Synthesis of conductive elastic film and conductive fabric based on crosslinked carboxymethyl starch-AgNPs composite

Manal A. El-Sheikh

National Research Centre, Textile Research Division, El-Behouth St., Dokki, Egypt. P.O. 12311

ABSTRACT

The current work is developing a novel, facile and eco-friendly method for synthesis of highly concentrated silver nanoparticles (AgNPs) using $AgNO_3$ as a precursor, the eco-friendly carboxymethyl starch (CMS) polymer as both reducing and stabilizing agent and glycerol as a plasticizer. (4-trimethyl ammonium methyl) benzophenone chloride)/UV eco-friendly system was utilized for further synthesis of AgNPs and for grafting of N, N-methylene diacrylamide onto CMS-AgNPs composite to obtain crosslinked CMS-AgNPs. After crosslinking, the produced composite either: 1) dried in a Teflon coated petri dish followed by exposure to UV-irradiation or 2) dried on the surface of a textile fabric followed by exposure to UV-irradiation. An insoluble elastic gel film was produced in both cases. The produced crosslinked CMS-AgNPs film or fabric coated crosslinked CMS-AgNPs film showed a measurable electrical conductivity, elasticity and water absorption properties. Colloidal solution of AgNPs was characterized by UV-Vis spectroscopy. Film and fabric were characterized by, TEM, SEM, EDS and TGA. The obtained properties of the film or fabric render it for utilization as a polymer gel electrolyte in the dye-sensitized solar cells (DSSC) fabrication

Keywords: carboxymethyl starch, Photoinitiator, uv-irradiation, silver nanoparticles, conductive fabric, conductive film.

1. INTRODUCTION

Increasing interest has been stirred up in lightweight, flexible, and wearable electronics to meet the up-and-coming applications such as high-performance sportswear, wearable displays, new classes of portable power, embedded health monitoring, and so on [1-5]. Textiles with flexibility, stretchability, and light mass are expected to be incorporated into a desirable wearable power as a component. However, as an electroactive material, good electronic conductivity is necessary for its efficient energy storage. Different synthetic approaches are possible for the fabrication of conductive textiles. Amongst are: in situ polymerization or coating of polyaniline and/or polypyrrole onto cotton fabric [2, 3, 6-9], coating fabric with graphene oxide nanosheet [3], metal nanoparticles such as silver [10], zinc oxide [11] or nickel hydroxide [12].

Silver nanoparticles have unique optical, electrical, and biological properties that have attracted significant attention due to their potential use in many applications. Polymers prevent agglomeration and precipitation of the particles, so they have been employed as capping and/or stabilizing agents in the chemical synthesis of metal nanoparticles. Among methods of green synthesis of silver nanoparticles, water is used as an environmentally benign solvent and cellulose, starch or CMS as both reducing and capping agent [13-20].

In a previous work [14], a novel green method was adopted to synthesize AgNPs using the water soluble 4-(trimethyl ammonium methyl) benzophenone chloride/UV system and silver nitrate as a precursor in the presence of CMS. While PI photogenerate AgNPs, CMS acts as both reducing and stabilizing agent. All components were water soluble, the process was "simple and easy," and the synthesis conditions used are mild. According to the process, AgNPs so-obtained were stable in aqueous solution, have a round shape morphology, the sizes of synthesized AgNPs were found in the range of 1–21 nm. However, little concentrations of AgNPs were achieved.

The current work aims at producing high concentrations of AgNPs, insoluble elastic conductive film and conductive cotton fabric. Concentrated AgNPs were obtained using a green method where CMS, glycerol, $AgNO_3$ and water were homogenized for one minute before going to the reaction course at 90°C for 6h under continuous stirring. While the conductive elastic films were produced using another green method by adding PI, and N, N-methylene diacrylamide to CMS-AgNPs colloidal solution followed drying and exposing the dried films to UV irradiation. Colloidal solution of AgNPs was characterized by UV-Vis spectroscopy. Film and fabric were characterized by TEM while the conductivity of the both film and fabric is measured using Keithley Digital Multimeter.

2. Experimental

2.1. Materials

100% bleached, scoured cotton fabric was supplied by Misr El–Beida Dyers, Egypt. The fabric was not subjected to any type of finishing treatments. The fabric was washed with a solution containing 5g/l sodium carbonate and 5g/l non–ionic detergent at boil for 3 hours. It was then rinsed with hot and cold water and left to dry at room temperature.

Native maize starch (St.) was kindly supplied by the Egyptian Company for Starch and Glucose Manufacture, Cairo, Egypt.

4-(trimethyl ammoniummethy) benzophenone chloride was supplied by "The associated Octel Ltd., Widnes, Great Britain", and used without further purification.

Monochloroacetic acid, sodium hydroxide, sodium carbonate, silver nitrate, MDA, hydrochloric acid, acetic acid, ethanol, glycerol and isopropanol were laboratory grade chemicals.

2.3. Methods

2.3.1. Carboxymethylation

Water soluble carboxymethyl starch with DS= 0.2 was prepared according to a reported method [21]. In this method, 100g of maize starch were placed in a sealable bottle and mixed together with a known volume of isopropanol. An aqueous solution of sodium hydroxide (0.5 mole/mole St.) was added drop wise to the starch–isopropanol mixture under stirring until the whole amount of sodium hydroxide was added. The sodium salt solution of monochloroacetic acid (0.2 mole/mole St.), prepared by the reaction of monochloroacetic acid with the equivalent amount of sodium carbonate, was added drop wise to the starch–isopropanol–sodium hydroxide mixture under continuous stirring until complete addition of the sodium monochloroacetate solution. Stirring was then stopped and the bottle was closed and kept at 30 ^{o}C for 24 hours. After carboxymethylation, the CMS samples were washed with ethanol:water solution (80:20) while excess alkali was neutralized using acetic acid. After washing, the CMS samples were filtered and oven-dried at 70 ^{o}C.

2.3.2. Synthesis of AgNPs

Two sets of experiments were performed, symbolized as "I" and "II". The two experiments are technically similar, however they differ in the concentration of $AgNO_3$ and glycerol related to the total volume of the mixture as well as the temperature and time of reaction. All reaction conditions are listed in the footnotes of the corresponding figure. A typical experimental work is performed as follows:

In a sealable bottle, a certain weight of CMS is dissolved in a known volume of distilled water, using mechanical stirrer, before a solution of silver nitrate is added dropwise under continuous homogenization. Glycerol is then added drop wise while keeping homogenization. Calculated amounts of PI and MDA were dissolved and mixed with the produced mixture. The whole contents were homogenized for one min then the bottle was then placed in water bath attachedwith magnetic stirrer. The temperature is allowed to rise to 90°C and the whole contents are kept under stirring for 6h. Amazingly, the silver metal could be observed floating on the surface of the solution during the synthesis reaction.

2.3.3. Preparation of silver coated cotton fabric

A cotton fabric was placed horizontally on Teflon coated "Petri" dish. 50 ml of the produced CMS-AgNPs colloidal solution were poured on the surface of the cotton fabric and allowed to dry at 50°C in an air oven. After drying, the treated cotton fabric was subjected to UV radiation (254 nm) for 12 h, 6 h for each side.

2.3.4. Preparation of CMS-AgNPs film

50 ml of the produced CMS-AgNPs colloidal solution were poured on Teflon coated "Petri" dish and allowed to dry at 50°C in an air oven. After drying, the treated cotton fabric was subjected to UV radiation (254 nm) for 12 h, 6 h for each side.

2.3.5. Preparation of CMS-AgNPs film on glass slide

Few drops of the produced CMS-AgNPg were poured on a glass slide and allowed to dry at 50°C in an air oven. After drying, glass slide was subjected to UV radiation (254 nm) for 6 h.

2.3.6. UV-irradiation

Cotton fabric treated CMS-AgNPs and CMS-AgNP film were subjected to UV radiation at 254 nm using Spectroline E-Series, Ultraviolet Hand Lamp with Filter Assembly, Spectronics Corporation, USA.

2.4. Characterizations and analyses

The DS of the carboxymethylated starch samples was determined via determination of the carboxyl content according to a reported method [22].

The UV–vis spectra of AgNPs were recorded using Jenway Spectrophotometer, Model 6800, Flight Deck Software, UK at wavelength range from 550 to 300 nm. λmax at 390-420 is characteristic to AgNPs. Synthesis of AgNPs is expressed as absorbance of the colloidal solution of the samples under test. The absorbance, the broadening and the wavelength of the band measure the intensity of the colloidal solution. i.e. the conversion of silver ions to AgNPs. Very concentrated AgNPs samples did not show one smooth band (either sharp or broad) but showed a number of crowded sharp bands. This behavior leads to false readings. So, all samples showed this behavior were diluted "100" times the original sample.

Transmission Electron Microscope was used to characterize AgNPs. Thus, the shape and size of the synthesized silver nanoparticles were characterized by means of a JEOLJEM- 1200 Transmission Electron Microscope. The samples were prepared by placing a drop of the colloidal solution on a 400-mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature. The average diameter of the silver nanoparticles was determined from the diameter of nanoparticles found in several chosen areas in enlarged microphotographs. The particle size was measured from the TEM image using the software "Revolution v1.6.0b195," a simple electron microscope tool for acquiring images, maps, and spectra using the Spectral Engine, 1999–2002 4pi analysis, Inc.

Resistivity of CMS-AgNPs coated cotton fabric and CMS-AgNPs elastic film was measured using Keithley 2100 6 1/2 Digital Multimeter using glass surface with dimensions of 3cm^2 and a load of 500g.

3. RESULTS AND DISCUSSION

3.1. Synthesis of CMS-AgNPs (Experiment I)

Figure 1 shows the UV-Vis spectrum of CMS-AgNPs colloidal solution of Exp. "I" at different reaction temperatures. Figure 1 shows intensive bands with bell

shapes and high absorbance values at about 415 nm. This indicates the formation of AgNPs [14, 17] and reflects the efficiency of the current system in synthesizing AgNPs at the synthesis conditions. As clear, synthesis of AgNPs at 90°C showed the highest absorbance, i.e. the highest concentration of AgNPs which reflects the favorable effect of temperature on synthesizing AgNPs.

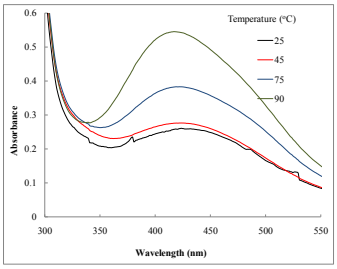

Figure 1: Effect of Reaction Temperature on synthesis of AgNPs (Exp. "I")

CMS, 10g; Ag, 2.5g; PI, 2.5g; MDA, 2.5g; Glycerol, 25g; Time 1h; Temperature 45-90°C; Total volume, 500ml; Sample dilution, all samples are diluted 100 times the original sample.

Figure 2 shows the UV-Vis spectra of CMS-AgNPs colloidal solution of Exp. "I" at different reaction durations (1-6h) while temperature is kept at 90°C. As clear, synthesis of AgNPs at 5h and 6h showed the highest absorbance, i.e. the highest concentration of AgNPs. Meaning that no more conversion of Ag ions to AgNPs is expected with prolonging the reaction time using this system.

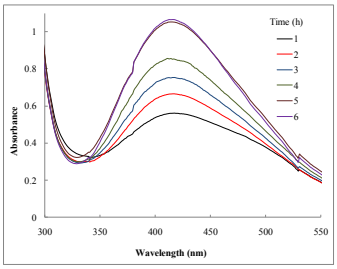

Figure 2: Effect of Reaction Time on synthesis of AgNPs

CMS, 10g; Ag, 2.5g; PI, 2.5g; MDA, 2.5g; Glycerol, 25g; Time 1-6h; Temperature 90°C; Total volume, 500ml; Sample dilution, all samples are diluted 100 times the original sample.

Figure 3 shows UV-Vis spectra of CMS-AgNPs (Exp. "I") before and after exposure to UV radiation for 12 h. The effect of PI/UV system could be noticed from the increase of absorbance of the colloidal solution after exposure of UV. The solution contains PI which in presence of UV acts as reducing system for Ag ions to AgNPs [14].

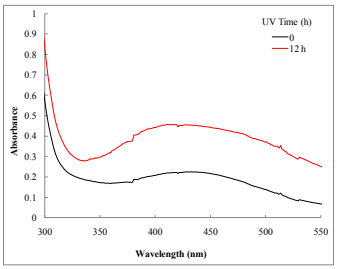

Figure 3: Effect of UV irradiation on Synthesis of CMS-AgNPs

CMS, 10g; Ag, 2.5g; PI, 2.5g; MDA, 2.5g; Glycerol, 25g; Time 1h; Temperature 25°C; Total volume, 500ml; Sample dilution, sample "0" is diluted 50 times the original sample and sample "12h" is diluted 100 times of the original sample.

3.2. Synthesis of CMS-AgNPs (Experiment II)

Figure 4 shows the consistency of the current system. Again, highest absorbance is obtained after 6h at 90°C. The system could be applied for different concentrations of reactants. The highest absorbance (Exp. II) is higher than that of (Exp. I) due to the increase in the concentration of glycerol (100% (of weight of CMS) compared to that of Exp. I (2.5% (of weight of CMS). Undoubtedly, the increase in the amount of OH (present in glycerol molecule) groups enhances the reduction of Ag ions to AgNPs.

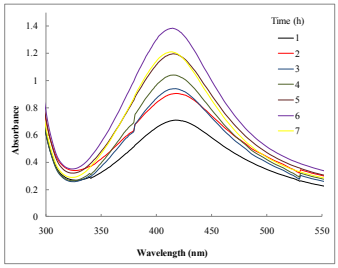

Figure 4: Effect of Glycerol Concentration on synthesis of AgNPs (Exp. "II")

CMS, 5g; Ag, 0.5g; PI, 0.5g; MDA, 0.5g; Glycerol, 5g; Time 1-7h; Temperature 90°C; Total volume, 100ml; Sample dilution, all samples are diluted 100 times.

Figure 5 shows UV-Vis spectra of CMS-AgNPs coated glass (Exp. "II") before and after exposure to UV radiation for 6 h. Because the reflectance of CMS-AgNPs-coated cotton fabrics could not be measured, glass is used instead. It was possible to measure the absorbance of the transparent CMS-AgNPs coated glass slide. The non smoothness of both lines reflects the high concentration of AgNPs although thin film of CMS-AgNPs is produced. This process could be utilized in fabrication of conductive glass.

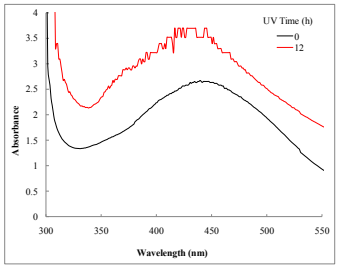

Figure 5: Effect of PI/UV system on synthesis of CMS-AgNPs thin film (Exp. "II")

CMS, 5g; Ag, 0.5g; PI, 0.5g; MDA, 0.5g; Glycerol, 5g; Time 7h; Temperature 90°C; Total volume, 100ml; Sample dilution, no dilution.

3.3. TEM of Exp. I and II

Figures 6 and 7 show the TEM micrographs and particle size distribution histogram of the CMS-AgNPs

colloidal solutions of samples I and II respectively. Generally, micrographs showed silver nanoparticles with fine dispersion. The nanoparticles mostly have round shape morphology with little irregularly shaped particles. The mean particle sizes are between 1–21 nm and 1–20 nm for samples I and II respectively. The highest count % was found for AgNPs between 6–9 nm and 3-6 nm samples I and II respectively.

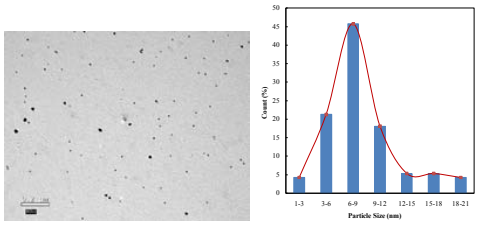

Figure 6: TEM and particle size distribution histogram of sample I

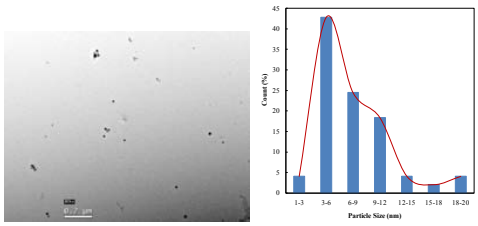

Figure 7: TEM and particle size distribution histogram of sample II

3.4. Conductivity of CMS-AgNPs coated cotton fabric and CMS-AgNPs elastic film

Figure 8 shows, from left to right 1) yellow-brown cotton fabric coated with CMS-AgNPs (characteristic for AgNPs) and metallic color (characteristic for silver metal) are both seen clearly on the fabric surface, 2) high elasticity of the fabric and 3) a rough measurable resistivity using traditional AVO meter (about 3.7 MΩ).

Figure 8: Conductivity and elasticity of CMS-AgNPs coated cotton fabric

Figure 9 shows, from left to right 1) brown color CMS-AgNPs film. (characteristic for AgNPs), 2 and 3) high elasticity of the film. The film is bendable in all directions and 4) a rough measurable resistivity using traditional AVO meter (about 2.5 MΩ).

Figure 9: Conductivity and elasticity of CMS-AgNPs film

Accurate resistivity of both CMS-AgNPs coated cotton fabric and CMS-AgNPs film was measured using Keithley 2100 6 1/2 Digital Multimeter according to the experimental section. Table 1 shows the resistivity of both CMS-AgNPs coated cotton fabric and CMS-AgNPs film.

Sample	Resistivity (MΩ)
CMS-AgNPs coated cotton fabric	0.4399
CMS-AgNPs film	0.544

Table 1: Conductivity of CMS-AgNPs coated cotton fabric and CMS-AgNPs film.

4. CONCLUSION

Highly concentrated AgNPs was prepared using facile and eco-friendly method where the eco-friendly CMS polymer was used as both reducing and stabilizing agent and glycerol as a plasticizer. TEM results showed round shape morphology with mean particle sizes between 1–21 nm. (4-trimethyl ammonium methyl) benzophenone chloride)/UV eco-friendly system was utilized for further synthesis of AgNPs and for grafting of N, N-methylene diacrylamide onto CMS-AgNPs composite to obtain crosslinked CMS-AgNPs. An insoluble elastic gel film was produced as CMS-AgNPs or CMS-AgNPs coated cotton fabric. The produced film and fabric showed resistivity of 0.4399 and 0.544 MΩ respectively and high elasticity.

REFERENCES

[1] Pasta, M., la Mantia, F., Hu, L., Deshazer, H. D., Cui, Y., "Aqueous supercapacitors on conductive cotton", Nano Research, vol. 3, no. 6, pp. 452-458, 2010.

[2] Zhang, Y., Dong, A., Wang, Q., Fan, X., Cavaco-Paulo, A., "Conductive cotton prepared by polyaniline in situ polymerization using laccase", Applied biochemistry and biotechnology, vol. 174, no. 2, pp. 820-831, 2014.

[3] Tang, X., Tian, M., Qu, L., Zhu, S., Guo, X., Han, G., Sun, K., Hu, X., Wang, Y., Xu, X., "Functionalization of cotton fabric with graphene oxide nanosheet and polyaniline for conductive and UV blocking properties", Synthetic Metals, vol. 202, pp. 82-88, 2015.

[4] Yuan, C., Hou, L., Li, D., Shen, L., Zhang, F., Zhang, X., "Synthesis of flexible and porous cobalt hydroxide/conductive cotton textile sheet and its application in electrochemical capacitors", Electrochimica Acta, vol. 56, no. 19, pp. 6683-6687, 2011.

[5] Hu, L., Pasta, M., Mantia, F. L., Cui, L., Jeong, S., Deshazer, H. D., Choi, J. W., Han, S. M., Cui, Y., "Stretchable, porous, and conductive energy textiles", Nano letters, vol. 10, no. 2, pp. 708-714, 2010.

[6] Otrokhov, G. V., Morozova, O. V., Vasil'eva, I. S., Shumakovich, G. P., Zaitseva, E. A., Khlupova, M. E., Yaropolov, A. I., "Biocatalytic synthesis of conducting polymers and prospects for its application", Biochemistry (Moscow), vol. 78, no. 13, pp. 1539-1553, 2013.

[7] Chaubey, A., Pande, K., Pandey, M., Singh, V., "Signal amplification by substrate recycling on

polyaniline/lactate oxidase/lactate dehydrogenase bienzyme electrodes", Applied Biochemistry and Biotechnology, vol. 96, no. 1-3, pp. 239-248, 2001.

[8] Stempien, Z., Rybicki, T., Rybicki, E., Kozanecki, M., Szynkowska, M. I., "In-situ deposition of polyaniline and polypyrrole electroconductive layers on textile surfaces by the reactive ink-jet printing technique", Synthetic Metals, vol. 202, pp. 49-62, 2015.

[9] Bowman, D., Mattes, B. R., "Conductive Fibre Prepared From Ultra-High Molecular Weight Polyaniline for Smart Fabric and Interactive Textile Applications", Synthetic Metals, vol. 154, no. 1–3, pp. 29-32, 2005.

[10] Xue, C.-H., Chen, J., Yin, W., Jia, S.-T., Ma, J.-Z., "Superhydrophobic conductive textiles with antibacterial property by coating fibers with silver nanoparticles", Applied Surface Science, vol. 258, no. 7, pp. 2468-2472, 2012.

[11] Lim, Z. H., Chia, Z. X., Kevin, M., Wong, A. S. W., Ho, G. W., "A facile approach towards ZnO nanorods conductive textile for room temperature multifunctional sensors", Sensors and Actuators B: Chemical, vol. 151, no. 1, pp. 121-126, 2010.

[12] Hwan Ko, Y., Kim, S., Su Yu, J., "Electrochemical synthesis of hierarchical β-Ni(OH)2 nanostructures on conductive textiles", Materials Letters, vol. 84, no. 0, pp. 132-135, 2012.

[13] El-Sheikh, M. A., Ibrahim, H. M., "One Step Photopolymerization of N, N-Methylene Diacrylamide and Photocuring of Carboxymethyl Starch-Silver Nanoparticles onto Cotton Fabrics for Durable Antibacterial Finishing", International Journal of Carbohydrate Chemistry, vol. 2014, pp. 1-9, 2014.

[14] El-Sheikh, M. A., "A Novel Photosynthesis of Carboxymethyl Starch-Stabilized Silver Nanoparticles", The Scientific World Journal, vol. 2014, pp. 1-11, 2014.

[15] Hebeish, A., El-Rafie, M. H., El-Sheikh, M. A., El-Naggar, M. E., "Nanostructural Features of Silver Nanoparticles Powder Synthesized through Concurrent Formation of the Nanosized Particles of Both Starch and Silver", Journal of Nanotechnology, vol. 2013, pp. 1-10, 2013.

[16] El-Sheikh, M. A., El-Gabry, L. K., Ibrahim, H. M., "Photosynthesis of Carboxymethyl Starch-Stabilized Silver Nanoparticles and Utilization to Impart Antibacterial Finishing for Wool and Acrylic Fabrics", Journal of Polymers, vol. 2013, pp. 1-9, 2013.

[17] El-Sheikh, M. A., "Synthesis of poly acrylamide-g-carboxymethyl starch silver nanoparticles composite and its corresponding hydrogel". 7th Aachen-Dresden International Textile Conference, pp. 1-43, Aachen, Germany, 2013.

[18] El-Feky, G. S., MH, E.-R., El-Sheikh, M., El-Naggar, M. E., A, H., "Utilization of Crosslinked Starch Nanoparticles as a Carrier for Indomethacin and Acyclovir Drugs", J Nanomed Nanotechnol, vol. 6, no. 1, pp. 1-8, 2015.

[19] Hebeish, El-Rafie, M. H., El-Sheikh, M. A., Seleem, A. A., El-Naggar, M. E., "Antimicrobial Wound Dressing and Anti-inflammatory Efficacy of Silver Nanoparticles", International Journal of Biological Macromolecules, vol. 65 no. 0, pp. 509–515, 2014.

[20] El-Sheikh, M. A., El-Rafie, S. M., Abdel-Halim, E. S., El-Rafie, M. H., "Green Synthesis of Hydroxyethyl Cellulose-Stabilized Silver Nanoparticles", Journal of Polymers, vol. 2013, pp. 1-11, 2013.

[21] El-Sheikh, M. A., "Carboxymethylation of maize starch at mild conditions", Carbohydrate Polymers, vol. 79, no. 4, pp. 875-881, 2010.

[22] Daul, G. C., Reinhardt, R. M., Reid, J. D., "Preparation of Soluble Yarns by the Carboxymethylation of Cotton", Textile Research Journal, vol. 23, no. 10, pp. 719-726, 1953.