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# Electrochemical growth of trijunction semiconductors for Renewable Energy applications

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## Abstract

In the present work, we report the growth of an electrode based on $TiO_2/Fe_2O_3/MnO_2$ trijunctionon stainless steel substrate,to develop a new electrode for electrochemical supercapacitor. The synthesized electrodes are characterized by X-ray diffraction (XRD) and Fourier Transform Infrared, Spectroscopy (FTIR). Electrochemical properties are studied using cyclic voltammetry (CV), and electrochemical impedance spectroscopy techniques. The observed results suggest that the trijunction electrode of the three metal oxide materials has a high electrochemical property due to its large surface area, porous structure, and low resistance to charge transfer. In fact, it exhibits capacitive in 1 M KOH electrolyte, indicating a promising electrode material for electrochemical supercapacitors.

**Keywords**: metal oxides thin films, electrochemical technique, trijunction electrode, supercapacitor application

## Fabrication of supercapacitor electrodes:

We have successfully developed an original process to synthesize $TiO_2/Fe_2O_3/MnO_2$ trijunction metal oxides onto stainless steel substrate as a supercapacitor electrode for energy storage, using three-step strategy methods. To understand the synthetic process of trijunction $SS/TiO_2/Fe_2O_3/MnO_2$, we have schematized the synthesis conditions in Fig. 1.


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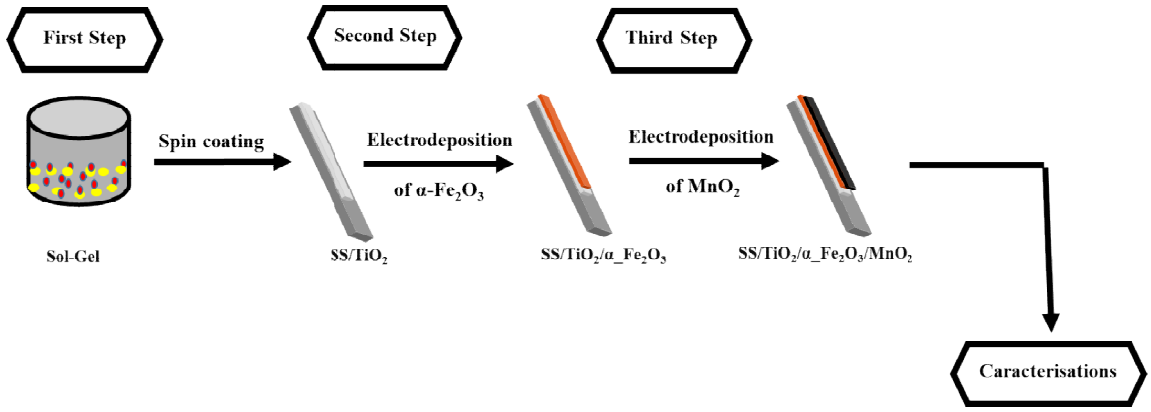


**Figure 1:** Electrochemical growth of $TiO_2/Fe_2O_3/MnO_2$ trijunction electrode

## Results and discussions

### 1.Structural analysis

Figure (2a) reveals the XRD pattern recorded for the stainless steel substrate (SS), The $TiO_2$,α-$Fe_2O_3$ and the heterojunction $TiO_2$/α-$Fe_2O_3$. The dashed lines represent the contribution of the 304L stainless substrate at 2θ = 43.8°, 44.6° and 50.8°. According to JCPDS (Joint committee on Power Difraction) database with card number 00–023-0298. The (+) represents the hematite peaks, it was observed that the rhombohedral α-$Fe_2O_3$ structural peaks at 2θ values of 24.21°, 33.23°, 35.70° were indexed to the (012), (104) and (110) planes, respectively (JCPDS card No. 86–0550)[1, 2]. The peak indicated by (*) correspond to$TiO_2$anatase phase characterized by the main orientations (101) at 2θ = 25.3° [3]. It is recalled that the crystal lattice of anatase is tetragonal (JCPDS-ICDD maps n° 01-084-1286). By comparison with the diffractograms of the materials alone, the peaks of the heterojunction were attributed to the SS substrate, $TiO_2$ anatase phase and hematite $Fe_2O_3$. This suggests on the one hand that the rhombohedral structure of α-$Fe_2O_3$ is well formed on the $TiO_2$ layer and on the other hand that thin layers of $TiO_2$ are stable during the second process of hematite synthesis.

For the electrodeposition of $MnO_2$(Figure 2b), we will not see any peak attributed to manganese oxide except that the characteristic peaks of the stainless-steel substrate. This behavior can be explained by the fact that this compound is amorphous and not detectable by XRD analysis [4]. Hammami and his group [5]showed that even with a heat treatment at 450°C for one hour the $MnO_2$material remained amorphous and no change in the XRD spectrum was observed. By comparison with $TiO_2/Fe_2O_3$ heterojunction electrode and $MnO_2$ spectrum, the spectrum of trijunction electrode contain only the peaks attributed to $TiO_2$


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(101), $Fe_2O_3$ (012), (104) and (110) planes and any peaks related to $MnO_2$ are obtained. This confirm another time that le manganese oxide is not detected by XRD analysis.

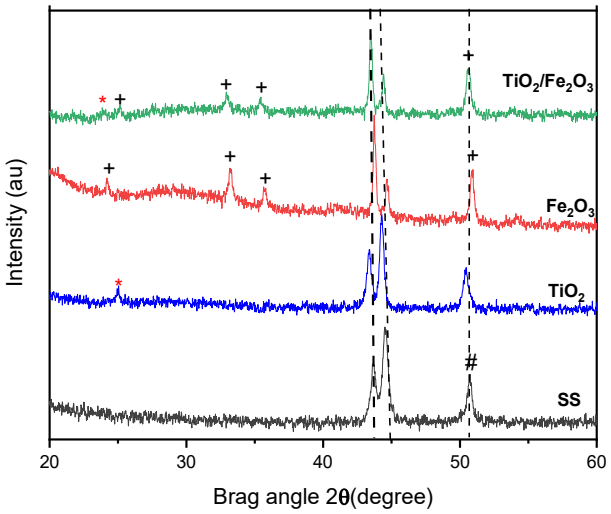


**Figure 2.** XRD diffraction pattern of thestainless-steel substrate (SS), $TiO_2$, α-$Fe_2O_3$ and the heterojunction $TiO_2$/α-$Fe_2O_3$

## 2. Electrochemical performance

In this work, the electrochemical capacitive performance of the metal oxide materials thin films grown by electrodeposition method onto SS substrate is determined using CV measurements in 1 M KOH solution at a fixed scan rate of 50 $mV.s^{-1}$ (Figure 3).To neglect the influence of the substrate, the CV measurement of stainless steel substrate was also performed with the same conditions. A slight difference is observed between the CV curve of the Stainless-steel substrate (SS) and $TiO_2/Fe_2O_3$, indicating that the combination of both $TiO_2$ and $Fe_2O_3$ is not suitable enoughto affect the capacitance electrode behavior. However, when $TiO_2/Fe_2O_3$ is recovered by $MnO_2$ (pink curve), we can see that the trijunction electrode at a potential scan rate of 50$mV.s^{-1}$exhibit nearly ideal EDLC behavior with quasi-rectangular form of CV curve along the potential current axis without evident redox peaks, indicating that the trijunction electrode has an ideal electric double-layer capacitive behavior [6]. Besides, the remarkable increase of the area of CV curve is indicating the capacitive nature of this trijunction. Comparing the trijunction electrode to only $MnO_2$ thin film electrode (black curve), we can clearly see that the prepared $TiO_2/Fe_2O_3/MnO_2$ electrode has a higher area curve, which means that the obtained trijunction has higher charge storage properties. In fact, we can note that the addition of $MnO_2$ on the $TiO_2$/a-$Fe_2O_3$ junction forms a porous structure,


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allowing an efficient ion exchange between the electrolyte and the active electrode, which promotes the rapid oxidation-reduction reaction to obtain a high specific capacity. All these characteristics ensure full contact between the electrolyte and the electrode in order to accelerate the diffusion of ions.

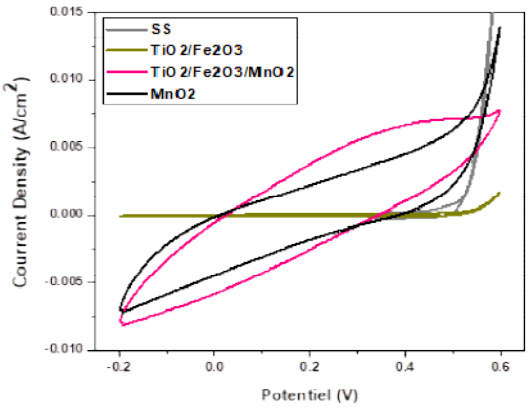


**Figure 3:** Superposition of CVs forSS, $TiO_2$/ $Fe_2O_3$, $MnO_2$, $TiO_2$/ $Fe_2O_3$/$MnO_2$of various films studied (at a scanning rateof 50 mV/s).

## Conclusion

In summary, $TiO_2$/α-$Fe_2O_3$/$MnO_2$ have been successfully elaborated onto SS substrate for the first time by a two-step process of combined Sol-Gel/spin coating technique followed by electrodeposition method.The capacitive effect of$MnO_2$ on the electrical properties of SS/$TiO_2$/$Fe_2O_3$electrode was investigated.The trijunction electrodeexhibited high efficiency supercapacitor properties comparing to $Fe_2O_3$/$TiO_2$ electrode. From this study, we can conclude that the proposed trijunction electrode can be available for electrochemical performance for supercapacitor application.

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