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CHEMICAL DEPOSITION OF NANO-SIZED ELECTROCHROMIC THIN FILMS OF $Na_{0.33}V_2O_5\cdot H_2O$ XEROGELS

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INTRODUCTION

One of the most important properties of the materials used in various fields of high technology is electrochromism. A material is electrochromic if it has the capability to maintain reversible and persistent change in the optical properties (color change) when an electrical potential is applied to it. The reversible change in the color is induced by the change in the oxidation state of the metal ions which is associated with relevant insertion/extraction of ions from the electrolyte into/from the material.

Nano-sized electrochromic sodium intercalated vanadium(V) oxide xerogels thin films with composition $Na_{0.33}V_2O_5\cdot H_2O$ have been deposited on electroconductive FTO coated glass substrates by a simple chemical bath method.

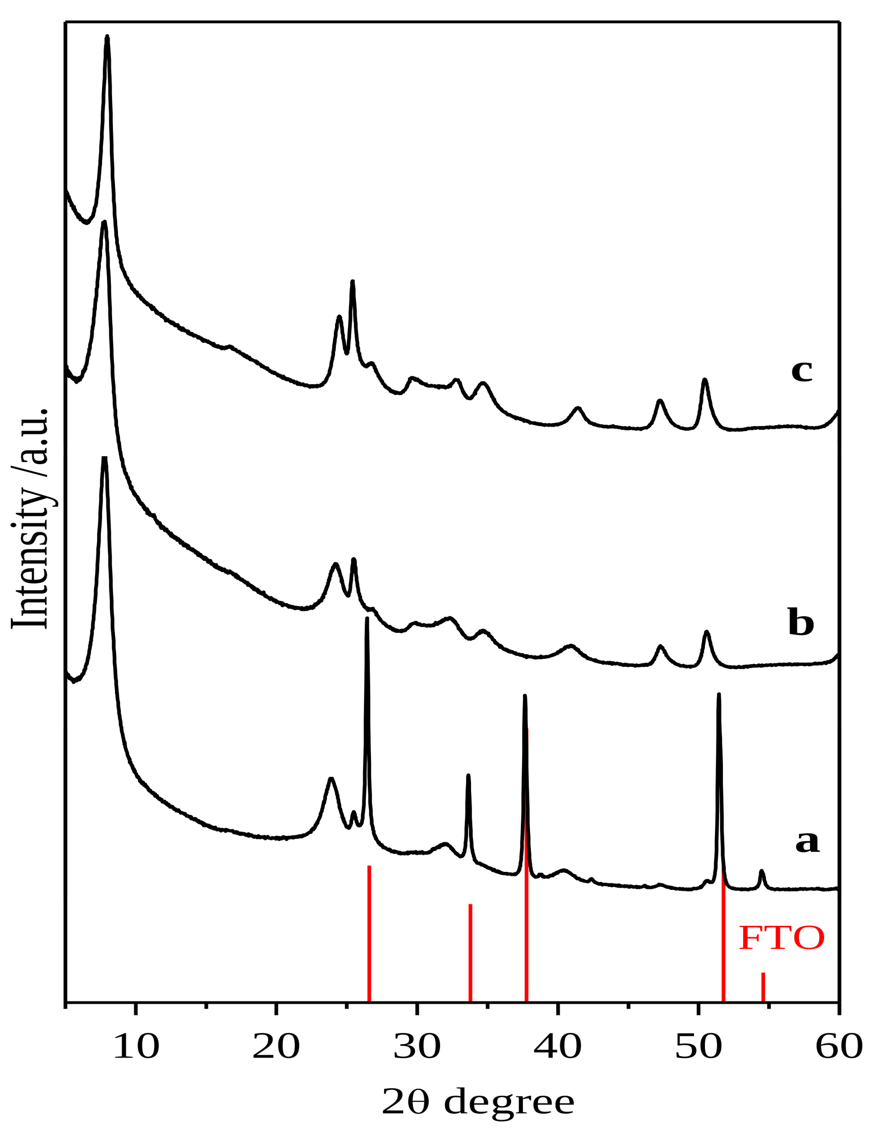
CHEMICAL BACKROUND OF THE PROCESS

The chemistry of the deposition process is complex and not fully understood and is based on hydrolysis of diethyl sulfate above 65 ˚C. The precipitate and the thin films of $Na_{0.33}V_2O_5\cdot H_2O$ are obtained in acidic media that is achieved by increasing the concentration of H_3O^+. Namely, the following reaction takes place:

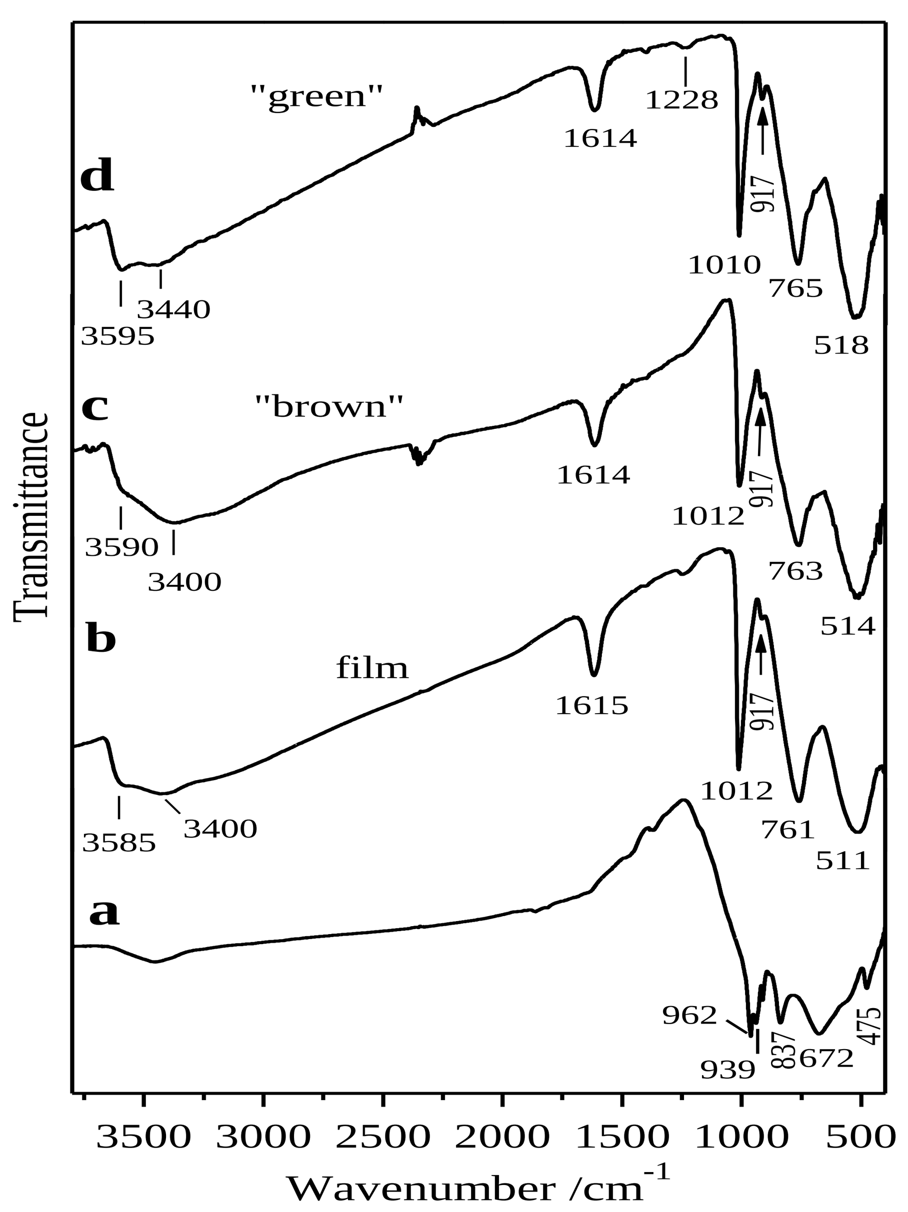
$$(CH_3CH_2O)_2SO_2(aq) + 4H_2O(l) \rightarrow 2CH_3CH_2OH(aq) + 2H_3O^+(aq) + SO_4^{2-}(aq)$$

The $Na_{0.33}V_2O_5\cdot H_2O$ "brown" colored xerogel thin films turn "green" after one week.

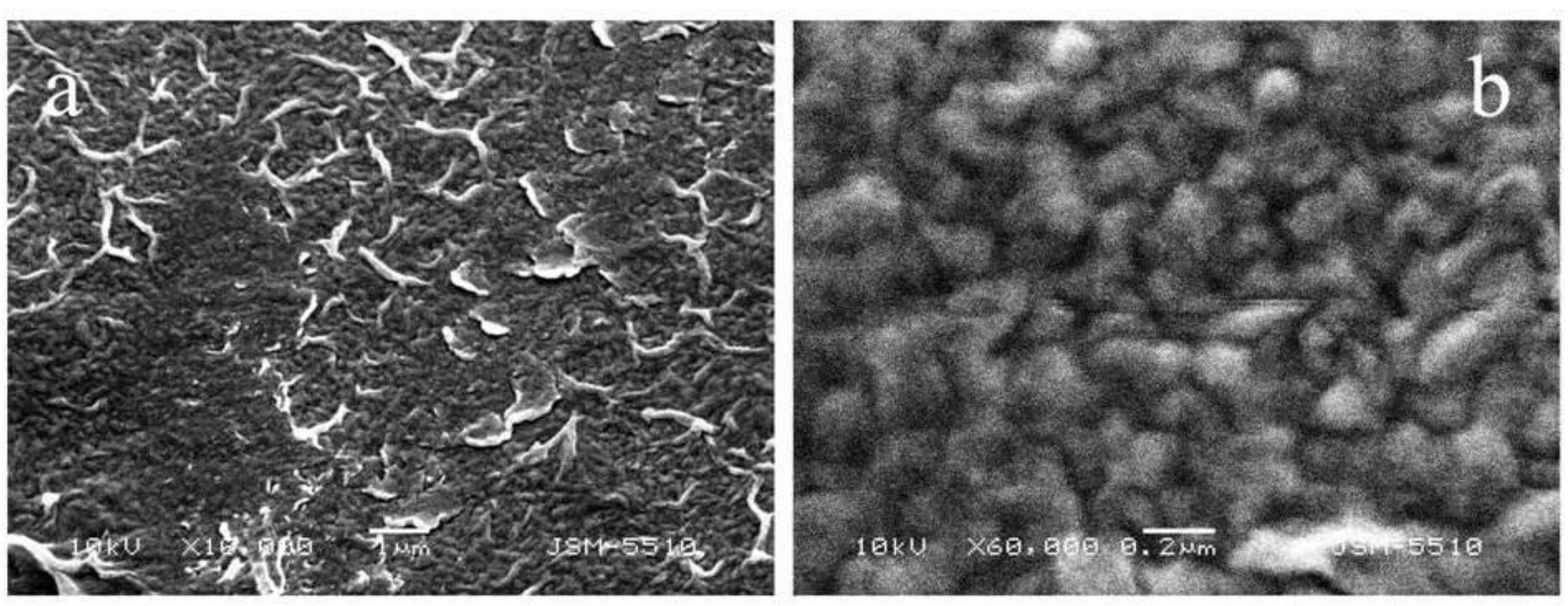
STRUCTURAL ANALYSIS



XRD patterns of as-deposited film (a), "brown" precipitate (b) and "green" precipitate (c)

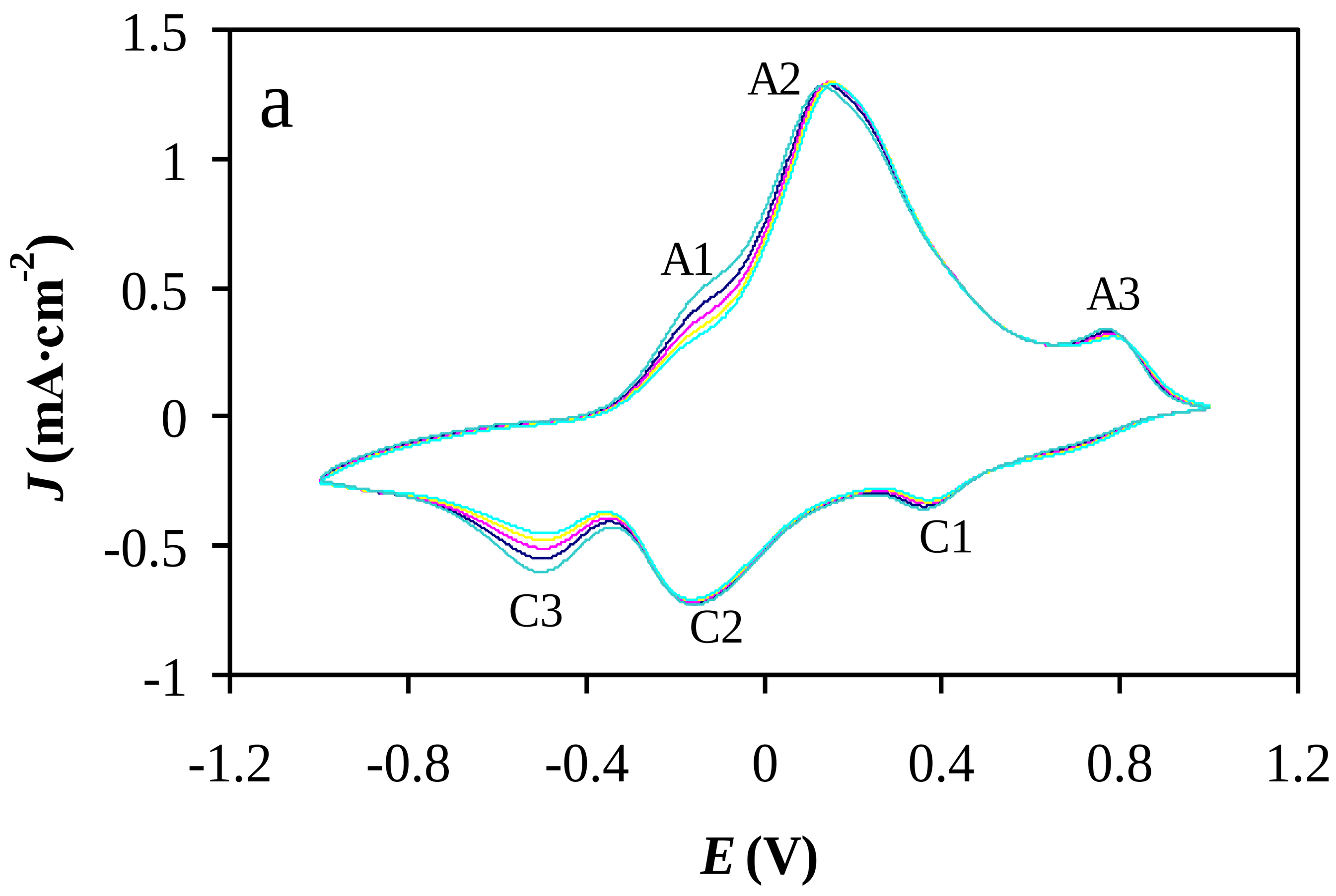


IR spectra of $NaVO_3$ (a), as-deposited scraped film (b), "brown" precipitate (c) and "green" precipitate (d)



SEM photomicrographs illustrating the morphology of $Na_{0.33}V_2O_5\cdot H_2O$ thin films

ELECTROCHEMICAL CHARACTERIZATION IN 1 M $LiClO_4$ IN PROPYLENE CARBONATE (PC)

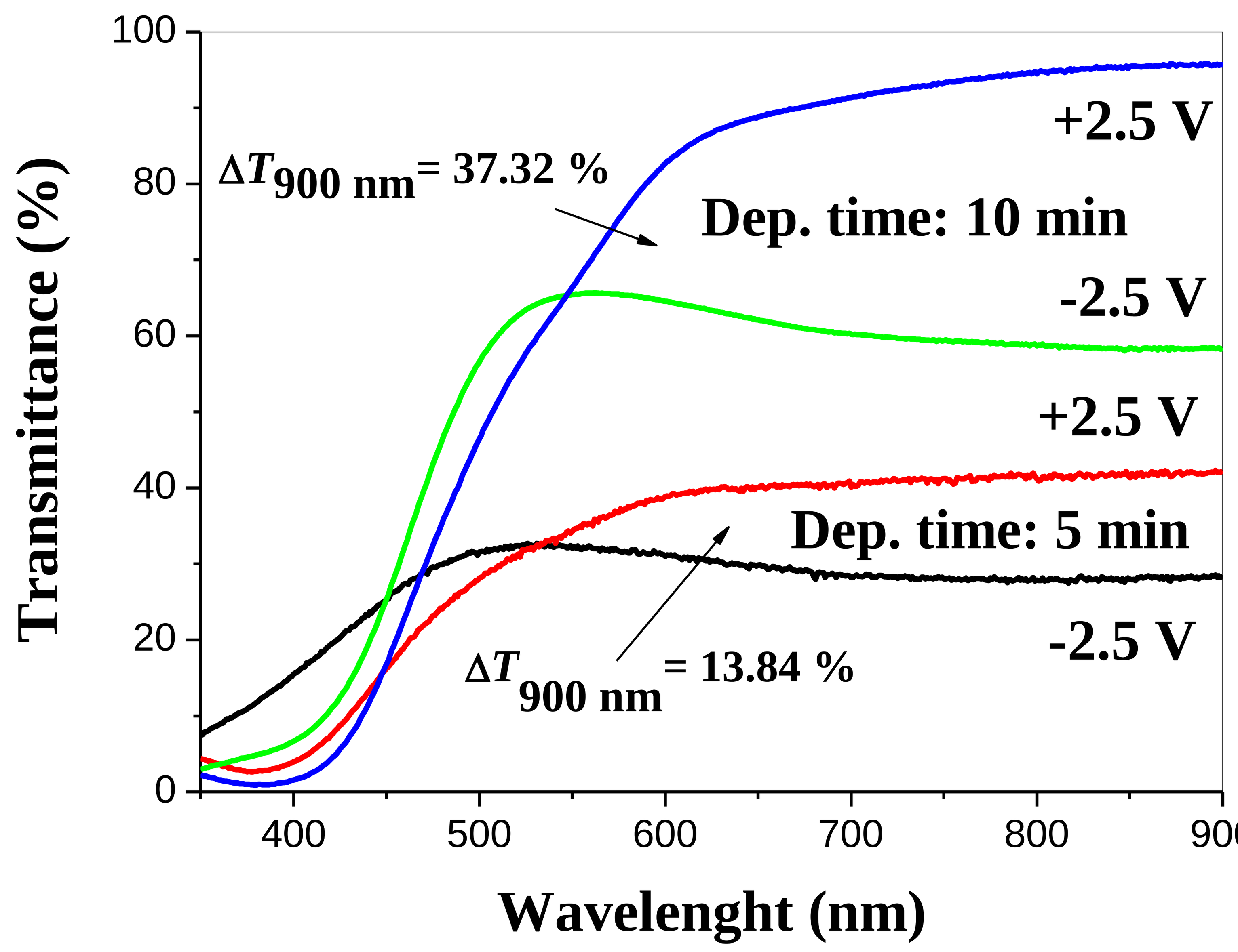


The observed three redox pairs are related to reversible intercalation/deintercalation of lithium ions accompanied with reversible reduction/oxidation processes between V(V) and V(IV) sites:

$$x\mathrm{Li}^+(aq) + Na_yV_z^{+4}V_{2-z}^{+5}O_5\cdot aH_2O(s) + xe^- \rightleftharpoons Li_xNa_yV_{z+x}^{+4}V_{2-z-x}^{+5}O_5\cdot aH_2O(s)$$

"brown" "blue-gray"

UV-VIS SPECTRA OF $Na_{0.33}V_2O_5\cdot H_2O$ THIN FILMS EXAMINED IN 1 M $LiClO_4$ IN PC



CONCLUSIONS

- A new method for chemical deposition of nano-sized $Na_{0.33}V_2O_5\cdot H_2O$ electrochromic thin films has been designed. It doesn't require expensive equipment and can be easily adopted for a large and small area deposition.
- The cyclic voltammetry shows that the Li^+ ions are reversibly intercalated/deintercalated within the prepared films.
- The prepared thin films exhibit two-step electrochromism: from orange to green and then from green to blue. The colour changes are related to the transitions between different oxidation vanadium states.
- The best electrochromic properties are obtained for a thin film with 110 nm thickness: ΔT for this film is ~ 37 % at 900 nm. The good value achieved for transmittance variance makes these films very promising for application in electrochromic devices.