

ELECTROSORPTION OF SALT IONS USING TITANIUM DIOXIDE- DECORATED rGO AS A PROMISING ELECTRODE CANDIDATE

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ABSTRACT

Transition metal oxide (TMO) nanoparticles are particularly important in capacitive deionization desalination due to their wide areas of application. The performance of rGO decorated with TiO₂ nanoparticles has been investigated. Hammer method synthesizes the electrodes, followed by a hydrothermal treatment. The morphological properties of the rGO and rGO-15TiO₂ were characterized by FE-SEM and TEM measurements. The TEM images indicated the random distribution of titanium oxides in the rGO layer, while SEM images showed that the TiO₂ homogeneously covered and distributed on rGO sheets for rGO-15TiO₂. The performance of the prepared nanocomposite electrode's electrochemical conduct was assessed by cyclic voltammetry (CV) ex-situ. In the three-electrode system, was observed from -0.6 to 0.6 V in 1 M aqueous NaCl. The results illustrated that rGO-15(TiO₂) electrode showed the best performance in the CDI, achieving the highest specific capacitance of 473.9/g at 25mV/sec. The results indicating that rGO-15TiO₂ is a novel electrode material for CDI.

Key words: Graphene, Titanium oxide, Nanocomposite, Electrosorption.

1. INTRODUCTION

These days, the use of non- traditional water resources to produce drinking water has become widespread [1]. Desalination is a good answer to the growing requirements for fresh water as a replacement for fresh water resources. Many desalination methods have been used today, such as membrane-based pressure-driven procedures like nanofiltration (NF) and reverse osmosis (RO) and electrochemically driven processes like electrodeionization (EDI) and electrodialysis (ED), which are considered to be the most widely used techniques for the production of fresh water from different sources of water [2, 3]. They

have drawbacks, such as rising energy consumption and fouling, despite major improvements in technologies of desalination[4, 5]. Capacitive deionization (CDI) is considered an electrochemical process that uses porous electrodes in a feed solution to remove salt or charged species as a method for next-generation desalination [6]. CDI is commonly used in the field of seawater desalination due to its benefits including minimum consumption of energy, high coulombic effectiveness and no secondary pollution [7-10]. Electrode materials play an significant role in the determination of electrosorption

capacity and reversibility of as a major element in CDI cells [11-13].

An optimal CDI electrode material must have continuous electrons transfer paths for electrochemical dual layer formation, rapid ion transport pathways, and huge active sites. Electrode materials would therefore have big available surfaces, hierarchical porous morphology and outstanding electrical conductivity, in addition to improved electrosorption behavior and getting high salt removal capacity. These materials must be good conductor, long cycling stability, low manufacturing cost, high specific capacitance, huge surface area and rapid charge/discharge rates [14-16].

Appropriate applicants are carbon materials of varied morphology, easy-tuning characteristics and outstanding chemical / electrochemical stability. CDI has been commonly used for activated carbon, carbon nanospheres, carbon nanotubes, carbon aerogels and graphene [17-22]

Graphene, a two-dimensional (2D) planar structure of one atomic thickness sp²-hybridized carbon, has attracted significant interest as it has many benefits, such as excellent electrical conductivity (~7200 S cm⁻¹), superior elasticity, outstanding mechanical strength, adjustable surface characteristics, high adsorption capacity, huge surface area (~2600m² g⁻¹) and exceptional physiological strength and outstanding physical properties [23-26].

Among them, For large-scale CDI applications, Attention was drawn to graphene with elevated carrier mobility up to 10 000 m² V⁻¹s⁻¹. Despite 2D graphene, aggregation in the manufacturing process of slurry-based electrodes suffers because of van de Waals forces, Resulting in sharp decrease in surface areas that can be accessed and leads to significant deterioration of CDI performance [27-29].

The best way to beat this drawbacks from the AC and 3D graphene hydrogel, are to dope carbon-based materials with transition metal oxides (TMOs). Due to their low price, hydrophilic characteristics, simple manufacturing, non-toxic nature, and elevated antibacterial performance, TiO₂ and

ZrO₂ are particularly appealing among several transition metal oxides [30, 31]. Graphene is generally used as a supporting matrix for most nanoparticles of metal oxide owing to its elevated electrical properties, wide surface area and great stability [32].

In this work, rGO was first synthesized and then incorporated with a TiO₂ nanocomposite. The TiO₂ effect on the physiochemical properties and structure of the electrode was investigated. The electrochemical properties of the fabricated electrodes and deionization performance were also examined in the three- and two-electrode cells, also the efficiency of reduced graphene oxide (rGO) decorated with different percentages of TiO₂ NPs was investigated to estimate the optimum loading of the TiO₂ NPs. In addition to characterizing the synthesized electrodes, the performance of the prepared nanocomposite electrodes was investigated using three-electrode (ex situ) and two-electrode structures (in situ; CDI cell).

2- EXPERIMENTAL

2.1. Synthesis and fabrication of rGO-TiO₂ composite

The composite was synthesized as follows; Graphene oxide (GO) was prepared by a modified Hummer's method [33]. A suitable quantity of GO is dispersed in ethanol by 2 h sonication for the synthesis of the nanocomposites. Then, titanium isopropoxide (TiO₂ precursor) are added to the GO under continuous stirring for one hour. The resulting mixture is stirred at 70°C overnight to confirm complete removal of the ethanol. Lastly, the obtained composite was calcinated at 850 °C for 1 h to produce rGO-xTiO₂ composite.

2.2. Characterization

A transmission electron microscopy (TEM) analysis also identified the morphology and surface of the samples at 200 kV that consider an accelerating voltage using a JEOL-100CXII microscope and scanning electron

microscopy (SEM) at 10 kV using a Hitachi S-4800 field emission scanning electron microscope.

2.3. Ex situ characterization of the synthesized electrode

The electrochemical characterization was performed using the Gamry potentiostat (reference 3000, Gamry instruments). A three-electrode cell structure composed of counter electrode (Pt wire), reference electrode (Ag/AgCl), and working electrode (a carbon electrode glassy coated with 1 mm Teflon) was used. NaCl solution (1 M) was used as an electrolyte and the sweeping potential range of -0.6 V to $+0.6$ V (compared to Ag / AgCl) was used for testing.

Cyclic voltammetry (CV) measurements were investigated by VersaStat4 potentiostat instrument, to investigate the electrochemical properties. According to Eq(1), the specific capacity (C) values were measured from CV curves (1) by the following [34] :

$$C = \frac{i(E)dE}{2(E_2 - E_1)v_m} \quad (1)$$

where C, $i(E)dE$, v, $(E_2 - E_1)$, and m are the specific capacitance, total voltammetric charge obtained via the integration of the negative and positive scans (from the CV results), potential sweep rate ($mV s^{-1}$),

potential window width (V), and catalyst mass (g), respectively.

2.4. Electrosorption experiment

The CDI cell was made of two Perspex sheets ($7 \times 7 \times 1$ cm) and two stainless-steel electrodes (both 5×5 cm) that contained the deposited materials.

A stock of a two-liter feed solution with different concentration was prepared. Peristaltic pump was used to circulate through CDI cell at a different flow rate. The freshwater effluent was redirected to the feed stream, and this process was repeated until the surfaces of the electrodes became saturated.

3 RESULTS AND DISCUSSION

3.1. Characterization of rGO and rGO-15TiO₂ nanocomposite

SEM and TEM have studied the microstructures of rGO-TiO₂ nanocomposites. The SEM pictures, show platelets of rGO sheets between TiO₂ nanoparticles that are not hard to find. As shown in Fig.1 (a) and (b) represents the SEM images that depict the structural characteristics of the rGO and rGO-15TiO₂ composite. Fig.1 (c) shows TEM picture that rGO's irregular surface; and TiO₂ were effectively deposited outside on top of the rGO's surface after hydrothermal treatment.

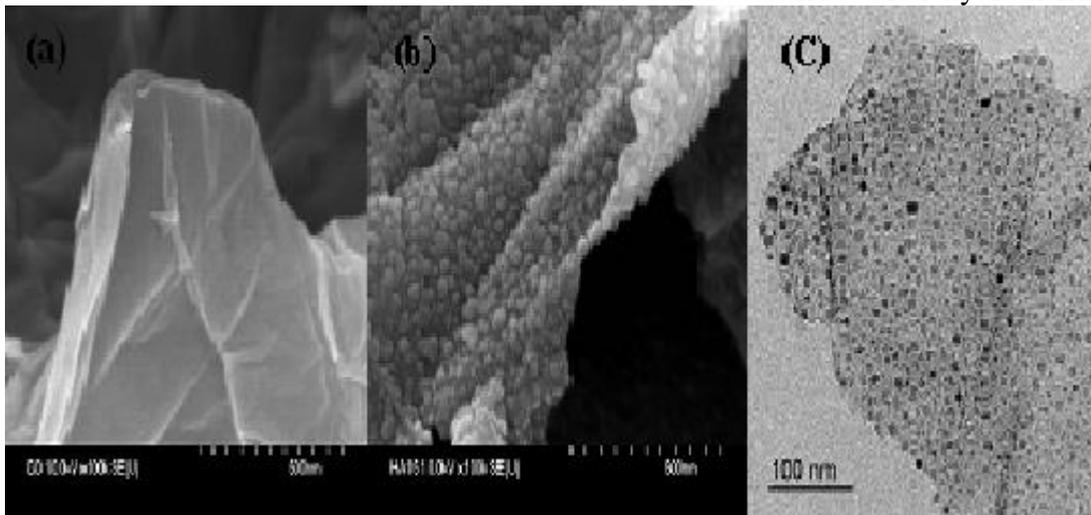


Fig.1. Characterization of rGO and rGO-15TiO₂: (a) and (b) SEM images, and (c) TEM image of rGO-15 TiO₂

3.2. Electrochemical performance

Cyclic voltammetry (CV) is used as an efficient method for detecting the performance of electrosorption and

examining CDI electrode materials by specific capacitance [35-37]. CV tests were performed in a three-electrode scheme to determine the electrochemical efficiency of

TiO₂-deposited rGO as electrodes. Figure 2(a) shows the range from -0.6 to 0.6 V of rGO-15TiO₂ electrode CV profiles with scanning rate (200 mv/sec). The specific capacitance of the electrode vs the scan/sweep rate is shown in Fig. 2(b).

Notably, by adding a small amount of TiO₂ to the rGO, the specific capacitance reaches 473.9/f at 25mV/sec by using equation (1). These results can be explained adding TiO₂ to rGO would enhance the CDI performance.

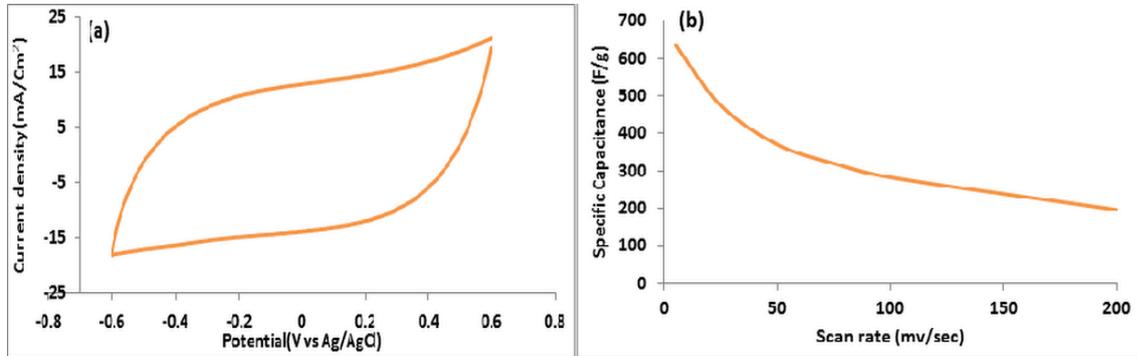


Fig. 2. (a) CV curve for the prepared electrode rGO-15TiO₂; (b) Specific capacitance for the obtained electrodes in a 1M NaCl aqueous solution

3.3. Two-electrode CDI performance

Because CDI performance is proportional to the electrode capacitance, rGO-15TiO₂ was chosen as an electrode to investigate the CDI desalination performance. The electrosorptive properties of rGO-15TiO₂ are described in Fig. 3(a,b,c,d), which compares the electrosorption profile of rGO-15TiO₂ with that of GO and rGO using an initial conductivity of 50 $\mu\text{S cm}^{-1}$, 100 $\mu\text{S cm}^{-1}$ and 150 $\mu\text{S cm}^{-1}$ under a cell potential of 1.2 V. As demonstrated, by applying a potential between the two electrodes, the conductivity of the salt solution declined owing to the

adsorption of ions from the feed solution onto the electrode surface. The conductivity decreased rapidly, and the electrode was saturated after 16 min of CDI operation. As expected, rGO-15 TiO₂ revealed the maximum electrosorption. This result was attributed to the very poor electrical conductivity of the GO, which resulted in uncharged electrodes. In contrast, rGO adsorbed ions, and the solution conductivity declined to 13.58 mg/g. Nevertheless, examining the stability of the sample during real application is vital prior to developing it as an effective catalyst.

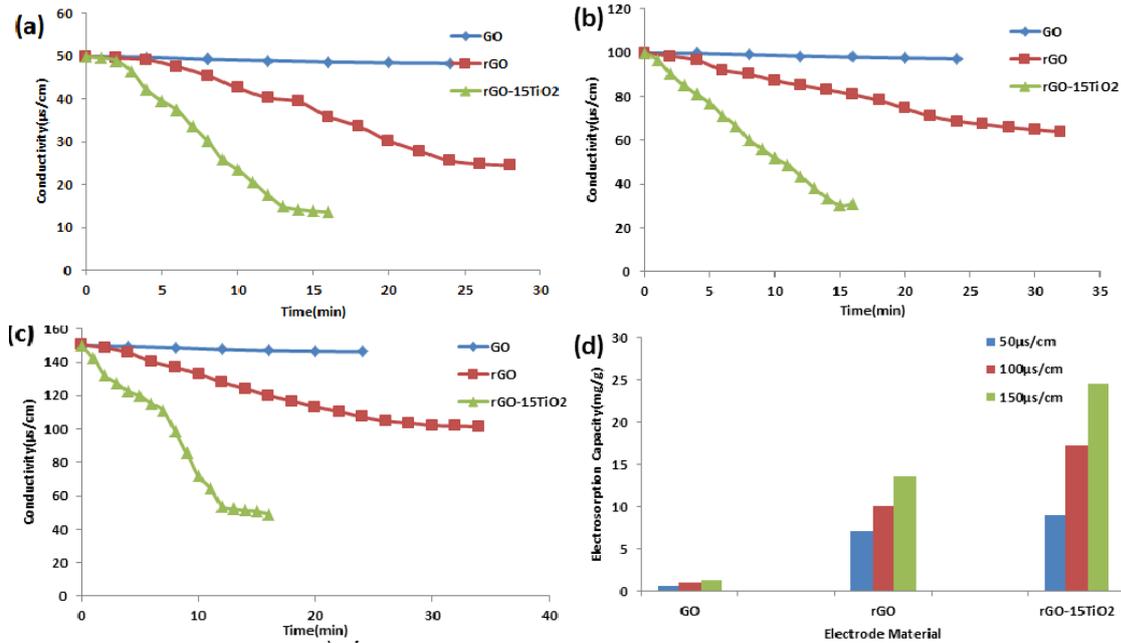


Fig. 3. Electro sorption of NaCl onto GO, rGO and rGO-15 TiO₂ at 1.2V voltage and 15ml / min flow rate at different initial concentrations: (a) 50μS/cm, (b) 100μS/cm and (c) 150μS/cm and (d) for comparison

For comparison Fig. 3(d) shows that when the electrodes are charged, the salt adsorption capacitance (SAC) improves rapidly and achieve a highest value after several mins, suggesting electrodes saturation. In different initial concentrations of NaCl solutions, the composite rGO-15TiO₂ indicate greater SAC than that of GO and rGO.

With the different initial conductivity of the prepared electrodes, rGO-15TiO₂ exhibits the maximum SAC of 9.04 mg/g, 17.17 mg/g, and 24.58 mg/g in 50 μS/cm, 100

μS/cm and 150 μS/cm NaCl solutions, respectively. Elevated performance of electro-sorption of manufactured electrodes at such a high saline concentration as compared to graphene electrodes (as shown in Table 1) due to constant ,various active ion-adsorption sites , fast ion transport pathways, and pseudocapacitive adsorption for functional oxygen groups. To form a uniform network, great dispersion of the TiO₂ in the graphene sheets and unique electrical conductivity of the graphene reduced by hydrothermal treatment.

Table 1.Electrosorption of GO, rGO and rGO-15TiO₂ at different concentrations

Initial Conductivity	Electrosorption Capacity(mg/g)		
	GO	rGO	rGO-15TiO ₂
50 μS/cm	0.55	7.094	9.043
100 μS/cm	0.93	10.08	17.17
150 μS/cm	1.31	13.58	24.58

The outstanding adsorption performance of the rGO / TiO₂ electrode can be ascribed of ion adsorption in both electrodes: (i) high hydrophilicity when the TiO₂ nanorods are decorated between graphene sheets, (ii) a morphological sandwich structure capable of preventing aggregation of sheet and offering fast ion accumulation on surface through the

intra-channel surface of the electrode, and (iii) a surface of TiO₂ charges resulting in reduced polarization of pristine rGO that can be seen as an efficient way of achieving better ion concentration and double-layer capacity [38, 39].

4. CONCLUSIONS

The TiO₂-decorated rGO reduced by hydrothermal treatment successfully synthesized, Both SEM and TEM images revealed the good dispersion of TiO₂ in the rGO sheets that formed a uniform network. rGO-15TiO₂ has good electrochemical performance compared to rGO and the highest values of rGO-15TiO₂ electrosorption capacities are 9.04 mg/g in 50 μs/cm, 17.17 mg/g in 100 μs/cm and 24.58 mg/g in 150 μs/cm NaCl solutions. The results indicated that TiO₂-decorated rGO is a suitable choice for electrodes to enhance desalination with CDI yield and to rapidly put the process into the market.

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الملخص العربي

تعتبر المواد الانتقالية النانوية مهمة بشكل خاص في تحلية التحلية المياه باستخدام الطريق الايوني السعوية بسبب مناطق تطبيقها الواسعة. تم التحقق من أداء الجرافين المختزل المزخرف بالجسيمات النانوية من التيتانيوم. ويتم في هذه الدراسة تحضير الجرافين بواسطة طريقة "هامرالمعدله" الذي تعمل على اكسدة الجرافيت، ثم تقشير الجرافيت المؤكسد ثم إختزال الجرافيت المؤكسد ثم اضافته التيتانيوم. وتم اجراء الاختبارات علي افضل العينات لمعرفة الخصائص المورفولوجية للجرافين المختزل بمفرده ثم مع وجود التيتانيوم. وأشارت الاختبارات التوزيع العشوائي لأكاسيد التيتانيوم في طبقة الجرافين المختزل، في حين أظهرت ايضا أن نسبة اكسيد التيتانيوم تغطي وتوزع بصورة عشوائية على العينة. تم تقييم أداء السلوك الكيميائي الكهربائي للقطب النانو المركب بواسطة الفولتاميتري. في النظام ثلاثي الإلكترود، تمت ملاحظته من -0.6 فولت الي 0.6 فولت في امولر من محلول كلوريد الصوديوم. أثبتت النتائج أن القطب ان 15% نانو تيتانيوم مع الجرافين حيث ان وصلت الي (F/g)473.9 أظهر أفضل أداء عند 25 مللي فولت/ثانية. تشير النتائج إلى أن 15% نانو تيتانيوم مع الجرافين هو مادة جديدة من الإلكترود لمادة CDI.

الكلمات الدالة: الجرافين ، اكسيد التيتانيوم، امتصاص الايونات بالكهروكيميائية