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Improving the effective photovoltaic performance in dye-sensitized solar cells using an azobenzenecarboxylic acid-based system

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Abstract

In this research, an azobenzenecarboxylic acid was used as a sufficient co-adsorbent in combination with N719 dye. As it is found from the results, an optimized concentration of the co-absorbent leads to the highest efficiency. The dye-sensitized solar cells (DSSCs) parameters such as short-circuit current (J_{sc}), open-circuit voltage (V_{oc}) and conversion efficiency (η) were obtained -14.87 mA/cm^2 , 0.765 V and 5.20% respectively. Based on the results, the N719/Azobenzenecarboxylic-based system shows a significant increase in V_{oc} and J_{sc} , resulting in an $\sim 21\%$ improvement in the efficiency. A higher conversion efficiency for the co-adsorbent-based systems was assigned to their enhanced η , which is attributed to reduced dye aggregation, higher electron injection and increased V_{oc} . This corresponded to the improved electron density in the TiO_2 conduction band of the photoanode and reduced charge recombination revealed through electrochemical impedance spectroscopy measurements. Also, evidence was provided for a long charge life time and a high resistance of charge recombination for the co-absorbed solar cells.

Keywords: Electrochemistry, Analytical chemistry

1. Introduction

The increasing need for energy has driven research towards efficient utilization of renewable resources such as low-cost, environmentally friendly, and abundant solar energy to electrical energy. The first reports of obtaining an conversion efficiency of 1–2% for DSSCs came in the 1960's and 70's [1]. In 1991, environmental friendly and high-efficiency DSSCs-based polypyridyl ruthenium (II) complex dyes were developed by Grätzel et al. with a reported η of >10% [2]. Since then, efforts have been made to improve the performance and increase the efficiency of these particular cells [3, 4, 5, 6]. Currently, the maximum reported η is 13% [7]; There are three unwanted processes that lead to losses in Voc and Jsc. First of all, electrons injected into the Fermi level of a semiconductor tend to recombine with the I^-/I_3^- couple and the cation of dye [known as charge recombination (CR)], decreasing the Voc of the cells. Secondly, a strong intermolecular interaction among the molecules of dye on the semiconductor surface results in the decline of the Jsc. Thirdly, TiO_2 surface protonation changes the amount of dye adsorption, resulting in a decrease of the stability of the device [8, 9, 10]. Therefore, there have been several attempts to suppress and prevent these occurrences, such as using additives, co-adsorbents, and metal oxides. Among them, the use of co-adsorbents has been very effective. Co-adsorbents are substances that can be adsorbed simultaneously onto the semiconductor surface of DSSCs in a competition with dye molecules, occupying the vacant sites on the semiconductor surface uncovered by dye molecules to depress CR [11, 12, 13]. In most cases, they are organic amphiphilic molecules containing anchoring groups such as carboxylic or phosphonic groups. The efficient grafting of co-adsorbents on the surface of a mesoporous semiconductor is due to these anchoring groups ($-COOH$, $-H_2PO_3$, $-SO_3H$, etc.) [4]. For carboxyl group binding to occur, there should be an electronic coupling between the cationic metal and oxygen atom of the carboxylic acid which promote electron transfer upon photoexcitation. The nature of linking of carboxyl group onto the metal oxide also plays a role in enhancing electron injection.

Herein, an N719-based dye/co-adsorbent system [N719 with (2-(N,N-dimethyl-4-aminophenyl) azobenzenecarboxylic acid), CA] is studied. The prepared device can protect the unoccupied free surface of TiO_2 against the approaching triiodide ions and, thereby, retard the back reaction of the injected electrons and improve the Voc. When the N719 dye with CA was adsorbed onto the TiO_2 film [4]deprotonation of the $-COOH$ group in the dye resulted in dye less adsorption on the semiconductor surface, due to the electrostatic repulsion of the ($-COO^-$) groups [14]. The larger molecular size of N719 incomparision with CA resulted in the lower dye adsorption on the TiO_2 surface. Moreover, here is an effective comparison between CA and N719 dye to locate in the empty spots on the TiO_2 surface. Co-adsorbent covers the vacant sites on TiO_2 , thus preventing dye aggregation,

retarding CR and improving both Voc and Jsc values in DSSC-based coadsorbent systems.

2. Experimental

2.1. Materials

N719 dye: [cis-bis(isothiocyanato)bis(2,2-bipyridyl-4,4-dicarboxylato)-ruthenium(II)bis-tetra butyl ammonium], acetonitrile, valeronitrile, guanidium thiocyanate, hexachloro platinic acid (H_2PtCl_6), 4-tert-butylpyridine (4-tBP) and 2-(N,N-dimethyl-4-aminophenyl) azobenzenecarboxylic acid were purchased from Sigma-Aldrich. Iodine (I_2) and lithium iodide (LiI) were obtained from Merck. Titania pastes were prepared in research laboratory [3]. Dye solutions (0.3 mM) containing different amounts of CA were prepared and used to sensitize the TiO_2 electrodes.

2.2. Dye-sensitized solar cell fabrication

DSSCs were fabricated according to the following procedure. FTO-coated glass substrates were washed in an ultrasonic bath for 15 min, rinsed with water and ethanol. A TiO_2 electrode (photoanode) with an optimized thickness (12 μm) was obtained by spreading a lab-made TiO_2 paste (containing 20-30-nm-sized TiO_2 particles) onto the conducting glass (FTO) using the doctor blade technique. The bladed paste was sintered at 500 °C for 30 min. The photoanodes were cooled to 80 °C and sensitized by being immersed in an N719 dye solution (0.3 mM) at room temperature for 20 h. Next, the dye-sensitized electrode was rinsed with an acetonitrile or ethanol solution and dried at room temperature. The active area of the TiO_2 surface was 0.16 cm^2 . If an FTO substrate was used as a photocathode, it had to be cleaned by distilled water, acetone and solutions of 0.1 M HCl in ethanol. To prepare a platinumized photocathode, a 0.6 M H_2PtCl_6 solution (in ethanol) was put on FTO dropwise, and then it was fired at 450 °C for 15 min. The two photoelectrodes were sealed with a 0.5-mm-wide strip of a thick Surlyn frame at 110 °C. After sealing, the cells were filled on the photocathode side with I^-/I_3^- redox couple-based electrolyte solution put in through a hole (diameter = 1 mm). The typical concentration of the electrolyte was as follows: 0.03 M I_2 , 0.6 M LiI, 0.1 M guanidium thiocyanate (GTS) and 0.5 M 4-tBP in 5 mL of acetonitrile: valeronitrile (85:15).

2.3. Characterizations

The amount of dye adsorption was measured by assessing dye desorption (detached from the semiconductor surface) into a basic solution (0.1 M KOH in EtOH (1/1)) followed by spectroscopic analysis. A spectrophotometer Optizen model 3220 was used to measure the UV-visible spectra of the N719 dye only or the N719 dye containing different concentrations of co adsorbent ((0.01, 0.05, 0.1 and 0.5

mM CA)) adsorbed onto a TiO_2 surface. A standard solar spectrum of an air mass of 1.5 was used for characterization (Luzchem-Solar). J-V curves were obtained by applying an external bias to the cell and measuring the photovoltaic characteristics with a computerized potentiostat/galvanostat instrument. In the dark condition, the electrochemical impedance spectroscopy (EIS) was performed using an electrochemical system (IVIUMstat).

3. Results and discussion

3.1. UV-Vis absorption

Two different efforts were studied for adsorption of the N719/co-adsorbent on the semiconductor surface, including simultaneous and sequential (post) adsorptions of the co-adsorbent (Fig. 1). Different concentrations of the dye in corporation with the co-adsorbent were prepared, and then they were investigated with photovoltaic measurements.

The factors such as the thickness of the barrier layer, morphology, the surface area of the TiO_2 electrode, etc have an effective role in the amount of semiconductor dye loading. Fig. 2 shows the Ultraviolet-Visible (UV-Vis) absorption spectra of a potassium hydroxide solution (0.1 M), which contains the dye molecules detached from the semiconducting surface. This amount of the dye decreased from 2.4 to 0.6, 0.8, 1.14, 1.4, and 1.6 for the concentrations of 0.5 mM (simultaneous), 0.5 mM (sequential), 0.1 mM, 0.05 mM and 0.01 mM respectively. This led to 75, 67, 52, 42 and 33% slumps in the adsorption of dye on the TiO_2 surface. After the adsorption of the co-adsorbent and the dye on the surface of TiO_2 , due to the protonation of the surface with the electrostatic repulsion of negatively charged carboxylic acid group,

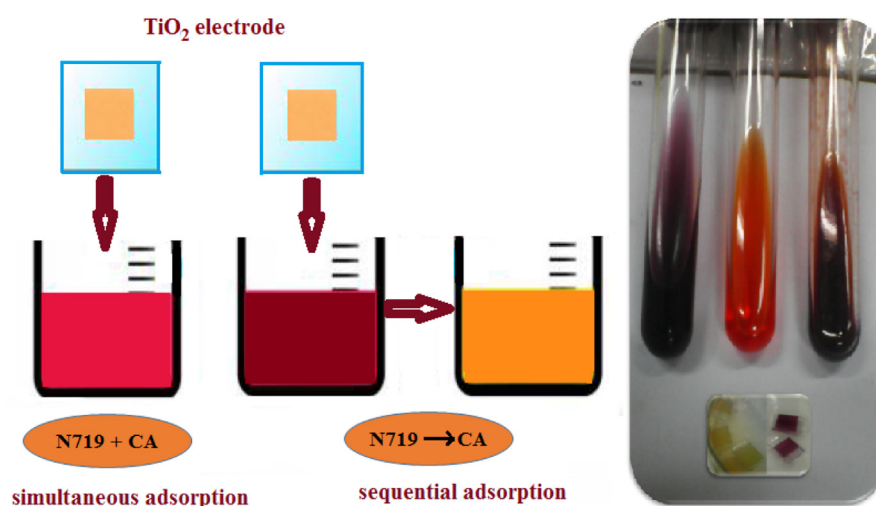


Fig. 1. Two different efforts for adsorption N719 and co-adsorbent on the semiconductor surface (simultaneous and the sequential adsorption).

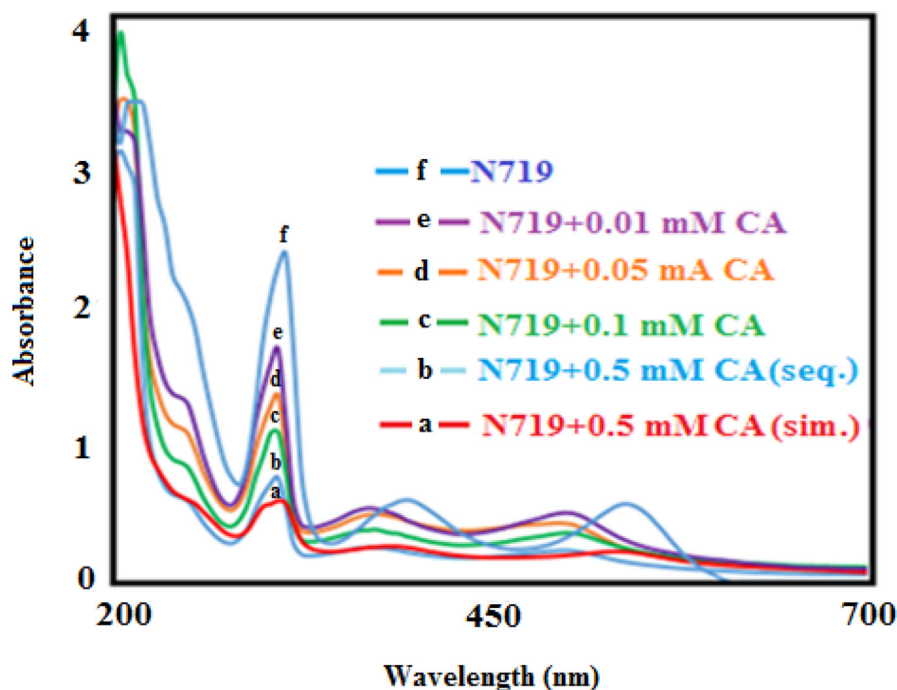


Fig. 2. Ultraviolet-Visible absorption spectra of the KOH (0.1 mol/L) in EtOH solution containing different concentration of desorbed-dye/co-adsorbent on the surface of TiO_2 . N719 (f, blue line), N719 + 0.01 mM CA (e, violet line), N719 + 0.05 mM CA (d, orange line), N719 + 0.1 mM CA (c, green line), N719 + 0.5 mM CA (b, pale blue line, sequential) and N719 + 0.5 mM CA (a, red line, simultaneous).

the amount of adsorbed dye on the semiconductor surface decreases effectively [14]. The N719/co-adsorbent system can inhibit competitive adsorption of dye molecules in the vacant spot on the TiO_2 surface and barricade the strong dyes intermolecular interaction on the semiconductor surface. This leads to an effective reduction of the interfacial charge recombination and improve the electron injection.

Fig. 3 presents the absorption spectra of the co-adsorbent, the dye, and the dye incorporated with the co-adsorbent in the solution and on the semiconductor surface. As it is found, CA displays a UV-Vis absorption spectrum in the solution at the wavelengths of 300–600 nm, which is beneficial for the light harvesting as presented in Fig. 3 (a). However, the dye only has a very weak absorption around 500 nm in the solution, as it is presented in Fig. 3 (b). The absorption spectra of N719 dye are shown at various wavelengths: metal-to-ligand charge transfer (534 nm and 390 nm), intraligand (π - π^*) charge transfer transitions (312 nm) [15]. The red shifted of co-adsorbent maximum absorption peak is shown in Fig. 3 (a) [from 462 nm (in the solution) to 480 nm (on the TiO_2 surface), known as a J-band]. This is due to the interaction with the TiO_2 surface [16]. Also, the blue shifted of N719 maximum absorption peak is shown in Fig. 3 (b) [from 534 nm (in the solution) to 480 nm (on the TiO_2 surface), known as a H-band] [17]. Fig. 3 (c) displays

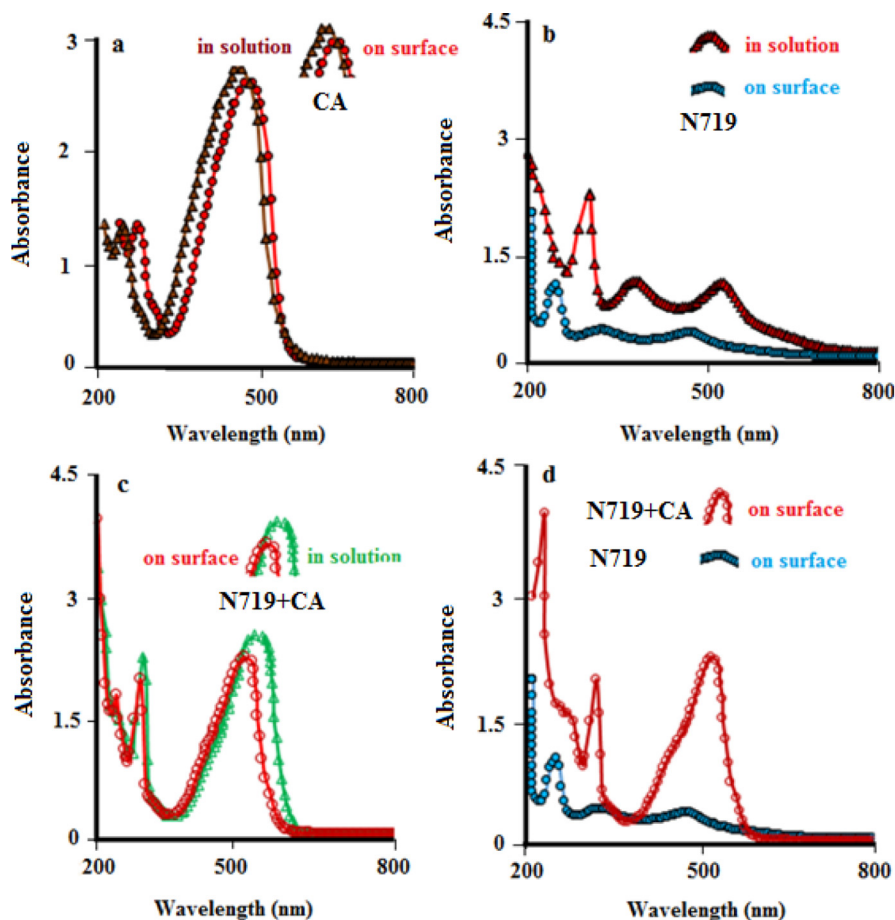


Fig. 3. (a–c) Ultraviolet-Visible absorption spectra of CA (0.5 mM), N719 (0.3 mM), and N719 (0.3 mM) + CA (0.5 mM) in acetonitrile (85)/valeronitrile (15) solution (triangle) and on the surface of TiO_2 (circle) respectively. (d) Ultraviolet-Visible absorption spectra of N719 (0.3 mM, Blue circle) and N719 (0.3 mM) + CA (0.5 mM, Red circle) on the TiO_2 surface.

N719 + CA on the TiO_2 surface and in the solution. The red shifted of N719 maximum absorption peak upon incorporation of CA as compared to that of dye alone on the TiO_2 surface (J-band) is shown in Fig. 3 (d), but it is still blue shifted in compare of the dye in the solution (J-band).

3.2. Photovoltaic performance

Typical current density-voltage measurements were done at a standard air mass of a 1.5 global illumination with a source set up at 100 mW/cm^2 to achieve photovoltaic features for DSSCs. are Fig. 4 and Table 1 display the typical J-V curves of N719 dye/CA-based DSSCs in simultaneous and sequential approaches and the photovoltaic characteristics respectively. A V_{oc} value of 0.74 V, a J_{sc} value of $-13.90 \text{ mA cm}^{-2}$ and a conversion efficiency of 4.30% resulted for the N719-based DSSCs. The J_{sc} value of the DSSCs for the N719 dye incorporation in different

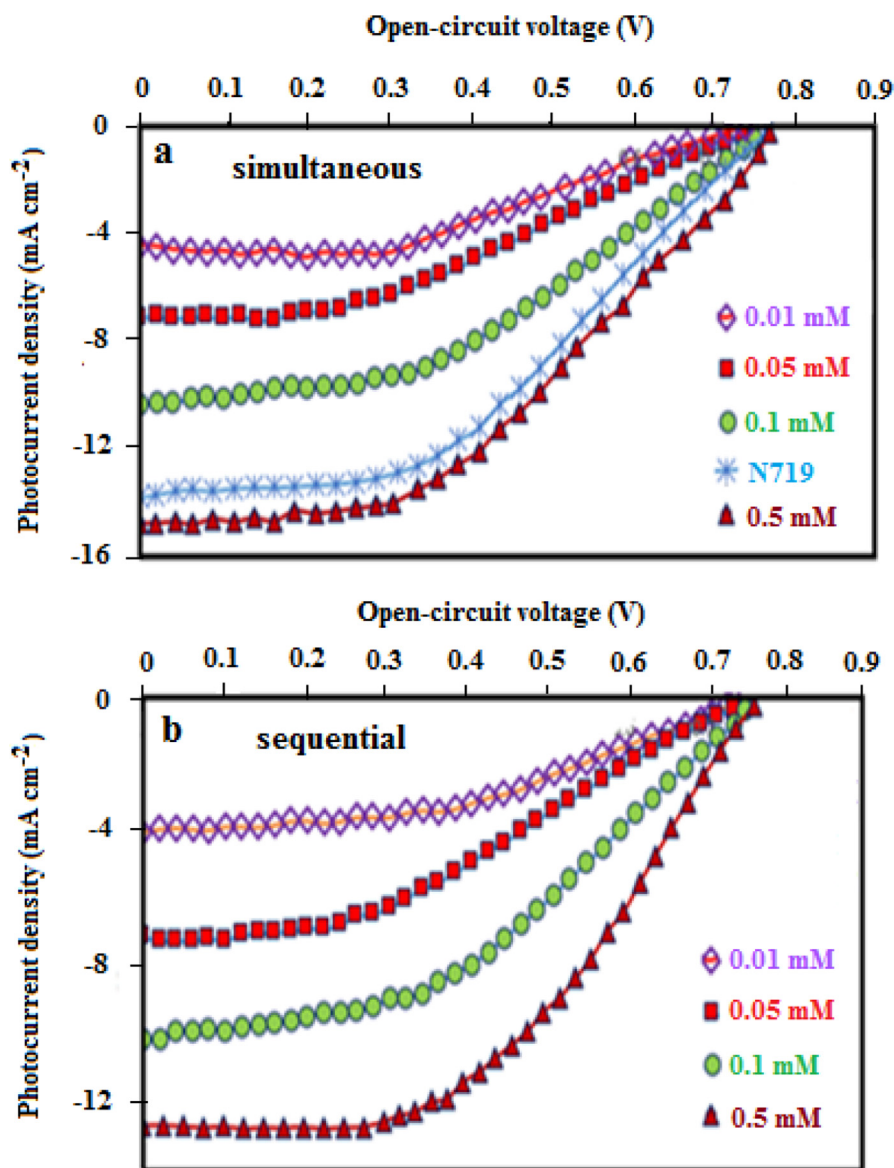


Fig. 4. J–V characteristics of N719/co-adsorbent system measured for different concentration of co-adsorbent: (a) N719 (star)+ [0.01 (diamond), 0.05 (square), 0.1 (circle) and 0.5 mM CA (triangle)]. (b) N719 → (0.01, 0.05, 0.1 and 0.5 mM CA).

concentrations of the co-adsorbent gradually increased according to the following order: dye/0.01 mM CA (-4.450 mAcm^{-2}) < dye/0.05 mM CA (-7.110 mAcm^{-2}) < dye/0.1 mM CA (-10.40 mAcm^{-2}) < dye/0.5 mM CA (-14.87 mAcm^{-2}) in the simultaneous manner and dye/0.01 mM CA (-4.040 mAcm^{-2}) < dye/0.05 mM CA (-7.150 mAcm^{-2}) < dye/0.1 mM CA (-10.47 mAcm^{-2}) < dye/0.5 mM CA (-12.80 mAcm^{-2}) in the sequential manner. The CR, the charge injection (CI) and light-harvesting efficiency (LHE) are the important factors that affect the value of J_{sc} in DSSCs. Based on the obtained results, the intermolecular interaction of dyes is obviously prevented in the N719/CA-based DSSCs due to the introduction

Table 1. Photovoltaic parameter for simultaneous adsorbent of co-adsorbent in different conditions.

CA/concentration	Voc (V)	Jsc (mA/cm ⁻²)	η%	R _{rec} (Ω)	τ _e (ms)
Simultaneous					
0.0	0.740	-13.90	4.30	564	27.31
0.5	0.765	-14.87	5.20	836	41.22
0.1	0.752	-10.40	3.28	417	19.83
0.05	0.748	-7.110	2.08	324	15.10
0.01	0.740	-4.450	1.47	279	11.84
Sequential					
0.0	0.740	-13.90	4.31	-	-
0.5	0.762	-12.80	4.47	-	-
0.1	0.752	-10.47	3.38	-	-
0.05	0.748	-7.150	2.06	-	-
0.01	0.740	-4.040	1.30	-	-

of CA among the dye molecules. This results in a faster CI rate from the non-aggregated dye molecules to the Fermi level of the photoanode electrode, in comparison with the aggregated dyes concluded in Jsc increasing. Therefore, the photovoltaic parameters for the N719/CA-based DSSC are as follows: Voc value of 0.765 V, Jsc value of -14.87 mAcm⁻², and a conversion efficiency of 5.20%. The Voc increasing is due to the occupation of the vacant spots of the semiconductor surface that were not touched by the dye alone in a higher concentration of the co-adsorbent in the simultaneous manner. Thereby, the charge recombination with the redox couple is retarded [13] while the enhancement of Jsc is related to the light absorption between 300 and 600 nm, according to Fig. 3 (a). An explanation in this regard is that CA occupies the free sites uncovered by the N719 dye on the semiconductor surface because of its small molecular size, leading to the enhanced electron lifetime [11], suppression of the CR, and enhancement of the η for the co-adsorbed DSSCs.

The characteristics of N719-CA-based cells in simultaneous and sequential approaches are presented in Fig. 5. The photovoltaics parameters and the dark current are obtained from the J-V measurements of DSSCs with different concentrations of the co-adsorbent. As it is obvious, CA might be effectual enough to screen iodine molecules or triiodide ions, which results in the improvement of Jsc, Voc, and the overall η in N719-CA-based cells. The results of this study are compared with the other works in Table 2 [18].

The dark current–voltage (J-V) characteristics provide a qualified measurement of the CR of the redox couple in the electrolyte and the TiO₂ conduction bond. The dark current-voltage parameters characteristics of the N719-CA-based cells are given in Fig. 5 (d). From the obtained results, the lowest dark current of the the solar cells with 0.5 mM CA, in comparison to the N719 dye alone and the other

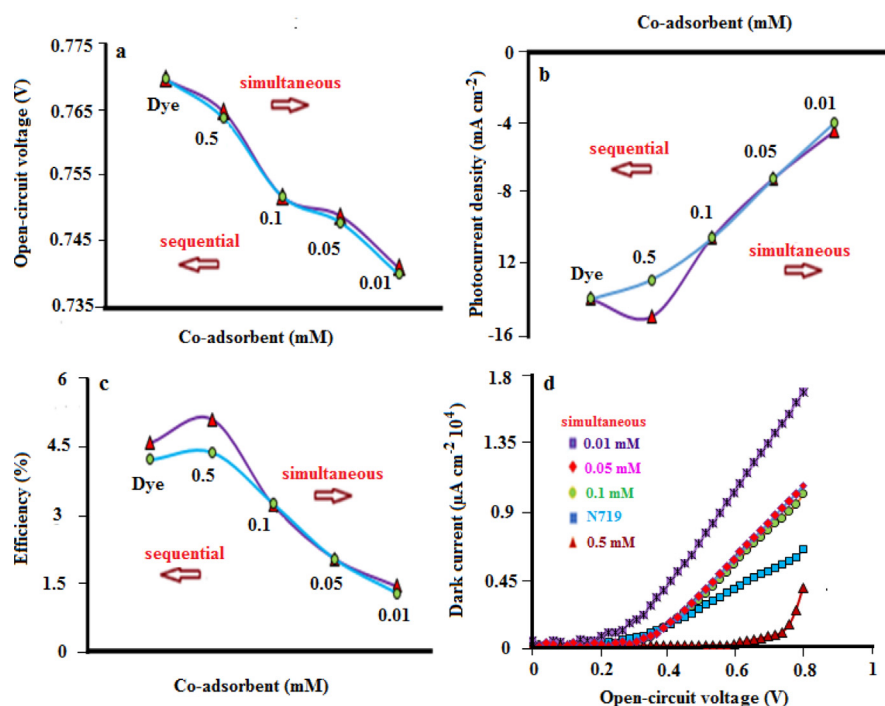


Fig. 5. The relationship between photovoltaic-characteristics of dye at different concentration of co-adsorbent: (a) N719 + (0.01, 0.05, 0.1 and 0.5 mM CA, triangle) and N719 → (0.01, 0.05, 0.1 and 0.5 mM CA, circle), (a) V_{oc} , (b) J_{sc} , and (c) η (%) respectively. (d) Dark current characteristics of dye at different concentration of co-adsorbent: N719 (blue square) + [0.01 (violet square), 0.05 (diamond), 0.1 (circle) and 0.5 mM CA (triangle)].

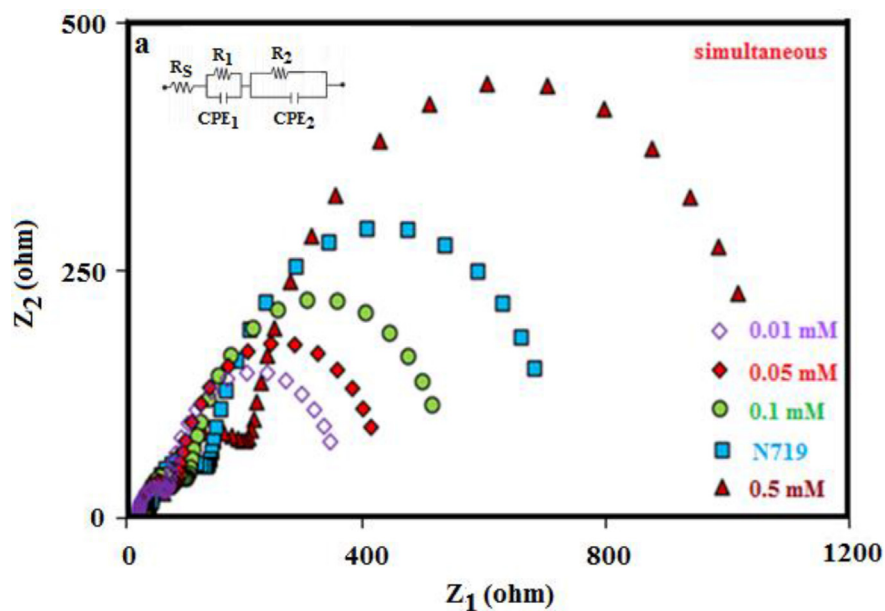
Table 2. The comparisons between different Coadsorbents in the various research studies.

Coadsorbent	$\eta\%$ (dye)	$\eta\%$ (dye + coadsorbent)	Increase percent	Ref.
Siloxane Derivatives	4.55	4.97	9.24%	[24]
Chenodeoxycholic acid	4.98	5.70	14.5%	[18]
3,4,5-Tris(dodecyloxy)benzoic acid	1.81	2.13	17.7%	[25]
Azobenzencarboxylic acid	4.30	5.20	20.9%	This work

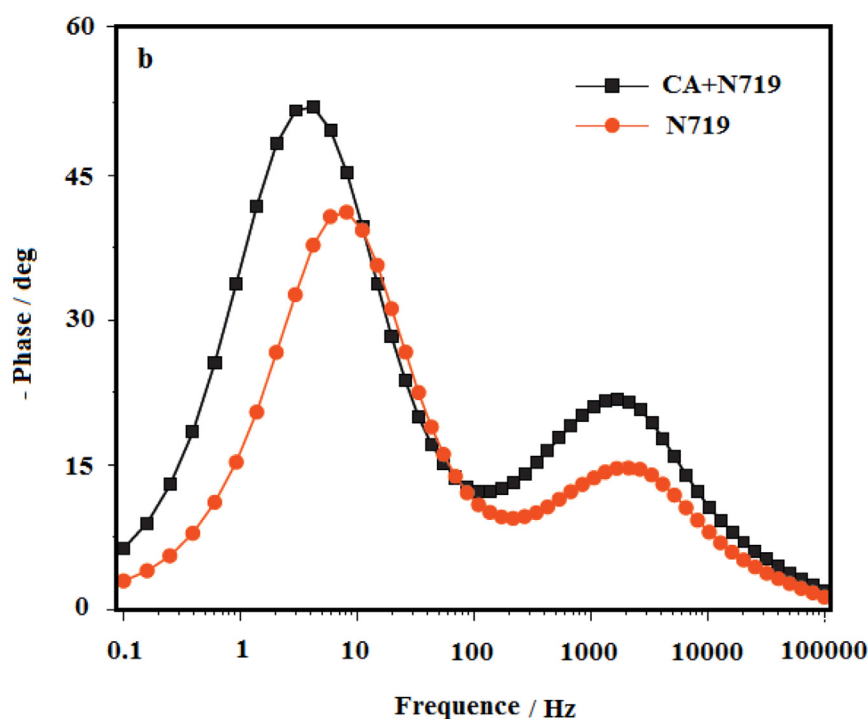
concentrations of the co-adsorbent, is related to the effective role of CA in screening I_2 or I_3^- and diminishing the CR rate. This is because the dark current is based on the flow of electrons from the semiconductor into the redox couple, resulting in a voltage reduction. On the other hand, a lower dark current suggests that CA acts as a barrier layer at the TiO_2 and electrolyte interface and, thus, increase the V_{oc} .

3.3. Electrochemical impedance spectroscopy

Using the EIS measurements, the CR value at the semiconductor/electrolyte interfacial can be determined. Fig. 6 (a) displays the Nyquist plots of the DSSCs for the



(a)



(b)

Fig. 6. (a) EIS spectra of DSSCs from 10^6 to 0.01 Hz for different concentration of co-adsorbent: N719 (square) + [0.01 (violet diamond), 0.05 (red diamond), 0.1 (circle) and 0.5 mM CA (triangle)]. The inset is an equivalent circuit used to analyses the device performance (see text for explanation). (b) Bode phase plots from EIS spectra for the DSSCs with an azobenzenecarboxylic acid co-adsorbent.

N719-CA-based solar cells system including the different concentrations of the co-adsorbent in dark. Furthermore, a simple equivalent circuit is shown at the top left of the Figure, and the fitting results are summarized in Table 1. Generally, the three semicircles of the EIS spectrum correspond to the photocathode electrode impedance (R_{Pt}), the dyed TiO_2 photoelectrode/electrolyte interfacial impedance (R_{TiO_2}), and the Nernst diffusion impedance (R_N) in the electrolyte. The studies indicate that the middle semicircle is related to the CR resistance at the interface of the TiO_2 /dye/electrolyte, and the increase in its diameter is due to retardation of the charge recombination resistance (R_{rec}) at the interface of the TiO_2 /dye/electrolyte [19, 20].

The co-adsorbent with a 0.5 mM concentration in the simultaneous approach demonstrates a larger middle frequency semicircle than the dye alone, and the other concentrations of the co-adsorbent of the sensitized device indicate an increase in the R_{rec} . Thus, co-adsorbents in high concentrations can serve as effective spacers to passive the semiconducting surface and, thereby, prevent the CR and improve the DSSCs overall efficiency [21].

According to suppress the back electron recombination with triiodide ion in the electrolyte, the electron life time (τ_e), at the photoanode/sensitizer (CA + N719 dye)/redox-based electrolyte [22] increased significantly. Fig. 6 (b) shows the Bode phase plots of the N719 dye only and the combination of CA and dye. The maximum frequency value (f_{max}) is defined as the electron transfer processes at the photoanode/sensitizer (CA + N719 dye)/electrolyte, were calculated 5.83 and 3.86 Hz, for the N719 and CA + N719 based systems, respectively. According to Eq. (1), for the 0.5 mM concentration of the co-adsorbent, the electron life time is found to be 41.22 ms, as compared to 19.83 ms estimated for 0.1 mM, 15.10 ms for 0.05 mM, 11.84 ms 0.01 mM, and 27.31 ms for the dye alone (Table 1).

$$\tau_e = 1/2\pi f_{max} \quad (1)$$

Because of the different degrees of occupation vacant sites (not covered by dye molecules) on the semiconducting surface, there exists a difference of electron lifetime values. The value of the later cell indicates a reduced rate of electron recombination. The higher R_{rec} value and the lower f_{max} resulted in the higher τ_e for the co-adsorbent based system (Table 1). Indeed, by increasing the electron lifetime, the V_{oc} increases effectively [23]. In the present case, incorporation of N719 with CA blocks the transfer of electrons from the conduction band of semiconductor to I_3^- effectively, retards the CR, and improves the electron lifetime which is accompanied with an increase in the V_{oc} value. Clearly, as follows, the results of the photovoltaic performance and EIS are in good agreement with each other due to observe a significant increase in the V_{oc} and η .

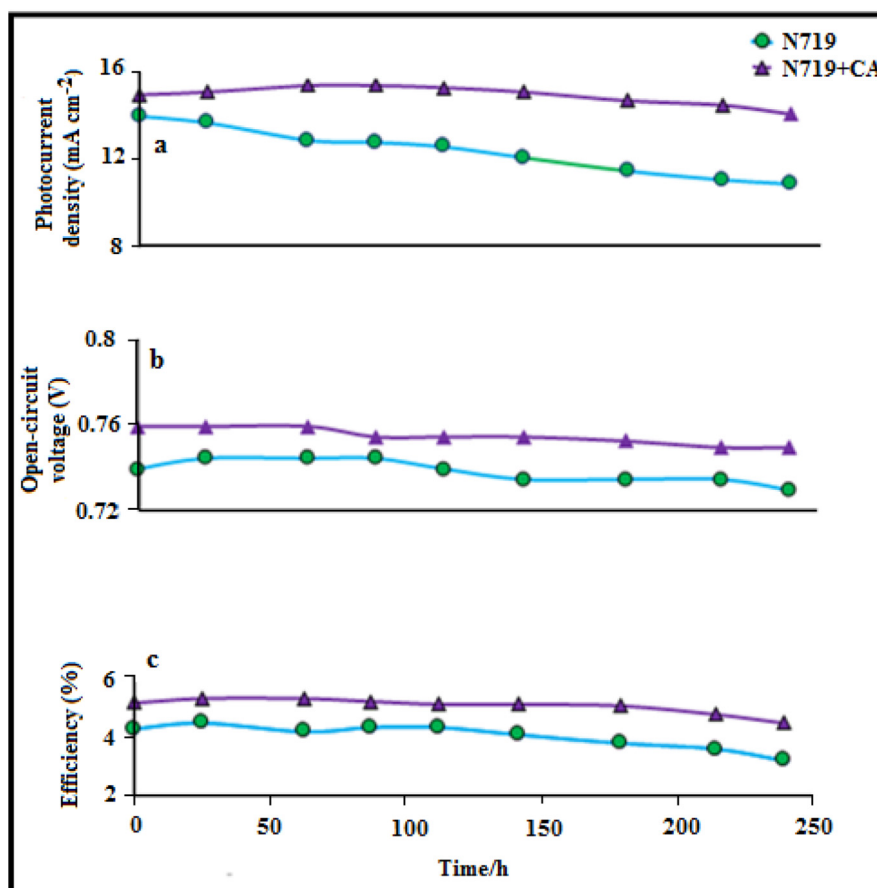


Fig. 7. A test of stability of N719 (circle) and N719 + CA (triangle) sensitized devices, (a) photocurrent density; (b) open-circuit voltage and (c) Efficiency (%).

3.4. Stability test

The stability test of N719 (circle) N719 + CA (triangle) sensitized solar cells was taken out for 240 h (Fig. 7). During the first 25 h, the N719-based systems overall conversion was increased slightly to 4.65%. After that, at hour 60 and hour 145 of the test, it decreased to 4.87% and to 7.50% respectively, resulting in a decreased J_{sc} . This is attributed to the desorption of dye molecules from the TiO_2 surface and, thereby, the light absorption reduction. In contrast, the overall conversion of the DSSCs was slightly increased to 2.9% in the first 25 h, further increased to 1.0% at hour 90, and then slowly approached the initial value (4.0%) at hour 145 of the test. These results indicate that the N719 + CA system is more stable than the N719 dye only due to the suppressed desorption of the N719 dye in the presence of the co-adsorbent.

4. Conclusion

In this study, an N719 dye/co-adsorbent system was evaluated by investigating the effects of different concentrations of the material on the photovoltaic performance.

The prepared device in this regard was found to have higher Voc, Jsc and overall η . There is an effective competition between dyes and CA molecules to block vacant spots (i.e. those not covered by dye molecules) on the semiconductor surface, to develop a blocking layer to elongate the lifetime of the photoelectrons, and to suppress the CR in a simultaneous manner. As a result, in the simultaneous manner, the Ru dye and the co-adsorbent are chemisorbed simultaneously, which is desirable for enhancing DSSCs characteristics. This process is in contrast with the post-chemisorption of the dye and the co-adsorbent.

Declarations

Author contribution statement

Mohammad Mazloun-Ardakani: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Rezvan Arazi: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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