

Synthesis and characterization of C-dots using composite carbon paste electrode as high performance in potentiometric sensors

M. Muthukumaran¹, S. Niranjani¹, K. Samuel Barnabas¹,
V. Narayanan², T. Raju^{1*}, K. Venkatachalam^{1*}

¹Department of Analytical Chemistry, University of Madras, Guindy Campus, Chennai-25.

²Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai-25.

*Corresponding author : kvenkatchemistry@gmail.com

Abstract -The newly synthesized C-dots as water-soluble materials using Sodium glucose xanthate (SGX), the composite electrode material was used for the potentiometric sensors for toxic metal ion. Composite carbon paste electrode (CCPE) was prepared from sodium glucose xanthate C-dots, graphite powder and paraffin wax (binder) for the application of metal ions sensing. C-dots fluorescent in nature. The formation of C-dots was confirmed by UV-Visible, photoluminescence and FT-IR, confocal raman spectroscopy. The effect of pHs on the UV-Visible and Fluorescence Spectroscopy of different pH was carried out at the solutions concentration (1mg/ml) at different pHs (pH=1-10). Surface morphology was analyzed using FE-SEM microscopy. The utility of composite carbon paste electrode with C-dots for the potentiometric determination of Cu(II) ion in aqueous medium was demonstrated with different electrolyte solutions and different pHs (pH=1-7). Interestingly C-dots exhibits a good response towards the Cu(II) ion when compared to other metal ions. In the potentiometric sensing the CCPE is the working (indicator) electrode and saturated calomel electrode (SCE) is the reference electrode.

Keywords: C-dots, composite carbon paste electrode (CCPE), potentiometric sensors, Toxic metal ions.

INTRODUCTION

Xanthate derivative was prepared by the chemical reaction of CS₂ under alkaline conditions. Xanthates, now classed under the more systematic but less evocative name of dithiocarbonates (or carbonodithioates), have been known for almost two centuries[1]. Xanthate, usually refers to a salt with the formula ROCS₂-M⁺ (R = alkyl; M⁺ = Na⁺, K⁺).The name of the xanthate is derived from Greek, meaning “yellowish, golden”, and indeed most xanthate salts are yellow coloured products. The sodium glucose xanthate is an organosulfur compound is important in two main areas, the production of cellophane and related polymers from cellulose and secondly in mining for the extraction of certain Chalcogen ores. They are also versatile intermediates in organic synthesis. Xanthate is also referred to functional group of esters of xanthic acid. These ester functional group have the structure ROC(=S) SR. Xanthates are family of organo sulphur compounds prepared by mixing alcoholic compound in alkaline condition with carbondisulphide. Xanthate reacts with metals to form metal-xanthate complexes.

The carbondisulphide is a hetero-allene which by its symmetric nature and possessing diverse bonding character, is a good complexing agent. Both free and complexes of allenes are highly reactive in nature. Ligands that are based on hetero allenes are called as heteroallyls[2]. Xanthate salts are produced by the reaction of equal molar quantities of an alcohol(OH) (glucose) with strong base such as sodium (Na⁺) or potassium (K⁺) hydroxide and carbondisulfide (CS₂)[3]. The mixture was stirred well and then excess of carbon disulphide was added with continued stirring [4] [5] [6] in the ice cold condition since the reaction is an exothermic reaction. Sodium ethoxide also be used in place of sodium hydroxide. Virtually any alcohol can be used in this reaction. Technical grade xanthate salts are usually of 90–95% purity. Impurities include alkali-metal and sulfide, sulfate, dithiocarbonates, thiosulfate, sulfite, or carbonate as well as residual raw material such as alcohol and alkali hydroxide.

These salts are available commercially as powder granules, flakes, sticks, and solutions. Sodium glucose xanthate (SGX) is an organosulfur compound with the chemical formula glucose-OCSS⁻ Na⁺. It is a yellow solution, which characteristically hydrolyzes to release malodorous products. Sodium glucose xanthate is predominantly used in the mining industry as a flotation agent. Several techniques and methodologies are described in literature such as HPLC[7] spectrophotometry[8], polarography etc. The present work is a simple inexpensive potentiometric sensing followed by the estimation of Cu (II) ion, Cd (II) ion, Zn (II) ion, Pb (II) ion and Hg (II) ion using composite carbon paste electrode prepared from sodium glucose xanthate C-dots.

Herein, the active C-dots was synthesized via facile one pot hydrothermal method using Sodium glucose xanthate. The synthesized C-dots was characterized using various techniques such as, Confocal raman, FT-IR, UV-vis, Photoluminescence and FESEM. As synthesized C-dots was highly active in potentiometric sensors studies for sensing toxic metal ions at different pH range (pH=1- pH=7). Further the following metal ions were selected for the potentiometric sensing and determination, which include Cu (II) ion, Cd (II) ion, Zn (II) ion, Pb (II) ion and Hg (II) ion at different pH conditions.

EXPERIMENTAL SECTION

CHEMICALS

All the chemicals and reagents used for this study were obtained from commercial sources, they are of analytical grade and were used without further purification. Double distilled water (DDW) was used in all solution preparations.

SYNTHESIS OF C-DOTS

A simple replacement for water in the reaction above is all that is required[9] An example would be the preparation of sodium glucose xanthate one mole of glucose and one mole of sodium hydroxide, one mole of carbondisulphide (CS₂) was slowly added. (1:1:1%). sodium hydroxide (0.4 g) was dissolved in 30 ml of water and the solution was exothermic and cooled with an ice bath. To the hydroxide solution, both glucose (1.801 g) and carbon disulfide (0.76 ml) were slowly added. The reaction mixture stirrer for 12 hrs. The reaction mixture is formed sodium glucose xanthate solution. Sodium glucose xanthate solution was transferred into Teflon coated autoclave and aged at 180°C for 12 hrs. The product of black powder was washed and filtered using methanol for several times[10]. The obtained C-dots was stored in vacuum desiccator.

INSTRUMENTATION

The C-dots prepared as above was characterized by fourier transform infrared spectroscopy (FT-IR), using Cary 630 FT-IR instrument. ultraviolet-visible spectrum was recorded using cary 8453 UV-Vis the diode array spectrophotometer, photoluminescence spectroscopy (PL) emission intensity measurements were carried out using perkin elmer LS-45 fluorescence spectrometer, field emission scanning electron microscopy (FE-SEM) was used to record micrographs from HITACHI S600N field emission scanning electron microscope (Japan), and raman spectrum was recorded using laser raman microscope, raman-11 nanophoton corporation (Japan). potentiometer measurements were made using a MP-1 plus susima pH-meter. the potentiometric sensing application was carried out from the C-dots prepared as above.

RESULT AND DISCUSSIONS

The FT-IR spectrum of sodium glucose xanthate C-dots was shown in Fig.1(a). According to FT-IR, spectrum of sodium glucose xanthate C-dots shows the stretching vibration of C=S at 1587 cm⁻¹, the stretching vibration of C-S at 922 cm⁻¹ and stretching vibration of CS₂ 1045 cm⁻¹, the bending vibration of C-O-C at 1202 cm⁻¹, and the wagging vibration of C-H at 1408 cm⁻¹, stretching vibration of CH₂ at 2931 cm⁻¹, the peak at 3437 cm⁻¹ is due to the stretching vibration O-H group respectively [11].

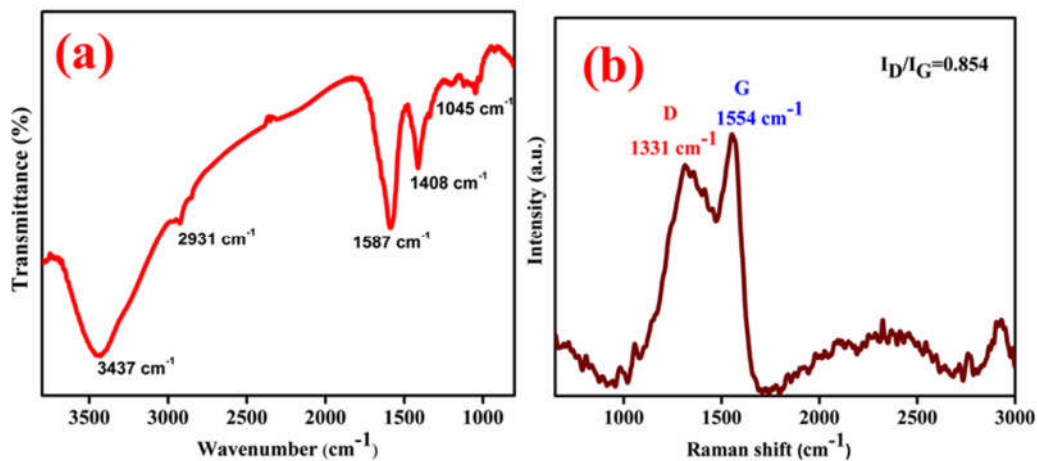


Fig. 1.(a). FT-IR Spectrum (b) Raman spectrum of Sodium glucose xanthate C-dots

The raman spectra of sodium glucose xanthate C-dots was shown in Fig. 1(b), the raman spectrum of sodium glucose xanthate C-dots shows the stretching vibrations of C=S at 1554 cm^{-1} , the stretching vibration of C-S at 976 cm^{-1} and stretching vibration of CS₂ at 1055 cm^{-1} , the bending vibration of C-O-C at 1554 cm^{-1} , and the wagging vibration of C-H at 1331 cm^{-1} , stretching vibration of CH₂ at 2918 cm^{-1} , respectively confirms the raman spectrum of sodium glucose xanthate C-dots.

The raman spectrum of sodium glucose xanthate C-dots. exhibits two major bands at 1331 and 1554 cm^{-1} , which are respectively assigned to Graphitic carbon G-band (sp²) and Diamond carbon D-band (sp³). In general, the G band corresponds to the vibration mode of a sp² carbon atom, while the D band represents a vibration mode of carbon atom in sp³ hybridized orbital (ID /IG) was about 0.854, which further confirmed the partial amorphous nature of the SGX CDs.

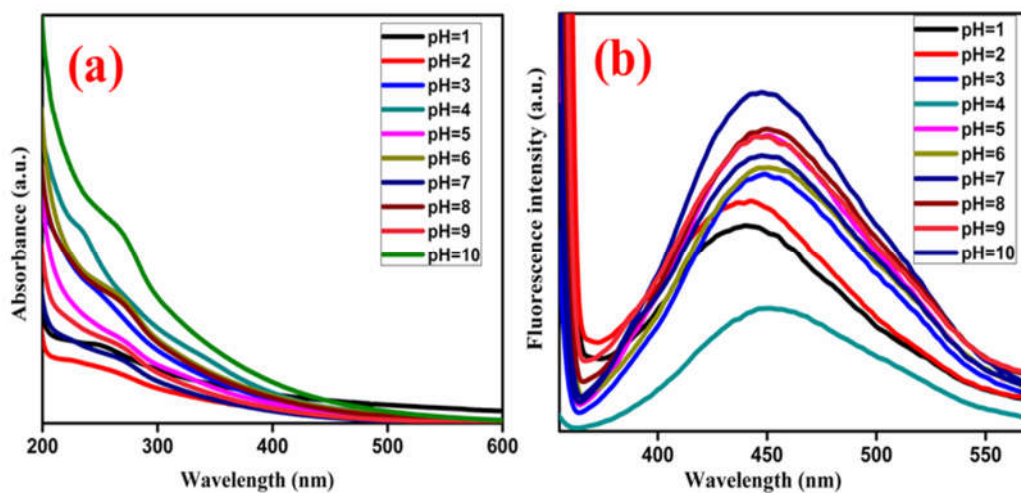


Fig.2(a). Ultraviolet-Visible (UV-Vis) spectrum (b). Photoluminescence Spectrum of Sodium glucose xanthate C-Dots- under the influence pH=1-10.

The ultraviolet-visible (UV-Vis) spectra of sodium glucose xanthate C-dots are shown in Figs.2 (a), the absorption measurements were performed for the solution of sodium glucose xanthate C-dots. During sodium glucose xanthate C-dots from the solution of the uv-visible spectrum of sodium glucose xanthate C-dots in effect of (pH=1-10) solutions shows the intensity ingress in effect of pH solutions. Absorption band at 268 nm , this shows the presence of $\pi-\pi^*$ transition. This transition occurs from the C=S bond, this bond is a part of the C-dots characteristic of the sodium glucose xanthate C-dots is observed[12].

The photoluminescence spectra of sodium glucose xanthate C-dots at effect of pH solutions Fig.2 (b), exhibits broad peaks with maxima at 454 nm, This shows the presence of π - π^* transition[13]. This transition occurs from the C=S bond, this bond is a part of the SGX C-dots. The PL peaks has been ascribed to different effects of pHs Nisha et. al[14]. The PL spectra of sodium glucose xanthate C-dots in effect of (pH=1-10) solutions shows the intensity ingress in effect pH solutions.

The surface morphology and size of the C-dots was observed by field emission scanning electron microscopy (FE-SEM) analysis. Fig.3 (a) the FE-SEM morphology image of sodium glucose xanthate C-dots shows an elongated spherical shape that to without any surfactant. The average particle size of the sodium glucose xanthate C-dots obtained was 177 nm. From Fig. 3(b) EDX of the sodium glucose xanthate C-dots peak shows corresponding to the elements C, O, S, and Na.

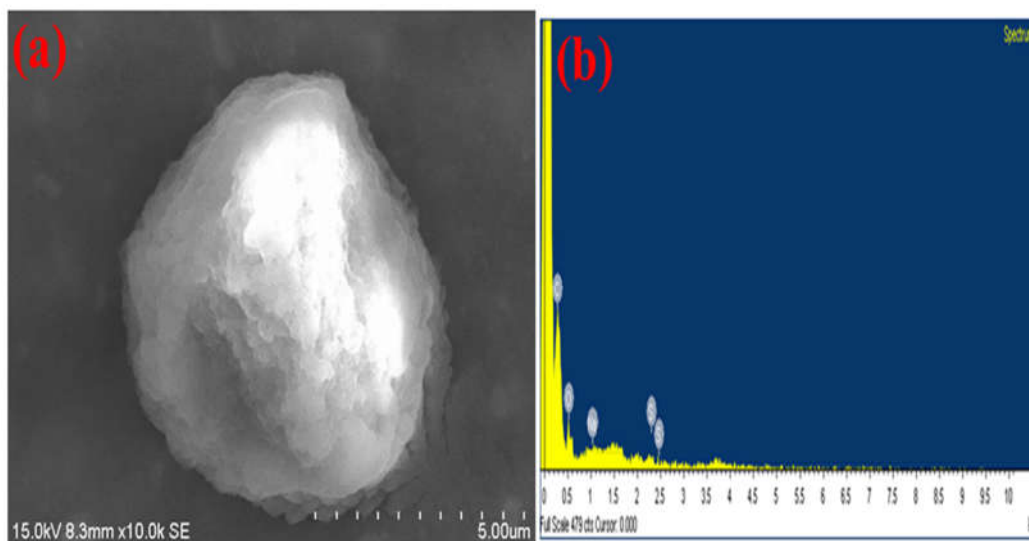


Fig. 3(a). Field emission scanning electron microscopy (b).EDX spectrum of Sodium glucose xanthate C-Dots

The sensitivity of potentiometric CCPE depends on the composite carbon paste composition [15]. The influence of ligand in the composite carbon paste was studied. The potentiometric sensing of sodium glucose xanthate C-dots. The reference electrode (SCE) and working electrode is (CCPE) taking equal molar quantities of electrolyte solution (1.0×10^{-3} M KCl) added, and DD water taken into beaker. The metal ion influence on the potentiometric responses were tested copper solutions, maintaining the ionic strength of the corresponding test solution constant with KCl.

The burette different metal ions added in the (CCPE) solution metal behavior is (Cd^{2+} , Hg^{2+} , Zn^{2+} , Pb^{2+}) is not behavior the metal of (Cu^{2+}) is very good sensing the CCPE can be employed with successful results, as for other reported potentiometric sensors[16]. Shows the Fig,4(a).

The potentiometric sensing C-dots with copper chloride & copper sulphate solution carried out electrochemical reaction by taking equal molar quantities buffer solution added, and 5ml water taken into beaker. Then reference electrode (calomel electrode) and indicator electrodes (CCPE) are immersed in that beaker solution. The solution is constantly stirring using magnetic stirrer. Electrodes are connected to potentiometer and sensing against 1.0×10^{-3} M of copper chloride (CuCl_2) & 1.0×10^{-3} M of copper sulphate (CuSO_4) solution. pH range 1-7 against the sensing. Dipped in to the solution of both electrodes saturated calomel acts reference electrode (SCE). Composite carbon past electrode (CCPE) acts as a working electrode Fig,4(b) & (c). Sensing was indicating concordant potential value was noted. Adding one ml of the copper (II) potential value was noted. The maximum speed of magnetic stirrer to this solution was allowed. The graph was plotted against volume of copper (1.0×10^{-3} M) as a function with C-dots potential noted.

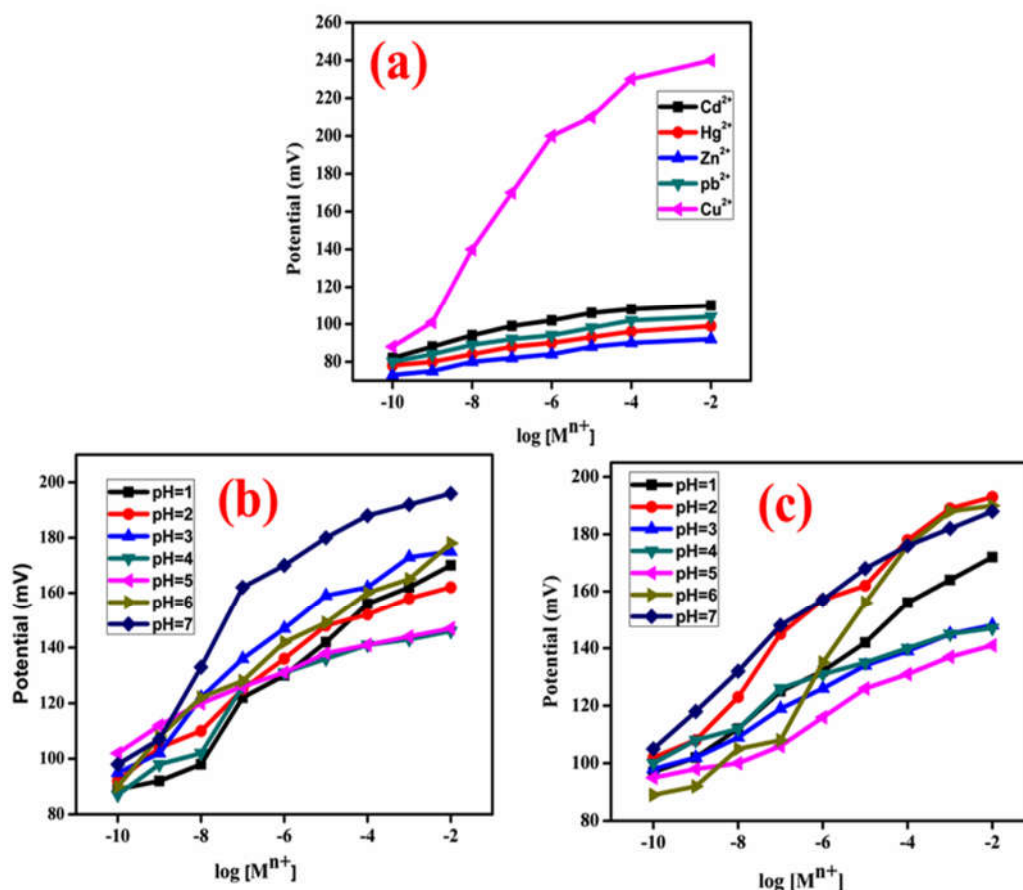


Fig:4(a)Potentiometric Sensing of C-Dots for Different Metal ions solutions (b). Effect of pH (pH=1-7) for Cl⁻ ion in CuCl₂ (c).Effect of pH (pH=1-7) for SO₄ ion of CuSO₄.

For pH=1-7, the difference of potential obtained at the initial stage of the sensing are higher than that of the potential difference obtained in copper ions. This indicates that the interaction of copper ions higher. Here the complex between xanthate anion and the copper ions is completed, which is known from the loop shape and bend increase line of the curve. The starting potential is very less due to the decomposition of C-dots at low pH.

The curve is still loop shape at higher pH from pH=8-10, because the xanthate completely ionize and are sufficiently stable at higher pH. The potential obtained are less in magnitude when compared to that of the potentials obtained at low pH. The incomplete complexation might be due to the formation of copper hydroxide at this pHs. The graph clearly separated at lower pH from higher pH distinctively. According to HSAB principle soft acids prefer binding to soft bases to give covalent complexes and hard acids prefer binding to hard bases to give ionic complexes. So here copper ion (II) act as a soft acid so it's prefer binding to xanthate like soft bases to give covalent complexes. During this reaction certain amount of potential is released that potential is measured our composite carbon paste electrode (CCPE). Oxidation and intermediate electronegativity 2.5-3.0. The sulfur act as a soft base. Copper act as a soft acid because it's large radius, low or partial positive charge, completely filled in the valance shells. That is copper act as a soft acid.

The different types of reaction that takes place in the solution and with electrode material

Stage 1: At the electrode

At the electrode (being more positive and anodic in nature) the C-dots solution being more negative, interaction takes place very strongly, hence adsorption overcoming the outer and inner Helmholtz plane which lead to the formation of complex at the electrode material and is pictorially represented as Fig,5.

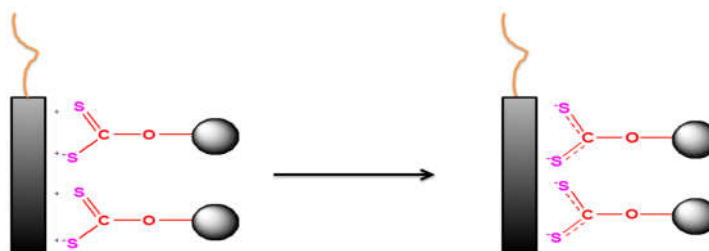
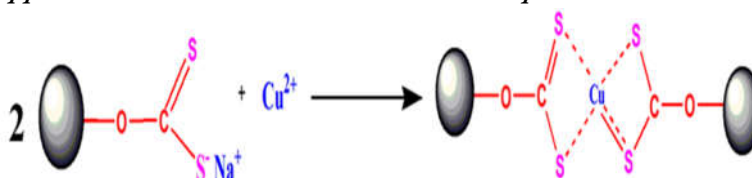


Fig.5, Pictorially representation of the formation of complex at the electrode material

Since a lone pair of electrons was available on the other sulphur atom and being in close proximity with the metal electrode, the unique cyclization (four membered ring formations on complexation) which is characteristic of C-Dots takes place, and ultimately di anion results following strong complexation.

Stage-2 Interaction of copper ions with electrode and its surface complexes



As the sensing progressed, the available excess copper ions competes a place for the electrode to form the Copper, C-Dots complex on the electrode. Copper ions plug ligands from the electrode surface owing to the higher stability of the copper complex formed. There is a possibility for the formation of a mixed hetero metallic complex of copper. This takes place at the surface of the electrode, and thereby making the electrode surface unavailable for sensing the ongoing reaction i.e. sensing the decrease of C-Dots or complexation.

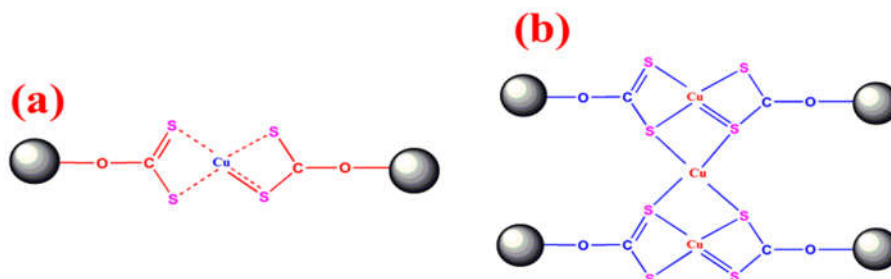


Fig.6(a). Complex (I) formed with copper(b).Complex (II) formed with excess of copper ions

The differentiation between the structure I & II can be established by two methods. By complex (I) formed with copper (1:2) ; complex (II) formed with excess of copper ions 3:4 complexes[17].

CONCLUSION

The C-dots were synthesized and characterize by UV-Visible and FT-IR studies. The synthesized compounds were sensing against d^{10} and d^9 metals to know their behavior in presence of buffer. The composite carbon paste electrode modified with SGX C-dots reveals an adequate response to copper ions. The potentiometric composite carbon paste sensor shows better selectivity to copper ions. However, the copper response CCPE has a minor dependence on the pH a shorter response time. Sodium glucose xanthate C-dots exhibited different behavior with respect to that of buffer. The deposition onto the electrode was found in case of copper complexes of C-dots. The deposition was not found in case of zinc, lead, and mercury complex. The stability and low solubility of the copper complex made the complexes to deposit on the electrode.

From these observations it is clear that copper complex of sodium glucose xanthate were less positively charge ions come to get reduced by the electrons coming from anode through the cathode

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