EFFECT OF SPIN COATING ON ELECTRICAL PROPERTIES OF MXENE FILMS DEPOSITED FROM NON-AQUEOUS SOLVENTS

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Abstract

We investigated the effect of spin coating parameters on the electrical properties of Ti_3C_2 MXene thin films deposited from non-aqueous suspensions in N,N-dimethyl formamide (DMF) and N-methyl-2-pyrrolidone (NMP) on gold interdigitated electrodes (IDE). The electrical properties of DMF-MXenes and NMP-MXenes films are characterized by impedance spectroscopy (4 Hz - 8 MHz at 1 V) using gold IDE with 25 μm gap. The electrical conductivity of MXene films decreases with increasing spin coating speed from 300 to 900 rpm. The series resistance (R_s) and double layer capacitance remain similar (C_{dl}). In all cases, MXenes deposited from DMF have five orders of magnitude higher electrical conductivity (lower R_{ct}) than MXene films deposited from NMP. It is correlated with the thin film morphology obtained by scanning electron microscopy (SEM). These findings can be useful for possible application of MXenes as charge transport layers in hybrid photovoltaic devices.

Keywords: MXene, thin films, impedance spectroscopy, electrical conductivity, spin coating

1. INTRODUCTION

MXenes are a new class of two-dimensional materials that can be denoted by the general formula $M_{n+1}X_nT_x$, where M is a transition metal, X is carbon or nitrogen, and T is a surface functional group (-OH, -O, and/or -F) [1]. Modified 2D MXenes are promising materials in energy conversion and storage, such as lithium-ion batteries and supercapacitors, with the possibility of using them to develop new electrode designs. Due to the microporous structure of MXenes, the process of transferring ions to the oxidative regenerative centers is much faster, which allows faster recharging of batteries. So, MXenes are also attractive in terms of the development of sustainable energy technologies due to a wide range of extraordinary properties, such as high electrical conductivity, hydrophilicity, excellent thermal stability, large surface area, etc. In the form of highly concentrated suspensions of MXenes in water, due to the functional groups on the surface, its hydrophilicity and stability during storage is ensured [2]. MXenes have a significant advantage over other nanomaterials, including reduced graphene oxide, for obtaining conductive nanocomposites, precisely due to their high conductivity [3-5]. MXenes are characterized by dependence between the electrical conductivity and their morphology, for example, ultrathin, compact MXenes films with highly aligned scales exhibit very high electrical conductivity. Grain boundaries can also affect electron hopping transport behavior, smaller flakes correspond to more particle boundaries and therefore more interparticle contacts, resulting in lower electrical conductivity of the films. This is best confirmed by the significantly higher conductivity of the flakes obtained by the spin coating method, which allows for more compact films (easier electron hopping).

An urgent task given by the promising use of MXenes in organic or perovskite solar cells is to study the conductive properties and structural features of MXenes thin films obtained from polar non-aqueous solvents.

This work aims to determine the effects on the electrical conductivity of MXenes deposited from suspensions of NMP and DMF on a sensor platform with gold IDE depending on the spin coater rotation speed by impedance spectroscopy. Impedance spectroscopy is used as an effective method for studying the electrical characteristics of interfaces in a wide frequency range [6-10]. The surface morphology of MXene thin films in terms of IDE sensor coating is evaluated from secondary electron images obtained by SEM.

2. EXPERIMENTAL METHODS

2.1. Preparation of MXenes in polar aprotic solvents

A solvent replacement method was used to prepare the suspensions. A known volume (0.5 mL) of the 0.9 mg/mL dispersion of Ti_3C_2based MXenes in deionized water was centrifuged at a rotation speed of 13000 rpm (15115 g) for 30 minutes, after which the supernatant above the sediment was pipetted off. The precipitated MXene was re-dispersed in polar aprotic solvents - NMP and DMF, respectively. Then the second stage of centrifugation was carried out at 13000 rpm (15115 g) for 5 minutes, the supernatant was removed by pipette and NMP or DMF solvent was added to 1 mL. This is a simplified and faster procedure than the previously reported [11]. To prevent particle aggregation, the resulting suspension was sonicated in an ultrasonic bath at 37 kHz for 30 minutes and stored for further analysis.

2.2. Sample Preparation

The interdigitated microelectrode sensor platform was used for the preparation and characterization of the MXenes thin films. Multilayer NiCr/Ni/Au interdigitated electrodes were deposited on a ceramic substrate of 5.5 × 8.8 × 0.6 mm^3. The IDE electrode structure consists of repeated lines/gaps with the width of 25 μm for both. The IDE was first cleaned with ethanol, then 1 μL of MXenes from NMP and DMF suspensions was applied by drop casting, followed by spin coating (Ossila Ltd). Samples with deposited thin films of MXenes from NMP and DMF suspensions were prepared at three different spin coating rotation speeds (300, 600 and 900 rpm) for 60 seconds, followed by evaporation of the liquid at T=100°C to form a dry thin film of MXenes.

2.3. Morphology Characterizations

The scanning electron microscope (SEM, MAIA3 Tescan) was used for the characterization of the surface morphology of the prepared samples. All presented SEM images of samples were acquired at 10 kV in the regime of secondary electrons.

2.4. Electrical Impedance Measurements

The IM 3536 LCR METER Hioki device was used to measure impedance spectra. All measurements were carried out in the frequency range from 4 Hz to 8 MHz at a constant voltage of 1 V. The sample was placed in a Faraday cage, the electrodes we fixed by a clamp, and connected to the LCR meter. LCR Meter Software was used to measure the impedance spectroscopy. Experimental Nyquist plots of the impedance $-Z_{im}=f(Z_{rel})$ were constructed to analyze the electron transport processes occurring at the interface of the gold IDE sensor and DMF-MXenes or NMP-MXenes.

3. RESULTS AND DISCUSSION

3.1. Methodology of MXene thin films preparation

For this study, we prepared samples of MXenes thin films deposited from NMP and DMF suspensions by spin coating on the surface of the IDE sensor. A drop of the suspension with a volume of 1 μl was deposited on a gold IDE sensor platform followed by spin coating at different spin speeds: 300, 600, 900 rpm for 60 seconds

and evaporation at T=100 ºC. A schematic representation of all stages of the preparation process of the studied samples is shown in **Figure 1a**. The spin coating method was used to obtain a thin coating of MXenes deposited on the surface of the IDE sensor. The general four stages of the spin coating process are shown: 1 - application of a drop of MXenes suspension on the substrate; 2 - the process of rotation of the sample with the suspension applied to its surface in the form of a drop, during which there is a uniform distribution of the layer of liquid applied to the surface; 3 - in the process of spin coater rotation there is a uniform distribution of liquid and MXenes on the surface of the IDE. A detailed schematic representation of the spin coating process is shown in **Figure 1b**.

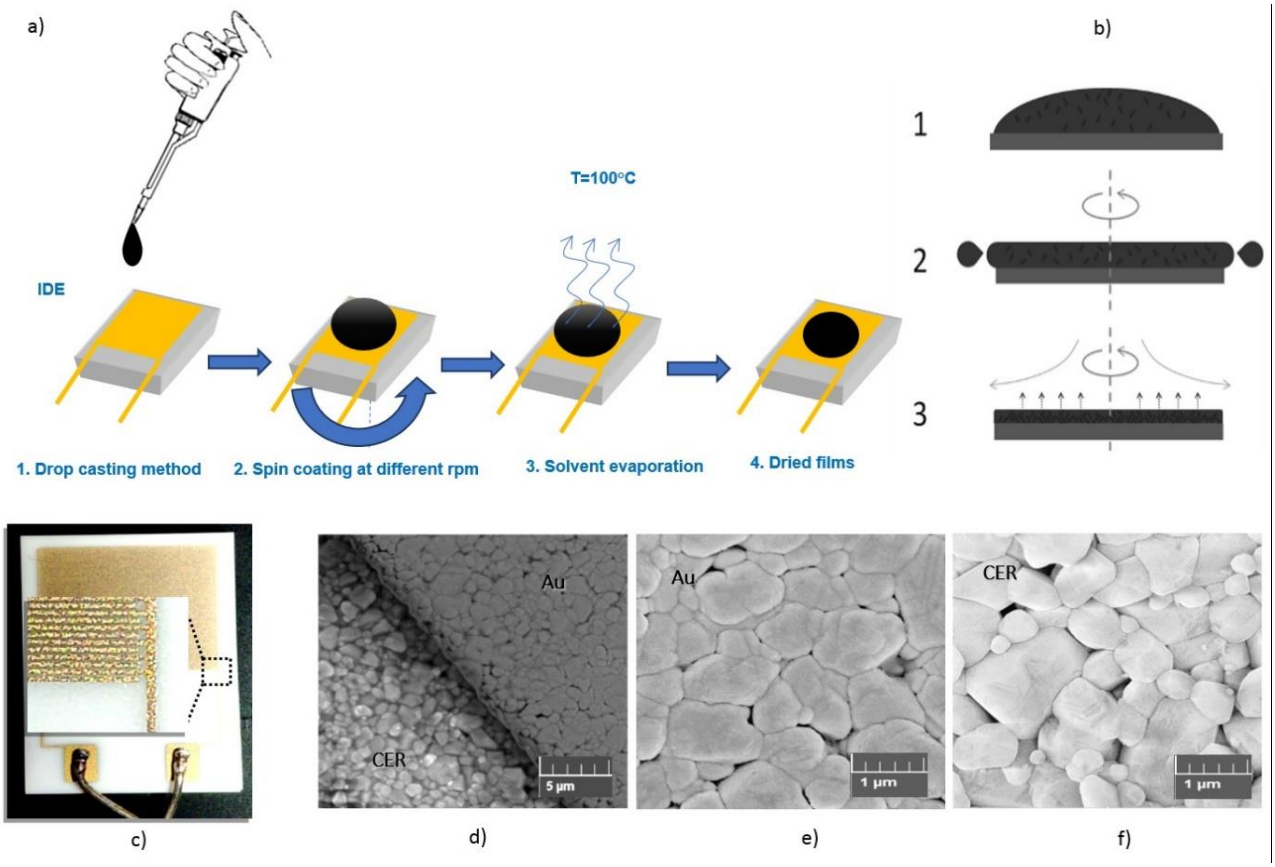

Figure 1 Scheme of MXene layer deposition process stages (a) and detail of the spin coating process (b). Photographs of bare gold IDE impedance sensor (c), its SEM surface morphology the border between Au electrode and ceramic substrate (d), and detail of gold electrode (e), ceramic substrate surface (f)

A photo of a bare IDE with an enlarged detail for better visualization of the structure of the gold electrodes on the ceramic surface is shown in **Figure 1c**. In order to compare the surface morphology of the deposited MXenes on the surface in terms of the uniformity of the sensor surface coating, the secondary electron images of the bare sensor were first obtained in three positions: at the interface between the gold electrode (Au) and the ceramic (CER), a scale of 5 µm, and the surface of the gold electrode and the between electrode space, the surface of the ceramic substrate **Figure 1e-f**.

3.2. Surface Morphology of MXene films

To analyze the morphology of MXenes thin films deposited from NMP and DMF suspensions on the surface of gold IDE by spin coating at different rotational speeds: 300, 600 and 900 rpm, SEM images of the samples were obtained, which are shown in **Figure 2a,b** (the scales bar are 1 mm for the overview image on the left and 1 µm for the detailed image on the right). For the investigated samples, thin homogeneous coatings are

observed at lower rotational speeds of 300 and 600 rpm for both types of MXenes suspensions (NMP and DMF). For a rotation speed of 900 rpm, inhomogeneities and breaks are observed on the surface of the obtained films. By analyzing the acquired SEM images, it can be concluded that the spin coating method for allows obtaining more homogeneous MXenes coatings at lower rotational speeds (300 and 600 rpm) than at higher speeds (900 rpm).

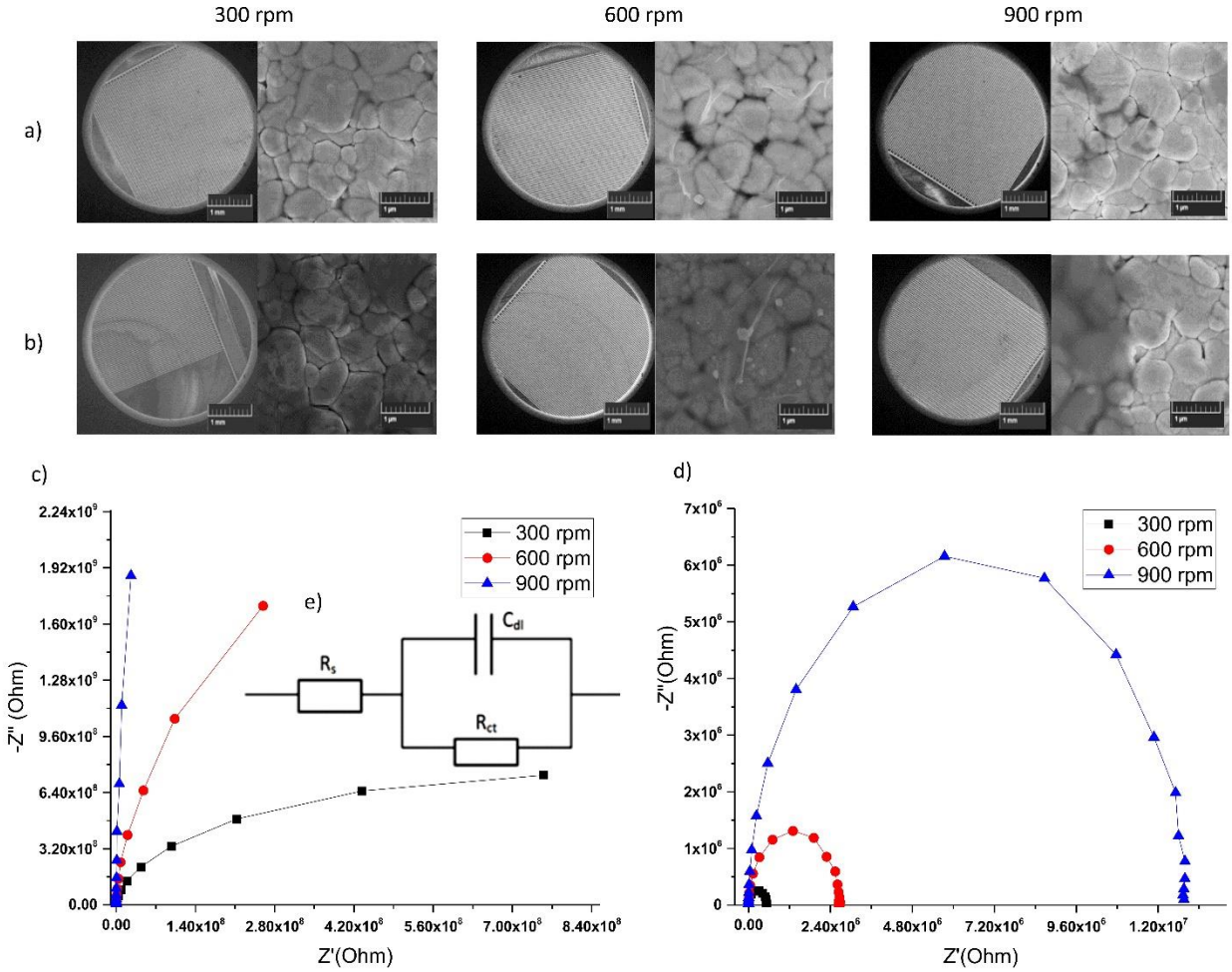

Figure 2 SEM morphology of the MXenes thin films deposited from NMP (a) and DMF (b) at different spin coating speeds (300, 600, 900 rpm). Nyquist plots of NMP-MXene (c) and DMF-MXene (d) obtained by Electrical Impedance Spectroscopy. Scheme of the equivalent model of the circuit (e)

3.3. Electrical properties of MXenes films

The results of electrical impedance spectroscopy measurements of MXenes thin films deposited from NMP and DMF suspensions on a gold IDE sensor platform at different spin coater rotation speeds (300, 600 and 900 rpm) are shown in **Figures 2c** and **2d**. Analyzing the Nyquist plots, we can see a tendency of decreasing of electrical conductivity of MXenes thin films with increasing rotation speed for MXenes deposited from both types of suspensions. For the NMP-MXenes films, the Nyquist plot shows only a small part of the semicircle in the given frequency range, indicating that the role of the charge transfer resistivity component decreases. The radius of the semicircle arcs approaches the real part of the impedance. The decrease in the radius of curvature with decreasing rotation speed indicates an increase in electrical conductivity. The impedance spectra were fitted using series resistance R_s, charge transfer resistance R_{ct} and double layer capacitance C_{dl} using the equivalent circuit model shown in **Figure 2e**. The resulting values of R_s, R_{ct} and C_{dl} parameters for all NMP-MXenes and DMF-MXenes samples are summarized in **Table 1**.

Table 1 Evaluated parameters R_s, R_{ct}, C_{dl} of MXenes deposited from NMP and DMF suspensions on the gold IDE platform

Speed of rotation (rpm)	NMP-MXenes			DMF-MXenes		
	R_s (Ω)	R_{ct} (Ω)	C_{dl} (pF)	R_s (Ω)	R_{ct} (Ω)	C_{dl} (pF)
300	58.00	0.15×10^{10}	26.6	62.92	5.25×10^5	21.3
600	63.42	6.63×10^{10}	21.3	61.29	26.6×10^5	22.7
900	63.57	6.63×10^{10}	20.9	53.73	1280×10^5	23.4

In general, the MXenes thin films formed at different spin coating speeds are highly resistive and there is a tendency to increase the electrical conductivity of the films with decreasing spin coating speed. At the spin coating speeds of 300 rpm, MXenes thin films deposited from both types of NMP and DMF suspensions had the lowest resistance. Comparing the total resistivity of MXenes thin films deposited from DMF and NMP solutions at different rpm, it can be seen that DMF-MXenes had better conductive properties (by 5 orders of magnitude) than NMP-MXenes. The series resistance R_s and double layer capacitance C_{dl} are about similar and remain similar independent of spin coating speed. The series resistance R_s is also quite low, around 60 Ω for both types of MXenes. Thus, the determining factor for R_s and C_{dl} are not the differences in surface functional groups that were indicated previously by Raman spectroscopy [11]. It is known that the grain boundaries can also influence the behavior of electron hopping, smaller flakes correspond to a larger number of particle boundaries and hence more inter-particle contacts, which leads to a decrease in the electrical conductivity of the films. However, the average size of DMF-MXenes and NMP-MXenes particles is similar (36 nm and 42 nm) and thus the effect of internal structure can also be excluded. It is thus the MXene/Au-electrode interface that limits the charge transfer and leads to the very high resistance R_{ct} despite low series resistance R_s. During the spin coating and drying process the MXene flakes are most likely not sufficiently well connected to the IDE electrode below them. The lower R_{ct} of DMF-MXenes compared to NMP-MXenes may be due to better electrode coverage, at the lowest 300 rpm speed, as indicated by darker SEM images.

4. CONCLUSIONS

The study of spin coating parameters' effect on MXenes thin films deposited from suspensions of DMF and NMP on a gold/ceramic IDE sensor platform. For the spin coating speeds 300-900 rpm, series resistance (related to actual electrical conductivity) and double layer capacitance (related to actual microstructure) of MXenes remained similar for both types of suspensions independent of rotation speeds. The highest charge transfer conductivity, i.e. the lower charge transfer resistance, was systematically achieved at the lowest rotation speed of 300 rpm, irrespective of NMP or DMF solvent. We assume that it is mainly due to the highest density and uniformity of MXenes distribution by spin coating on the IDE surface as shown by the SEM images. Interestingly, MXenes spin coated from DMF solution had better charge transfer compared to NMP. This difference can be explained by better coverage and contact with the electrodes (again noticeable in SEM images) due to differences in the surface functional groups of NMP-MXenes and DMF-MXenes. The conclusions made in this work regarding the dependence of electrical properties on the spin coating process parameters may serve as a guide for the possible use of MXenes in non-aqueous solvents as charge transporting layers in organic-based photovoltaic devices.

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