

Application of Convolution-deconvolution voltammetry for investigation of 4,4'-bipyridine with benzoquinone derivatives

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Convolution, deconvolution cyclic voltammetry, chronoamperometric, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed for clarifying the characterization of charge transfer complex (CT) of 4,4'-bipyridine with benzoquinone derivatives. These studies were achieved at a gold electrode in TBAPL/CH₂Cl₂. The kind of the electrode reaction and the kinetic parameters of the CT complex under study were suggested and calculated via the above methods, then confirmed via digital simulation. SEM and TEM were performed for characterization of the structural morphology of the presented complex as well as showing the nanostructured of the complex.

Keywords: Convolution, deconvolution voltammetry, Chronoamperometry, SEM, TEM.

1. INTRODUCTION

Literature survey revealed that the complexes of bipyridine absorbed strongly in the region of the visible spectra. The CT complexes were characterized from six-coordinated, octahedral structures and two enantiomers [1-3]. One of the important studied and used in the field of electrocatalysis, photocatalysis and photoelectrochemical cells are CT complex of ([Ru- (bpy)₃]²⁺) [4-6]. The good merger of redox properties, chemical stability and excited reactivity state has interested engaged much consideration of many research units. Literature survey revealed that the electrochemistry study on this complex are confined within limits only in solution and at electrodes modified chemical [5-7]. The electrochemical behavior of ruthenium (II)/polypyridyl complexes have been the issuable of several investigations [8-14]. An adequate method of changing the properties of CT complex is to adapt the bipyridine ligand by orientation the electron-withdrawing or electron-donating substituents in various positions [15-18]. 4,4'-Bipyridine appertain to a valuable kind of compounds with ample utilization in various fields and since the creation of CT substances produce opportunity to enhance

the physical and chemical properties of different donors, so charge transfer substances of 4,4'-bipyridine (Bpy) with 2,3-dichloro-5,6-dicyano-1,4'-benzoquinone (DDQ), 2,5-dichloro-3,6-dihydroxy-1,4-benz-oquinone [chloranilic acid] (CHA) and 2,3,5,6-tetrachloro-1,4'-benzoquinone [chloranil] (CHL) was observed.

Bipyridine is an aromatic heterocyclic substance presenting vital class of substances which retain a system of π and n-electrons. Paraquat (1,1'-dimethyl-4,4'-bipyridilium ion), also known as methyl viologen gave many utilizations such as electron transfer hindrance, a redox indicator in analytical systems and monomers in polymer creation [17,18].

The IR and ^1H NMR analysis show that a charge transfer combined with a proton motion from acceptor to donor followed by intramolecular hydrogen bonding [19, 20]. No data record has arose in the literature including CT complexes of 4,4'-bipyridine with different benzoquinone derivatives as π acceptors.

So the present work is aimed to extend our previous study [21] on CT complex of 4,4'-bipyridine with derivatives of benzoquinone at working gold electrode via additional electrochemical methods such as I_2 convolution voltammetry and chronoamperometry. Also, the morphology of CT complex of 4,4'-bipyridine with benzoquinone derivatives was examined by SEM and TEM techniques.

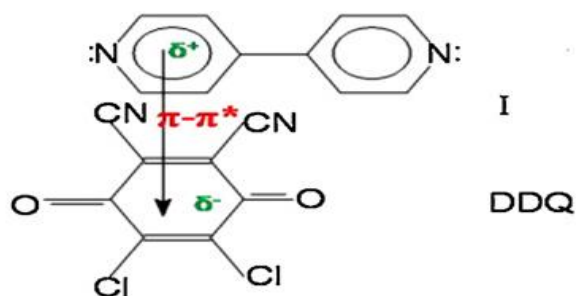
2. EXPERIMENTAL

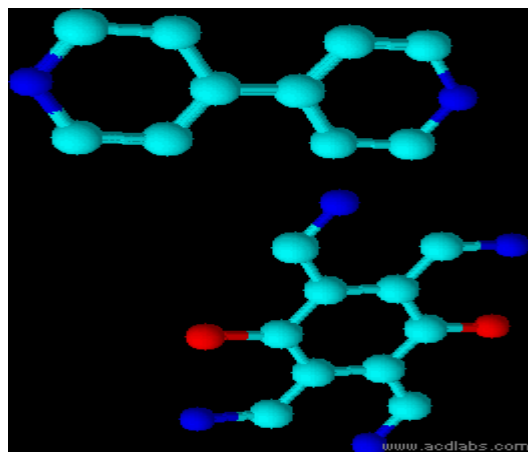
2.1. Materials

DDQ and 4,4'-Bipyridine were obtained and supplied from Aldrich Chemical Co. The solvents used in this article were of spectral pure grade.

2.2. Synthesis of the solid CT complexes

Preparation of 1:1 solid charge transfer complex was carried out by mixing of 4,4'-bipyridine (3.0 mmol) with acceptor DDQ (3.0 mmol) in ethanolic solution. The prepared solid of CT complex was filtered then washed numerous times with minimal quantities of ethanol and then dried.





Scheme 1. The structure of CT complex of Bpy-DDQ,

2.2. Voltammetric measurements

Cyclic voltammetry, convolution-deconvolution voltammetry and chronoamperometric experiments were carried out using Potentiostat Model 283 and PAR Model 175 from EG and G and three electrode electrochemical cell. The gold working electrode has a surface area of $6.75 \times 10^{-3} \text{ cm}^2$, coiled platinum wire as a counter electrode and saturated Ag/AgCl as a reference electrode. The potential was measured relative to the Ag/AgCl reference electrode at 25°C and 0.1 mol/L tetraethyl ammonium perchlorate (TEAP) as indifferent electrolyte.

Cyclic voltammetry experiments were achieved at scan rate ranging from 0.02 to $5 \text{ V}\cdot\text{s}^{-1}$ in CH_2Cl_2 at $(23 \pm 2)^\circ\text{C}$.

EG & G condosim software package was used for generation of the theoretical cyclic voltammograms via digital simulation on PC computer. Algorithms for the simulation program were codified and accomplished into the condosim software package provided by EG & G. All working solutions were completely degassed with oxygen free nitrogen and a nitrogen atmosphere was kept up above the solution during the experiments.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry study

To examine the redox characteristics of 4,4'-bipyridine with benzoquinone, cyclic voltammetry (CV) and convolution voltammetry investigations were performed in methylene chloride (CH_2Cl_2) solution at ambient temperature $23 \pm 2^\circ\text{C}$ with supporting electrolyte (TEAP). Fig.1 displays the cyclic voltammogram of the CT complex at sweep rate of $0.2 \text{ V}\cdot\text{s}^{-1}$ in 0.1 mol/L TEAP at working gold electrode.

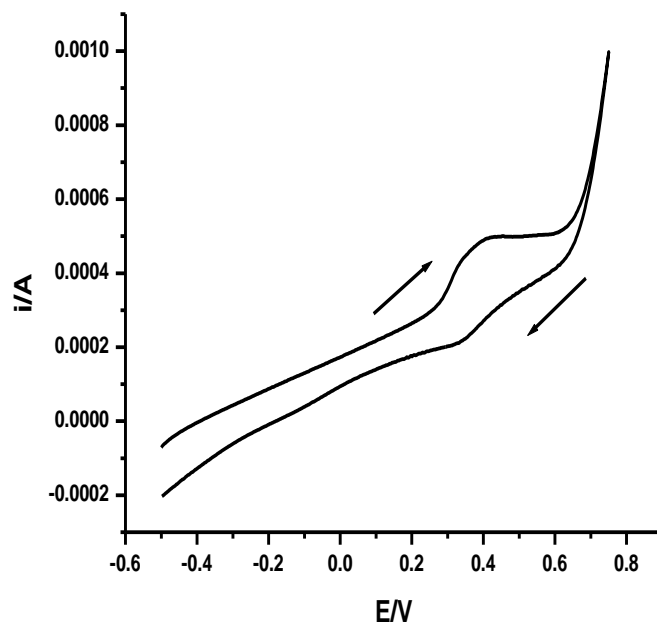


Figure 1. Cyclic voltammogram curve of CT complex at gold electrode, sweep rate $0.2 \text{ V}\cdot\text{s}^{-1}$ and $T = 23 \text{ }^\circ\text{C}$

The cyclic voltammogram revealed a single oxidative peak ($E_{pa} = 0.451 \text{ V}$) coupled with small reductive peak ($E_{pc} = 0.323 \text{ V}$) at $25 \text{ }^\circ\text{C}$ (figure 1). The coupled peaks describe a quasi-reversible electron transfer precedes a moderate fast chemical step (EC scheme) [21,22]. It was observed that the peak isolation of CT complex ($\Delta E_p = E_{pc} - E_{pa}$) lie in the region $120.5 - 220.5 \pm 5 \text{ mV}$ which exceeded than the calculated value (58 mV) for single-electron Nernstian transfer [21]. This may be due to a slight sluggishness of the rate of electron transfer and further due to some solution resistance of the CH_2Cl_2 media [23]. The estimation of the formal potential ($E^{0'}$) was carried out from the mean values of the peak potentials position of the voltammograms and was cited in Table 1. The rate constant of electron transfer (k_s) was calculated *via* the peak separation using ΔE_p values *versus* rate constants [24]. Values of $E_p - E_{p/2}$ (Table 2) was used for estimation of the transfer coefficient (α) *via* equation (1) and found to be 0.33 ± 0.01

$$E_p - E_{p/2} = 48/(\alpha n_a) \quad (1)$$

where $E_{p/2}$ is the magnitude of the potential at $i_p/2$ of peak current and E_p is the oxidative peak potential. After elimination the effect of background and solution resistance, the value of D was calculated from the following Randles-Sevcik equation [21],

$$i_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} S C^{\text{bulk}} D^{1/2} \nu^{1/2} \quad (2)$$

where i_p is the height of the peak current, n is the number of electrons involved in electrode reaction, α is the symmetry coefficient and the remaining symbols have their usual definition. The value of calculated D was found to be $3.47 \pm 0.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Table 1. Values of the kinetic parameters obtained for 4,4'-bipyridine with benzoquinone complex at a gold electrode in this work and at platinum electrode [21] at sweep rate of 0.2 Vs^{-1} .

Technique	$k_s \times 10^{-3}$ (cm s^{-1})	E^0 / V	$D \times 10^5$ ($\text{cm}^2 \text{ s}^{-1}$)	α	k_c, s^{-1}	Reference
Sim	3.35	0.395	3.16	0.33	0.52	This work
	3.55	0.385	3.18	0.43	0.21	[21]
CV	3.20	0.397	3.10	0.34	----	This work
	3.50	0.387	3.12	0.44	----	[21]
I_1 Conv.	----	----	3.22	----	----	This work
	----	----	3.29	----	----	[21]
Decon.	----	0.393	3.23	----	----	This work
	----	0.383	3.27	----	----	[21]
CA	3.38	----	3.65	0.32	----	This work
I_2 Conv.	---	0.392	---	---	0.51	This work

Sim: simulation, CV: Cyclic voltammetry, conv: Convolution voltammetry, Decon: Deconvolution voltammetry, CA: Chronoamperometry.

3.2. Convolution-deconvolution voltammetry

It was established that in case of a simple electron transfer mechanism for electroactive species A, Fick's Second Law is describes as:

$$[\partial C_A / \partial t]_x = D_A [\partial^2 C_A / \partial x^2]_x \quad (3)$$

This equation may be solved at the electrode to produce

$$I_1(t) = (C_A^b - C_A(t)) \cdot [nFAD^{1/2}_A] \quad (4)$$

The surface electrode area is referred by the symbol A and I_1 is the semi-integration of current and is defined as:

$$I_1(t) = \pi^{-1/2} \int_0^t [i(u)/(t-u)^{1/2}] du \quad (5)$$

under condition of pure diffusion-controlled [i.e., $C_{(0,t)=0}$], $I_1(t)$ gives its limiting value, I_{lim} :

$$I_{lim} = nFSC\sqrt{D} \quad (6)$$

Therefore the semi integration convert the cyclic curve ($i-E$) shape to a S shape plot $I(t) -E$ curve which produces a steady-state curve and in some cases is more adjustable for data analysis [25-29].

The evaluation of the $I_1(t)$ was performed via the following algorithms [30, 31]:

$$I(t) = I(k\Delta t) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{j=k} \frac{\Gamma(k-j + 1/2)}{(k-j)} \cdot \Delta t^{1/2} i(j \Delta t) \quad (7)$$

At equally intervals of Δt the current is represented by $I(j\Delta t)$ and $\Gamma(x)$ is the Gamma function of x .

The diffusion coefficient of CT complex was calculated, from a relationship [26] (6), where I_{lim} is the limiting value accomplished for I_1 when the potential is forced to a sufficiently value past the peak and the other terms has their normal meanings.

The I_1 convolution voltammogram of the investigated complex under consideration shows an obvious estrangement between the forward and reverse scan [21] and clearly clarify the moderate speed of electron transport of the redox step. Also as established in previous work [21] the backward direction of the I_1 convolution does not reach to initial value due to chemical reaction appears at longer time scales of the experiment. The values of D calculated *via* equations 2 and 6 [21] are summarized in Table 1. The homogeneous chemical rate constant (k_c) of the chemical step can be precisely evaluated via the kinetic convolution (I_2) by putting trial value of the homogeneous chemical rate constant (k_c) into the convolution calculation until I_2 returned to zero immediately after the peak [21,31]. This is entirely a rumination of the nonappearance of the reductive species at the electrode at potentials prior the peak when the bulk concentration of this species is zero. The true k_c value determined from I_2 convolution was found to be $0.52s^{-1}$ which agrees with the value used in simulated cyclic voltammograms [21].

The true homogeneous chemical rate constant (k_c) and reduction potential (E^0) were extracted via a simple and accurate method using equation 8, [28, 29]

$$I_{lim} - I_1 = I_2 \exp - ((E - E^0)(nF/RT)) \quad (8)$$

Where I_2 is the kinetic convolution and remain the symbols have their usual interpretation. Presentation of equation 8 are summarized in Figure 2 which indicate that when $E = E^0$ the terms $I_{lim} - I_1$ and I_2 become equal and the intersection of the plot happen at E^0 when kc is true.

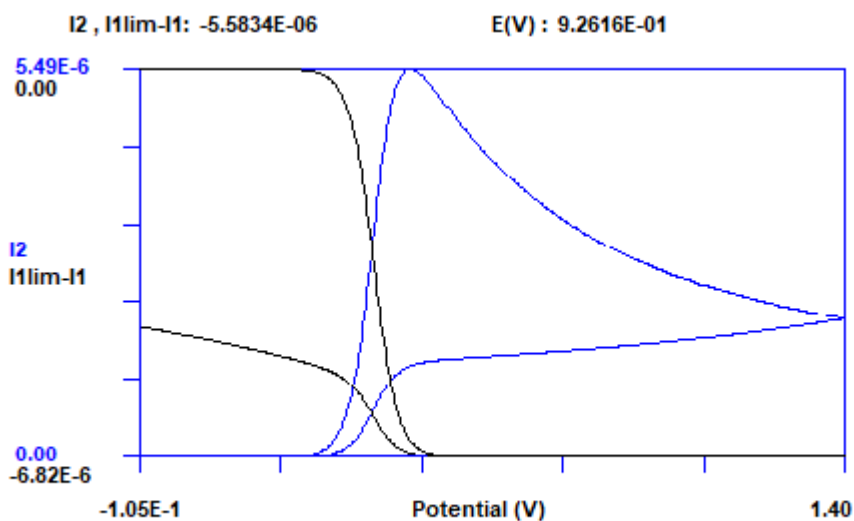


Figure 2. Display the I_2 convolution and $I_{lim} - I_1$ of CT complex at gold electrode, sweep rate of 0.5 V s^{-1} , $T = 25 \text{ }^\circ\text{C}$.

The diffusion coefficient was also determined from deconvolution voltammometry using equation 9 [21]

$$e_p = 1.12 \times 10^6 \alpha n^2 \nu C^{\text{bulk}} D^{1/2} \tag{9}$$

where e_p is the height of the forward peak of deconvolution voltammometry (in Ampere) and the other symbols have their normal meanings. The magnitude of D calculated from Eq. (9) is cited in Table 1. Also from the arrangement between convolution and deconvolution transforms the relationship (10) was obtained and used for determination the number of electrons consumed in electrode reaction and found to be equal one as established in our previous work [21]:

$$n = \frac{0.086 e_p}{I_{lim} \alpha \nu} \tag{10}$$

Inspection of the tables 1 and 2 revealed that the values of reduction potential (E^0) determined at a gold electrode in this work is slightly more positive than that obtained in case of the platinum electrode in our previous work. The values of the remaining kinetic parameters at the gold electrode are less than the values recorded at the platinum electrode. Also, the peak characteristics listed in table

2 reflect the rate of electron transfer at gold electrode is little lower than that measured at platinum electrode. These results can be attributed to the lower electrocatalytic activity of the gold electrode than platinum electrode.

Table 2. Peak characteristics of the investigated CT complex 4,4'-bipyridine with benzoquinone extracted from cyclic voltammetry, deconvolution voltammetry and digital simulation techniques obtained in this work and from reference [21] at 0.5 V s^{-1} .

$E_p - E_{p/2} / \text{mV}$	86(a) 84*	87(c) 85*
$E_p - E_{o'} / \text{mV}$	87(a) 86*	88(c) 86*
W_p / mV	126(b) 124*	124 (c) 123*
$\Delta e_p \text{ Decon} / \text{mV}$	84(b) 82*	83(c) 81*
$e_{pf} / e_{pb} \text{ (Decon)}$	1.11 (b) 1.15*	1.12(c) 1.12*

(a) Values determined from Cyclic Voltammetry (b) values determined from deconvolution (c) values determined from digital simulation and * from reference [21].

3.3. Digital simulation

In this work, Digital simulation was achieved via EG & G Condesim software program. The simulation was accomplished using finite differences techniques [21, 32-37]. A direct examination of the electrochemical parameters was performed by generating the theoretical cyclic voltammogram of the investigated CT complex using the mean values of electrochemical parameters attained experimentally and comparing it with the voltammogram recorded experimentally. The electrochemical and chemical parameters which exhibit good matching for the examined CT complex which proceeds as EC scheme are listed in table 1

3.4. Chronoamperometry of CT complex.

Chronoamperometric experiments were achieved by stepping the potential from the initial value (0.3 V) where no electron transfer occurs, to a value in the region of 0.32 V to 0.39 V and the current was recorded as a function of time. Chronoamperogram of the CT complex in 0.1 mol L^{-1} TBAP/ CH_2Cl_2 at a gold electrode at potential step from E_i (0.3 V) to E_f (0.34 V) is displayed in Figure 3. The rate constant k_f was calculated via equation (11) [30]

$$i(t) = -\beta I_1 + u \quad (11)$$

where $u = nFSC^{bulk}k_f(D)^{1/2}$ and $\beta = k_f(D)^{1/2}$. Measurements of the intercept at $I_1 = 0$ and the slope of the straight line of $i(t)$ versus I_1 produce k_f . Here, the basic relation between the rate constant of the electron transfer and the potential of the electrode is considered in the treatment of the Butler-Volmer relationship which can be written in the equation (12) [28]

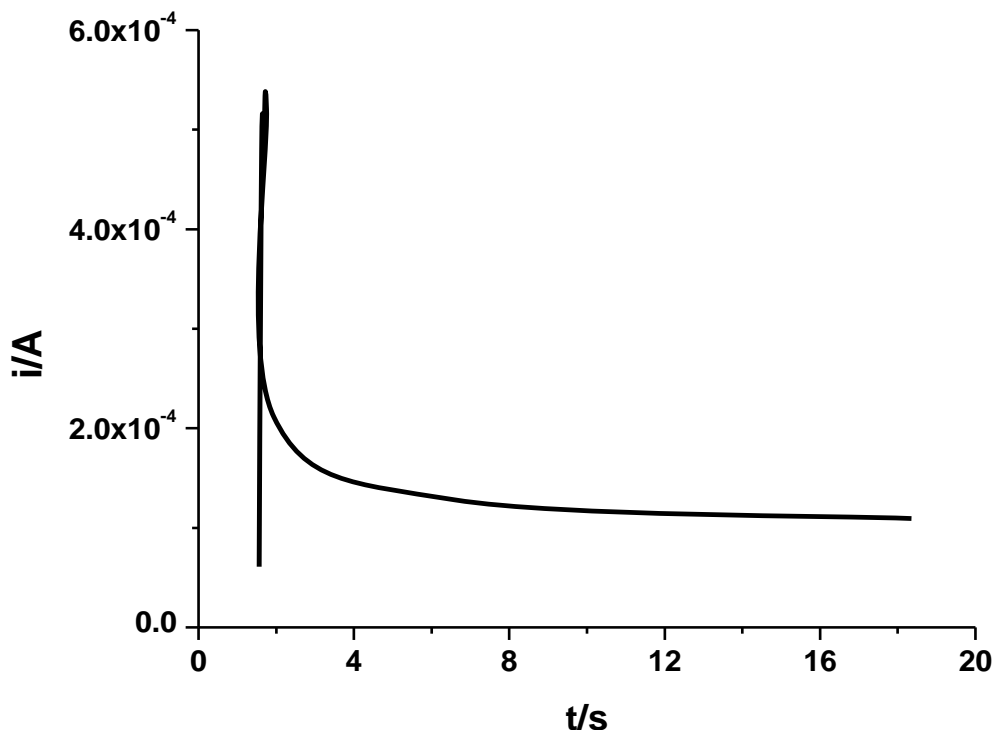


Figure 3. Chronoamperogram curve of CT complex of 4,4'-bipyridine with benzoquinone at gold electrode and at $T = 25\text{ }^\circ\text{C}$.

$$\ln k_f = \frac{\alpha nF}{RT} (E_f - E^{o'}) + \ln k_s \tag{12}$$

The value of α was computed from slope of the linear line of $\ln k_f$ vs. $(E_f - E^{o'})$ and was being to be 0.32, while value of k_s was calculated at the point at which $E_f = E^{o'}$ and was estimated to be $3.65 \times 10^{-3} \text{ cm s}^{-1}$. Both values are adhering well with those found from the experimental and theoretical calculations used in this work and our previous work [21] (Table 1).

3.5. SEM and TEM Techniques

The morphology of the CT complex in the present article was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) due to their good

resoluteness and great imaging quickness. Bpy-DDQ charge transfer complex was examined under scanning electron microscope (SEM) Fig. 4 A & B. Size dissemination and average particle radius were determined analyzing 4–6 pictures, presenting accumulation of more than 2000 particles. SEM images indicate that these nanoparticles attend to accumulate to produce clusters in the region of 50 nm to 100 nm. The appearance of Bpy-DDQ single-crystalline particles similar to such as rectangular like structures. TEM photograph of Bpy- DDQ exhibited that 10–15 nm particles are spherical in the sample (Fig. 4).

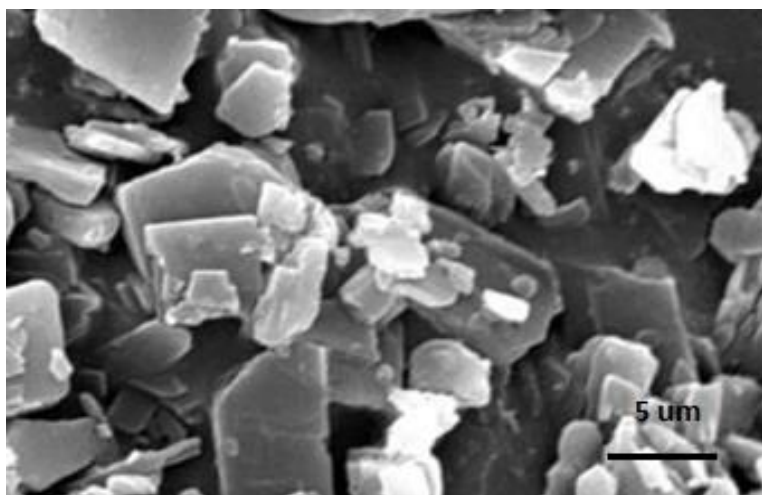
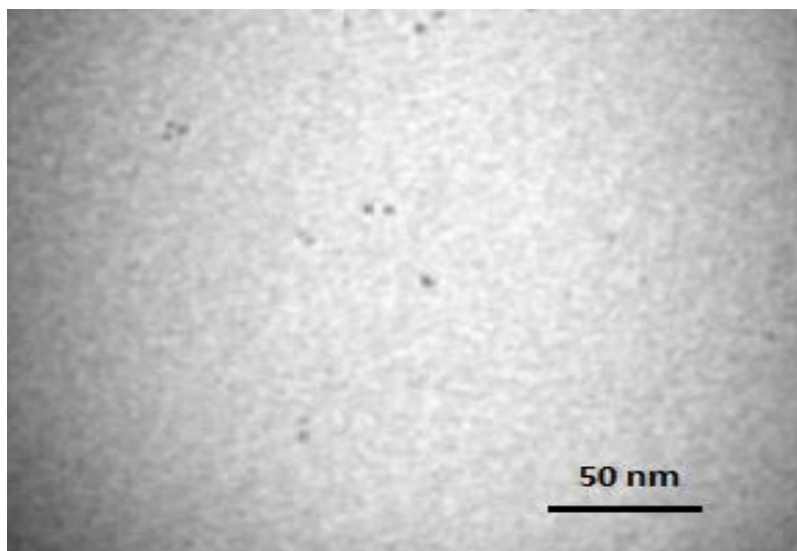
**A****B**

Figure 4. (A) The scanning electron image (SEM) and (B) transmission electron image for Bpy-DDQ complex.

4. CONCLUSION

In this article the electrochemistry of CT 4,4'-bipyridine with benzoquinone complex was explained at a working electrode (gold) in 0.1 mol L⁻¹ TBAP/CH₂Cl₂ solution by cyclic voltammetry, convolution deconvolution voltammetry and chronoamperometry experiments. The chemical and electrochemical constants of the investigated CT of 4,4'-bipyridine with benzoquinone complex have been determined experimentally via different methods. The electrode reaction was found to behave as moderate speed charge transform continued by chemical reaction step i.e., EC mechanism. Transmission electron microscope and scanning electron microscope were used to explain and clarify the morphology of the CT compound. It was concluded that the chemical and electrochemical parameters obtained in this work compare well with those obtained from our previous work confirming that the accuracy and validation of all the methods used for investigation of the CT complex.

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