida, S., Costanzo, L. L., Ventimiglia, G., & Bongiorno, C. (2008). Photochemical synthesis of copper nanoparticles incorporated in poly (vinyl pyrrolidone). Journal of Nanoparticle Research, 10(7), 1183-1192.

[9] Magdassi, S., Grouchko, M., & Kamyshny, A. (2010). Copper nanoparticles for printed electronics: routes towards achieving oxidation stability. Materials, 3(9), 4626-4638.

[10] Tauran, Y., Brioude, A., Coleman, A. W., Rhimi, M., & Kim, B. (2013). Molecular recognition by gold, silver and copper nanoparticles. World journal of biological chemistry, 4(3), 35.

[11] Liz-Marzán, L. M., Giersig, M., & Mulvaney, P. (1996). Synthesis of nanosized gold− silica core− shell particles. Langmuir, 12(18), 4329-4335.

[12] Kobayashi, Y., Correa-Duarte, M. A., & Liz-Marzán, L. M. (2001). Sol− gel processing of silica-coated gold nanoparticles. Langmuir, 17(20), 6375-6379.

[13] Kobayashi, Y., & Sakuraba, T. (2008). Silica-coating of metallic copper nanoparticles in aqueous solution. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 317(1), 756-759.

[14] Ang, T. P., Wee, T. S. A., & Chin, W. S. (2004). Three-dimensional self-assembled monolayer (3D SAM) of n-alkanethiols on copper nanoclusters. The Journal of Physical Chemistry B, 108(30), 11001-11010.

[15] Lisiecki, I., Billoudet, F., & Pileni, M. P. (1996). Control of the shape and the size of copper metallic particles. The Journal of Physical Chemistry, 100(10), 4160-4166.

[16] Kapoor, S., & Mukherjee, T. (2003). Photochemical formation of copper nanoparticles in poly (N-vinylpyrrolidone). Chemical physics letters, 370(1), 83-87.

[17] Xiong, Y., Washio, I., Chen, J., Cai, H., Li, Z. Y., & Xia, Y. (2006). Poly (vinyl pyrrolidone): a dual functional reductant and stabilizer for the facile synthesis of noble metal nanoplates in aqueous solutions. Langmuir, 22(20), 8563-8570.

[18] Jeong, S., Woo, K., Kim, D., Lim, S., Kim, J. S., Shin, H., ... & Moon, J. (2008). Controlling the thickness of the surface oxide layer on Cu nanoparticles for the fabrication of conductive structures by ink-jet printing. Advanced Functional Materials, 18(5), 679-686.

[19] Brege, J. J., Hamilton, C. E., Crouse, C. A., & Barron, A. R. (2009). Ultrasmall copper nanoparticles from a hydrophobically immobilized surfactant template. Nano letters, 9(6), 2239-2242.

[20] Park, B. K., Jeong, S., Kim, D., Moon, J., Lim, S., & Kim, J. S. (2007). Synthesis and size control of monodisperse copper nanoparticles by polyol method. Journal of colloid and interface science, 311(2), 417-424.

[21] Qi, L., Ma, J., & Shen, J. (1997). Synthesis of copper nanoparticles in nonionic water-in-oil microemulsions. Journal of colloid and interface science, 186(2), 498-500.

[22] Vitulli, G., Bernini, M., Bertozzi, S., Pitzalis, E., Salvadori, P., Coluccia, S., & Martra, G. (2002). Nanoscale copper particles derived from solvated Cu atoms in the activation of molecular oxygen. Chemistry of materials, 14(3), 1183-1186.

[23] Raja, M. (2008). Production of copper nanoparticles by electrochemical process. Powder Metallurgy and Metal Ceramics. 47(7), 402–405

[24] Itakura, T., Torigoe, K., & Esumi, K. (1995). Preparation and characterization of ultrafine metal particles in ethanol by UV irradiation using a photoinitiator. Langmuir, 11(10), 4129-4134.

[25] Condorelli, G. G., Costanzo, L. L., Fragalà, I. L., Giuffrida, S., & Ventimiglia, G. (2003). A single photochemical route for the formation of both copper nanoparticles and patterned nanostructured films. Journal of Materials Chemistry, 13(10), 2409-2411.

[26] Zhu, X., Wang, B., Shi, F., & Nie, J. (2012). Direct, rapid, facile photochemical method for preparing copper nanoparticles and copper patterns. Langmuir, 28(40), 14461-14469.

[27] Karadag, A., Yilmaz, V. T., & Thoene, C. (2001). Di-and triethanolamine complexes of Co (II), Ni (II), Cu (II) and Zn (II) with thiocyanate: synthesis, spectral and thermal studies. Crystal structure of dimeric Cu (II) complex with deprotonated diethanolamine,[Cu 2 (μ-dea) 2 (NCS) 2]. Polyhedron, 20(7), 635-641.

[28] Sun, Y., Mayers, B., Herricks, T., & Xia, Y. (2003). Polyol synthesis of uniform silver nanowires: a plausible growth mechanism and the supporting evidence. Nano letters, 3(7), 955-960.

[29] Dang, T. M. D., Le, T. T. T., Fribourg-Blanc, E., & Dang, M. C. (2011). Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method. Advances in Natural Sciences: Nanoscience and Nanotechnology, 2(1), 015009.

[30] Lisiecki, I., & Pileni, M. P. (1993). Synthesis of copper metallic clusters using reverse micelles as microreactors. Journal of the American Chemical Society, 115(10), 3887-3896.

[31] Nazar, R., Ronchetti, S., Roppolo, I., Sangermano, M., & Bongiovanni, R. M. (2015). In situ synthesis of polymer embedded silver nanoparticles via photopolymerization. Macromolecular Materials and Engineering, 300(2), 226-233.

[32] Priola, A., Gozzelino, G., Ferrero, F., & Malucelli, G. (1993). Properties of polymeric films obtained from uv cured poly (ethylene glycol) diacrylates. Polymer, 34(17), 3653-3657.

[33] Halin, D. S. C., Talib, I. A., Daud, A. R., & Abd Hamid, M. A. (2012). Cuprous Oxide Thin Films for a Photoelectrochemical Cell of ITO/Cu2O/PVC-LiClO4/ Graphite. In Advanced Materials Research (Vol. 501, pp. 247-251). Trans Tech Publications.