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Characterization of carbon derived from candle by flame-soot method for counter electrodes of dye-sensitized solar cells

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Abstract

Candle soot, carbon samples prepared by flame-soot method, was characterized and investigated for its catalytic ability for the reduction of tri-iodide ions aiming to substitute expensive platinum based electrode used in dye-sensitized solar cells (DSCs). The Energy Dispersive X-ray Spectroscopy of the candle soot samples revealed that the soot contains 96% carbon. Similarly, Scanning Electron Microscopy images show that the candle soot consists of interconnected carbon nanoparticles of size ∼50 nm. Furthermore, X-ray Diffraction and Raman spectroscopy showed that the candle soot consists of disordered and ordered graphitic carbons in a comparable proportion. The catalytic ability of the candle soot was compared with that of platinum by Electrochemical Impedance Spectroscopy of the symmetrical electrochemical cells. The charge transfer resistance (Rct) at the candle soot-electrolyte interface was observed to be $\sim 4.42\ \Omega\ cm^2$ *compared to* $\sim 5.04\ \Omega\ cm^2$ *that of the platinum-electrolyte interface. The candle soot was prepared by a simple method using low-cost material; hence, it can be a low-cost and efficient counter electrode material alternate to the platinum used in counter electrodes of DSCs.*

Keywords
Candle soot, Flame-soot method, Counter electrode, Catalyst, Dye-sensitize solar cells, Charge transfer resistance.

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1 Introduction

Carbonaceous materials are chemically stable, readily available, and low-cost [1] and these materials have been adopted in the preparation of counter electrodes of dye-sensitized solar cells (DSCs). The DSCs, developed by O'Ragen and Gratzel in 1991, are a relatively new type of solar cells and these photovoltaic devices can be low-cost compared to silicon based solar cells [2, 3]. The major components of a DSC are photoelectrode, liquid electrolyte, and counter electrode. Photoelectrode is the front electrode while the counter electrode (CE) is the back electrode, and the liquid electrolyte is enclosed in the gap between the two electrodes. Both the photoelectrode and CE use a transparent and conducting Fluorine-doped tin oxide (FTO)-glass substrate as a base. For the photoelectrode, the FTO-glass substrate is coated with a few microns thick film of mesoporous nanocrystalline Titanium dioxide (TiO_2) particles. Then, a monolayer of light sensitive dye molecules is chemically adsorbed on the TiO_2 film. For the CE, the glass substrate is generally coated with a platinum.

When the sunlight is incident at the photoelectrode, the dye molecules absorb the solar photons and inject their loosely bound electrons into the conduction band of the TiO2. After diffusion of the electrons in the TiO_2 film, they arrive at the conducting part of the photoelectrode. The photoelectrode is connected to the CE via an external circuit with an electric load. Thus, the electrons at the photoelectrode pass through the electric load in the external circuit and generate electric power. Then the electrons arrive at the CE [3, 4]. In order to enable the oxidized dye molecules to emit photoelectrons continuously (by absorbing the incident flux of solar photons), the dye molecules should be regenerated. The iodide ions in the electrolyte donate electrons to the dye molecules and the dye molecules are regenerated. After donating the electrons, the iodide ions are oxidized to tri-iodide ions, and they diffuse toward the CE which is generally coated with a thin film of platinum. The photoelectrons, arrived at the CE, are transferred to the diffused tri-iodide ions and the circulation of the electrons in the solar cell is completed. The tri-iodide ions after gaining the electrons are reduced to iodide ions [3–7].

The rate of reduction of tri-iodide ions into iodide ions is one of the factors that influence the light to electricity conversion efficiency of solar cells. Swift transfer of the tri-iodide ions into iodide ions results high efficiency of the solar cells. The platinum coated on the CE enhances the rate of electron transfer [6]. However, the use of platinum in DSCs has some issues like high cost of platinum and its instability in the electrolyte used in DSCs [6]. Hence, researchers have proposed various types of carbon as alternative catalyst to replace platinum [3–12]. Out of the carbonaceous materials, carbon nanotubes [5], carbon nanofibers [3,7,8], graphene [9,10] etc. have exhibited comparable catalytic ability for the reduction of the tri-iodide ions as the platinum. However, the synthesis process of these carbons is not simple. Consequently, these types of carbonaceous materials are still expensive.

In 2019, Joshi, Lawaju, and B.K. reported the composite of mustard oil lampblack and printer toner as a low-cost and novel counter electrode material. The light to electricity conversion efficiency of the composite based solar cells was 3.20% compared to 4.18% of the platinum based reference solar cells [4]. Similarly, Lawaju and Joshi used soybean oil lamp black/printer toner composite as another counter electrode material and reported an efficiency of 2.58% compared to 3.67% of the platinum based DSCs [11]. Our previous research has demonstrated that lampblack based CEs can serve as a catalyst for the reduction of tri-iodide ions although the catalytic ability of the CEs was not as efficient as that of the platinum based CEs. Herein, we have proposed low-cost and efficient CEs prepared with candle soot for the reduction of tri-iodide ions in DSCs. We prepared carbon samples derived from commercially available candle using flame-soot method and characterized the candle soot by using X-rays Diffraction (XRD), Raman spectroscopy, Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) for exploring structural and elemental compositions.

In order to evaluate the catalytic ability for the reduction of tri-iodide ions, impedance spectra can be obtained by using either a working DSC or a dummy cell [13]. The structure of a dummy cell is simpler than that of a working DSC as it is fabricated without dye-sensitized TiO2 film. A dummy cell is prepared by assembling two electrodes coated with catalyst. The electrodes are separated with a spacer and the gap between them is filled with an electrolyte [3,11,13]. A dummy cell fabricated with two identical electrodes (known as symmetrical electrochemcal cell) is generally employed in EIS [3, 11, 14]. The value of the charge transfer resistance, Rct at the catalyst-electrolyte interface of such cell indicates the ability of the catalyst for the reduction of tri-iodide ions. Smaller value of Rct at the catalyst-electrolyte interface implies better ablitity for the tri-iodide reduction [3, 13] and hence high efficiency. In this research, EIS of symmetrical dummy cells were carried out to evaluate the catalytic ability of the candle soot by measuring the Rct. The electrodes of the symmetrical electrochemical cells were prepared by coating a film of candle soot and value of the Rct at the interface of the candle soot based film and electrolyte was determined. The value of the Rct at the candle soot-electrolyte interface was ~4.42 Ω cm^2 compared to ~5.04 Ω cm^2 at the platinum-electrolyte interface.

2 Experimental

2.1 Sample preparation

Candles were bought at a grocery shop in Bhaktapur and carbon (soot) was prepared by flame-soot method (low-cost, traditional and simple method for the preparation of carbon). We have been using this method of preparing carbon samples for application in supercapacitors and dye-sensitized solar cells. The procedure of preparing the candle soot is similar to that described by Joshi et al., [4]. The experimental setup for the preparation of candle soot is shown in Figure 1. The flame of the candle lamp was obstructed by a porcelain bowl, Figure 1(a). The candle soot, deposited on the inner surface of the bowl, was collected for characterizations. A photograph of the collected candle soot sample is shown in Figure 1(b).

2.2 Characterization of candle soot for surface morphology and elemental composition

The elemental and structural composition of the carbon samples were investigated using SEM-EDS, XRD, and Raman spectroscopy. The SEM and SEM-EDS were carried out using FEI Helios Nanolab 400 Scanning Electron Microscope. Powder diffractometer (D2 PHASER, Bruker) was used for the XRD of the sample. Figure 2 shows the SEM images with different magnifications of the candle soot based carbon film prepared with carboxymethyl cellulose (CMC) as a binder. Figure 2(a) and Figure 2(b) are SEM images with ~6500X and ~20000X magnifications, respectively. These images show porous and rough surface of the film formed by interconnected carbon particles of a few tens of nanometers; particles of size ~50 nm were dominant ones in the film. Figure 3(a) is the EDS spectrum and the insets show the scanned area with elemental composition of the sample. The candle soot comprises ~96% of carbon and ~4% (atomic) oxygen. Figure 3(b) and Figure 3(c) depict the mapping of the elements in the film. Figure 4 is the XRD spectrum of the candle soot. The two broad peaks centered at 2 of ~25^0 and ~42^0 imply that the candle soot contains mainly amorphous form of graphitic carbon [3,15]. We also performed Raman spectroscopy of the samples. Figure 5 shows Raman spectra with two prominent peaks centered at wave number ~1361 cm^{-1} and ~1579 cm^{-1} which are known as D-band and G-band, respectively. The D-band is attributed to disoriented or defect riched carbonaceous material while the G-band arises due to ordered or graphitic carbon [3,15,16]. The findings of the Raman analysis is analogous to those from the XRD that the candle soot comprises both disordered and ordered forms of carbon. The portions of disordered carbon and ordered carbon (graphitic crystallites) in the candle soot were calculated by Lorentzian line shapes fitting of the Raman spectrum [17]. The content of disordered carbon was ~47% compared to ~53% of the ordered carbon and the value of ID/IG was ~0.9.

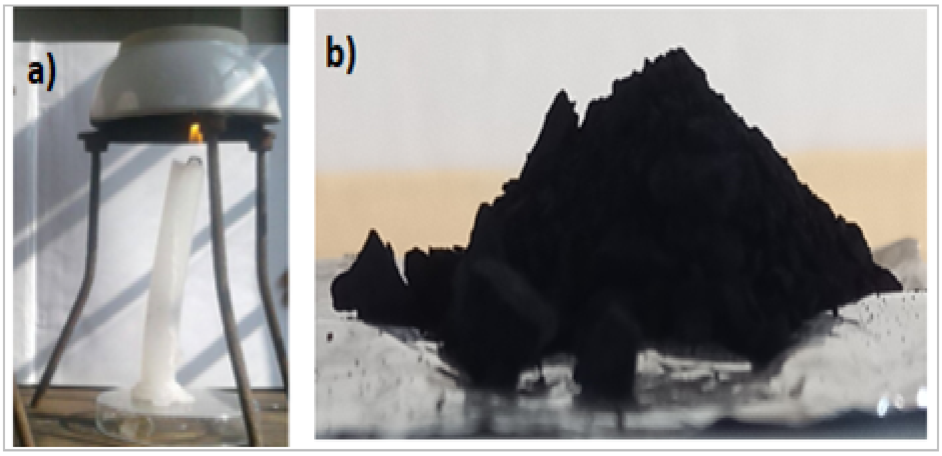

Figure 1: Preparation of carbon soot (a) experimental setup and (b) sample of candle soot.

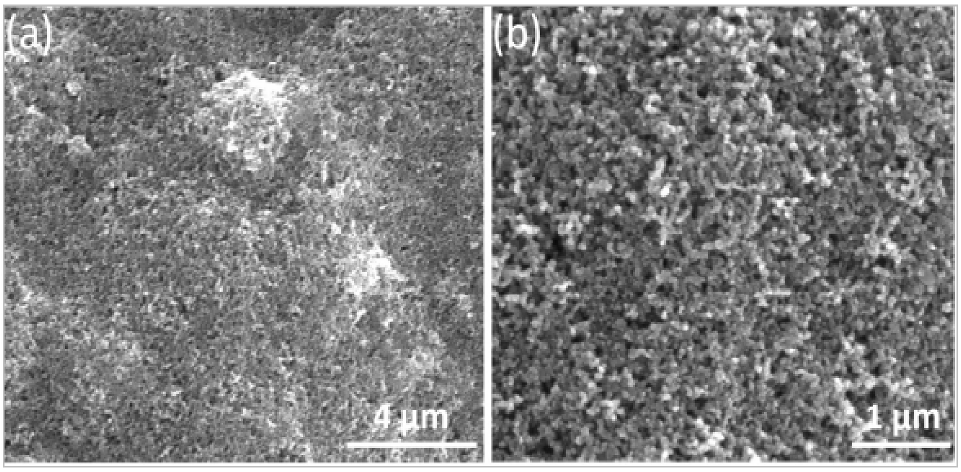

Figure 2: SEM images of candle soot based film with magnification of (a) ∼ 6500X and (b)∼20000X.

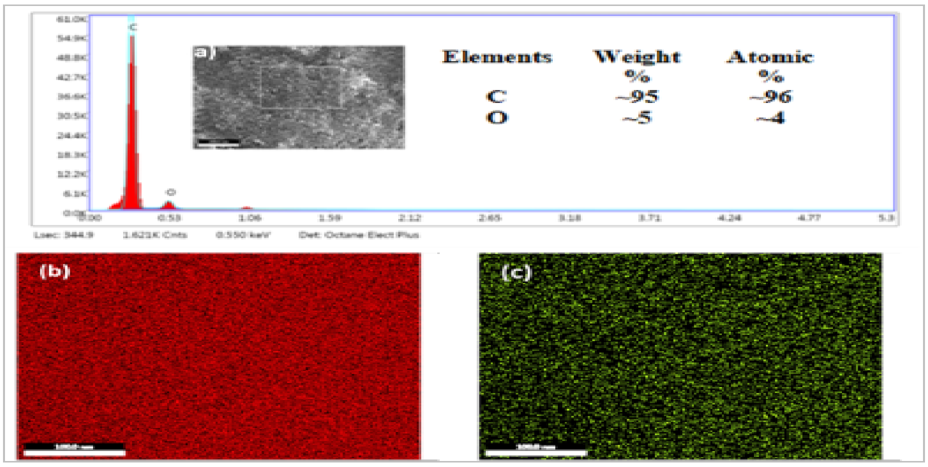

Figure 3: SEM images of candle soot based film with magnification of (a) ∼ 6500X and (b)∼20000X.

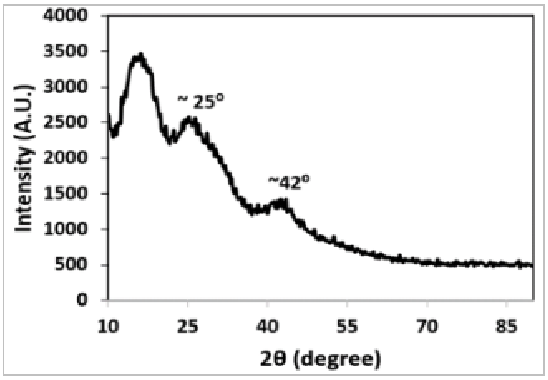

Figure 4: XRD spectrum of the candle soot.

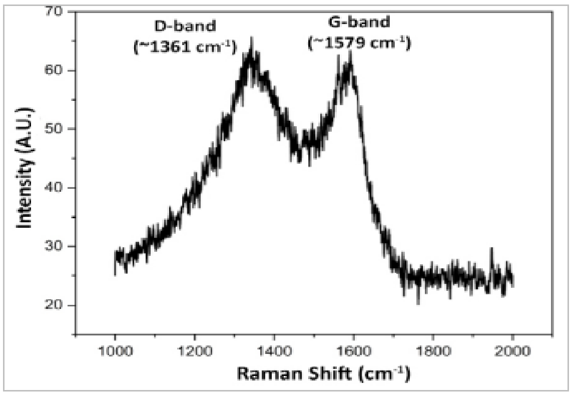

Figure 5: Raman spectrum of the candle soot.

3 Results and Discussion

The catalytic ability for the reduction of tri-iodide ions of candle soot was investigated by EIS of the electrochemical symmetrical cells prepared with two identical electrodes coated with the film of the candle soot.

A schematic diagram of the electrochemical cell is shown in Figure 6. In order to prepare the carbon based electrodes, first of all, the paste of candle soot was prepared by mixing ∼0.1 g of candle soot with ∼1.5 ml of aqueous solution of CMC (∼2%

concentration). The mixture was stirred and left in an ambient environment overnight. The mixture was centrifuged to remove excessive binder solution and doctorbladed onto clean FTO-glass substrates. The carbon film, coated on the FTO, was dried at a temperature of ∼80 ^{0}C for 12 hours. Two identical candle soot-based electrodes, prepared as described above, were assembled with a sealant and a liquid electrolyte containing iodide/tri-iodide ions (Iodolyte AN-50 purchased from Solaronix, Switzerland) was injected into the symmetrical cell. To compare the catalytic ability of the candle soot-based film, symmetrical electrochemical cells with platinum coated electrodes were also prepared. The EIS of the electrochemical cells were performed using Interface 1010E (Gamry Instruments, USA) in potentiostatic mode with 10 mV AC signals of frequencies ranging from 0.1 Hz to 100 KHz.

Figure 8 shows their equivalent circuits used to fit the Nyquist plots [14,18–20]. Figure 8(a) is the conventional equivalent circuit [14,20] in which Rs is the series resistance. The Rs is mainly attributed to the resistance of the electrodes and electrolyte of the symmetrical cell. Rct is the charge transfer resistance at electrode-electrolyte interface. Similarly, ZN is Nernst diffusion impedance and this deals with the impedance that arises from the diffusion of ions in the liquid electrolyte. CPE is a constant phase element, and this is related to the double layer capacitor formed at the electrode-electrolyte interface [3,11,14,18–20]. The equivalent circuit shown in Figure 8(a) was used to fit the Nyquist plot of the platinum based symmetrical cell. For better fitting of the Nyquist plot of the carbon soot based symmetrical cell, the equivalent circuit [18] shown in Figure 8(b) was used. This equivalent circuit was proposed by Kwon et al., to fit Nyquist plots of porous carbon electrodes. In this circuit C_{dl} is the double layer capacitor which is equivalent to CPE of the conventional equivalent circuit, Figure 8(a). In addition to the circuit elements mentioned above, electron transport resistance (R_{tms}) and trap capacitance (C_{trap}) were introduced in the new equivalent circuit [18]. R_{tms} and C_{trap} arise because of the carbon layer [18]. According to Kwon et al., carbon film is rich in superficial defects which exist mostly at grain boundaries and near carbon surface. Electrons are trapped in such regions and C_{trap} is formed [18]. The values of the parameters like Rtms, C_{trap}, R_s, R_{ct} of symmetrical cells were obtained by curve fitting of the Nyquist plots using Gamry Echem Analyst (Gamry Instrument, USA). The values of R_{tms} and C_{trap} were ∼0.79 Ωand∼3.4 μF, respectively. For the symmetrical cells with platinum electrodes, the values of these parameters are assumed to be negligibly small as platinum is highly conducting and the thickness of platinum used at the electrode is ultrathin compared to the carbon layer [18].

Rs of the symmetrical cells with platinum and candle soot were ∼24.17 Ω and ∼25.75 Ω, respectively, and these values are nearly equal. In a DSC, series resistance of the solar cell can affect its power conversion efficiency. An increase in series resistance of the solar cell decreases fill factor (FF), and low FF results lower efficiency of the solar cell [3]. The series resistance of the solar cell is mainly the sum of the ohmic resistances contributed from its components–photoelectrode, electrolyte, and counter electrode. As the values of the ohmic resistances of the platinum based symmetrical cell and candle soot based symmetrical cell are almost equal, it can be concluded that replacing a platinum with a candle soot in a DSC will not affect the power conversion efficiency of the solar cell. Along with the similarity of the R_s values of the symmetrical cells, their charge transfer resistance, R_{ct}, were also nearly equal. The values of the $R_{ct}$of the symmetrical cells with platinum and candle soot were ∼7.08 Ω (5.04 Ωcm^2) and 6.21 Ω (4.42 Ωcm^2), respectively. The R_{ct} at the catalyst-electrolyte interface of the symmetrical cells tells us effectiveness of the catalyst in the reduction of tri-iodide ions into iodide ions in the electrolyte. Smaller value of R_{ct} implies a faster rate of the reduction of the tri-iodide ions [3, 11, 14, 19, 20]. Hauch and Georg, in 2001, mentioned that the value of the R_{ct} of the catalyst should not be more than 10 Ωcm^2 for the fabrication of a good DSC [14]. In this research, R_{ct} of the candle soot based electrodes was lower than 10 Ωcm^2. Hence, the candle soot based electrodes can be used as counter electrodes of DSCs. Moreover, the comparable value of R_{ct} of the candle soot and platinum based cells indicate that the catalytic ability of candle soot based electrode for the reduction of tri-iodide ions was also comparable to that of the platinum based electrode.

The catalytic ability of the carbon based counter electrode depends upon its surface morphology and elemental composition. The SEM images shown in Figure 2 revealed rough and porous surface texture of the film. This yields a larger surface area and provides a large electrolyte-catalyst interface, which can be a merit for the fast reduction of tri-iodide ions. Also, the concentration of carbon in the candle soot is very high (∼96%) which could be another reason of low R_{ct}value of the candle soot. Similarly, Raman spectroscopy revealed the existence of disordered and ordered crystalline graphitic carbon in almost same proportion in the candle soot samples. Ordered crystalline graphitic carbon yields high electric conductivity. On the other hand, the presence of disorded carbon or defect rich carbon in the candle soots might have contributed in the fast reduction of tri-iodide ions. Graphitic crystallites exhibit a structural arrangement comprising basal planes, which are parallel to the layers of graphite, and edge planes, oriented perpendicular to the basal planes [21–23]. Notably, the electron transfer kinetics at the edge planes is more faster than that in the basal planes [21, 22]. Generally, graphitic particles of small size contain more edge planes than those of large particles. Veerappan et al., adopted submicron (700 - 900 nm) sized colloidal graphite (CG) and several micron sized graphite particles (AG20) for fabrication of counter electrodes of dye-sensitized solar cells. They reported that the smaller sized graphite particles (CG) have more edge planes than the larger ones. The symmetrical cells based on CG yielded lower Rct than the symmetrical cell based on AG20 [22]. The candle soot in this research has a particle size of ∼50 nm and the portion of the defective carbon in the candle soot is significantly high. So, it can be expected that the candle soot contains plenty of edge planes which contributed in fast reduction of tri-iodide ions.

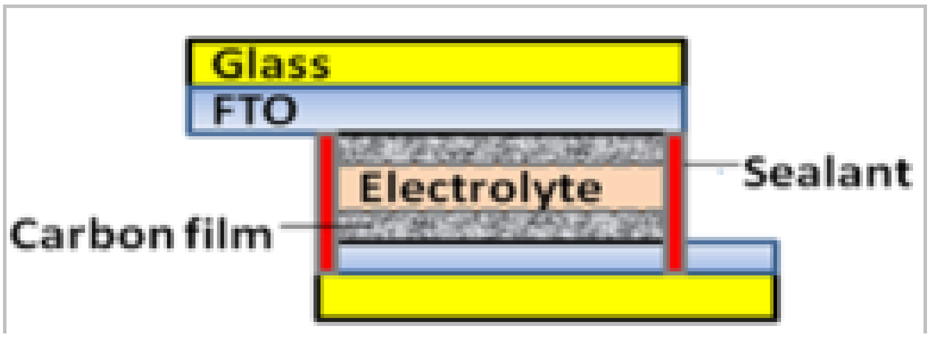

Figure 6: Schematic of electrochemical symmetrical cells. Modified from ref. [14]

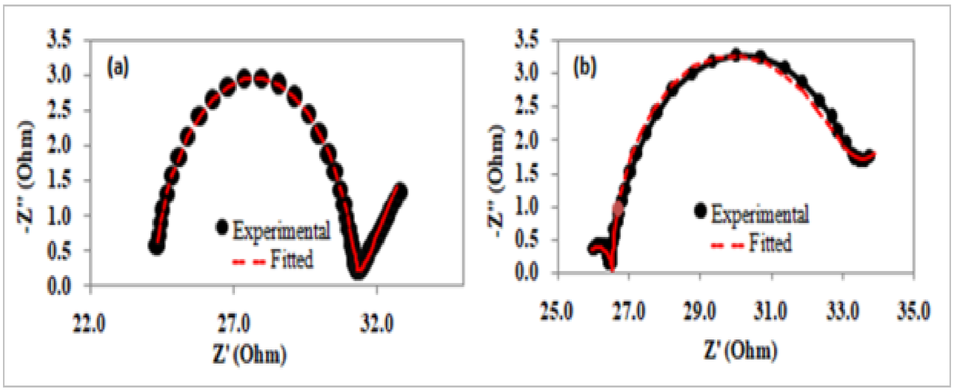

Figure 7: Nyquist plots of electrochemical symmetrical cells with (a) platinum coated electrodes and (b) candle soot coated electrodes.

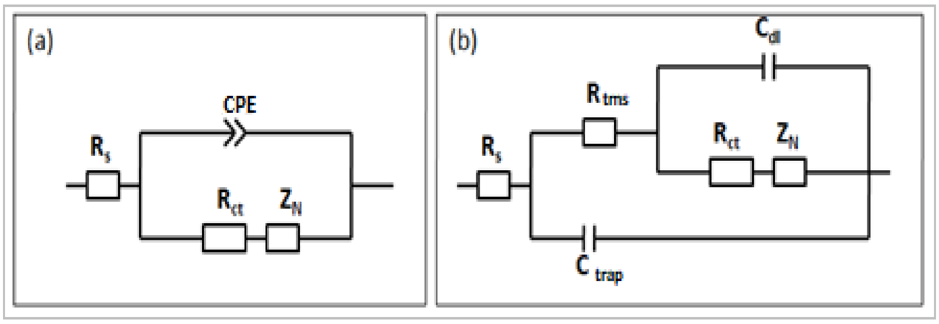

Figure 8: quivalent circuits used to fit Nyquist plots of electrochemical symmetrical cells with (a) platinum coated electrodes modified from ref. [14] and (b) candle soot coated electrodes modified from ref. [18].

4 Conclusion

Candle soot was investigated aiming to use it as a catalyst to replace expensive platinum used in DSCs. The candle soot consists of carbon nanoparticles comprising ordered and disordered carbon with a high concentration of carbon (∼96%, Atomic). The EIS of the symmetrical electrochemical cells with the candle soot based electrodes showed that their series resistance and charge transfer resistance are nearly equal to those of the platinum based symmetrical cells. Candle soot can be prepared with low-cost precursor and using simple techniques. So, this carbonaceous material can be a low-cost and efficient counter electrode material alternate to expensive platinum used in DSCs.

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References

[1] E. Frackowiak and F. Béguin. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon*, 39:937–950, 2001. https://doi.org/10.1016/S0008-6223(00)00183-4

[2] B. O'Regan and M. Grätzel. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal tio2 films. *Nature*, 353:737–740, 1991. https://doi.org/10.1038/353737a0

[3] P. Joshi et al. Electrospun carbon nanofibers as low-cost counter electrode for dye-sensitized solar cells. *ACS Appl Mater Interfaces*, 2:3572–3577, 2010. https://doi.org/10.1021/am100742s

[4] P. Joshi et al. Composite of lampblack and printer toner powder as a low-cost counter electrode material for dye-sensitized solar cells. *BIBECHANA*, 17:58–66, 2020. https://doi.org/10.3126/bibechana.v17i0.25598

[5] W. J. Lee et al. Efficient dye-sensitized solar cells with catalytic multiwall carbon nanotube counter electrodes. *ACS Appl. Mater. Interfaces*, 1:1145–1149, 2009. https://doi.org/10.1021/am800249k

[6] P. Joshi et al. Dye-sensitized solar cells based on low cost nanoscale carbon/tio2 composite counter electrode. *Energy Environ. Sci.*, 2:426–429, 2009. https://doi.org/10.1039/B815947P

[7] P. Joshi et al. Nickel incorporated carbon nanotube/nanofiber composites as counter electrodes for dye-sensitized solar cells. *Nanoscale*, 4:5659–5664, 2012. https://doi.org/10.1039/C2NR31379K

[8] J. Qiu et al. Morphology-controlled fabrication of nico2s4 nanostructures decorating carbon nanofibers as low-cost counter electrode for efficient dye-sensitized solar cells. *Electrochimica Acta*, 367:137451, 2021. https://doi.org/10.1016/j.electacta.2020.137451

[9] H. Wang and Y. H. Hu. Graphene as a counter electrode material for dye-sensitized solar cells. *Energy Environ. Sci.*, 5:8182–8188, 2012. https://doi.org/10.1039/C2EE21905K

[10] X. Meng et al. Scrutinizing defects and defect density of selenium-doped graphene for high-efficiency triiodide reduction in dye-sensitized solar cells. *Angewandte Chemie International Edition*, 57:4682–4686, 2018. https://doi.org/10.1002/anie.201801337

[11] U. Lawaju and P. Joshi. Dye-sensitized solar cells with cost-effective counter electrode based on soybean oil lampblack. *Journal of Nepal Physical Society*, 8:1–6, 2022. https://doi.org/10.3126/jnphyssoc.v8i1.48279

[12] P. Joshi. Characterization of bamboo based carbon powder applicable for fabrication of low-cost counter electrodes of dye-sensitized solar cells. *Tribhuvan University Journal*, 32:1–8, 2018. https://doi.org/10.3126/tuj.v32i1.24757

[13] T. N. Murakami et al. Highly efficient dye-sensitized solar cells based on carbon black counter electrodes. *J. Electrochem. Soc.*, 153:A2255, 2006. https://doi.org/10.1149/1.2358087

[14] A. Hauch and A. Georg. Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells. *Electrochimica Acta*, 46:3457–3466, 2001. https://doi.org/10.1016/S0013-4686(01)00540-0

[15] S. Singh et al. Candle soot-derived carbon nanoparticles: An inexpensive and efficient electrode for microbial fuel cells. *Electrochimica Acta*, 264:119–127, 2018. https://doi.org/10.1016/j.electacta.2018.01.110

[16] A. Sadezky et al. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon*, 43:1731–1742, 2005. https://doi.org/10.1016/j.carbon.2005.02.018

[17] A. K.C. et al. Heterogeneous integration of high-quality diamond on aluminum nitride with low and high seeding density. *Journal of Crystal Growth*, 610:127172, 2023. https://doi.org/10.1016/j.jcrysgro.2023.127172

[18] W. Kwon et al. A new equivalent circuit model for porous carbon electrodes in charge transfer reaction of iodide/triiodide redox couples. *Electrochimica Acta*, 68:110–113, 2012. https://doi.org/10.1016/j.electacta.2012.02.056

[19] S. M. Park and J. S. Yoo. Electrochemical impedance spectroscopy for better electrochemical measurements. *Anal. Chem.*, 75:455A–461A, 2003. https://doi.org/10.1021/ac0313973

[20] K. C. Sun et al. Electrocatalytic porous nanocomposite of graphite nanoplatelets anchored with exfoliated activated carbon filler as counter electrode for dye sensitized solar cells. *Solar Energy*, 167:95–101, 2018. https://doi.org/10.1016/j.solener.2018.04.002

[21] P. Poudel and Q. Qiao. Carbon nanostructure counter electrodes for low cost and stable dye-sensitized solar cells. *Nano Energy*, 4:157–175, 2014. https://doi.org/10.1016/j.nanoen.2013.10.012

[22] G. Veerappan et al. Sub-micrometer-sized graphite as a conducting and catalytic counter electrode for dye-sensitized solar cells. *ACS Appl. Mater. Interfaces*, 3:857–862, 2011. https://doi.org/10.1021/am101204f

[23] C. E. Banks et al. Electrocatalysis at graphite and carbon nanotube modified electrodes: Edge-plane sites and tube ends are the reactive sites. *Chem. Commun.*, pages 829–841, 2005. https://doi.org/10.1039/B413177K