



HAL
open science

UV treatment for enhanced electrochromic properties of spin coated NiO thin films

Khawla Zrikem, Giljoo Song, A. Aït Aghzzaf, M. Barek Amjoud, Daoud Mezzane, Aline Rougier

► **To cite this version:**

Khawla Zrikem, Giljoo Song, A. Aït Aghzzaf, M. Barek Amjoud, Daoud Mezzane, et al.. UV treatment for enhanced electrochromic properties of spin coated NiO thin films. Superlattices and Microstructures, 2019, 127, pp.35-42. 10.1016/j.spmi.2018.03.042 . hal-02057818

HAL Id: hal-02057818

<https://hal.science/hal-02057818>

Submitted on 13 Oct 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

UV treatment for enhanced electrochromic properties
of spin coated NiO thin films

K. Zrikem^{a,b}, G. Song^a, A. Ait Aghzzaf^b, M. Amjoud^b, D. Mezzane^b,
A. Rougier^{a*}

^a CNRS, Univ. Bordeaux, ICMCB, UMR 5026, F-33600 Pessac, France

^b LMCN-FST, Cadi Ayyad University, 112 Boulevard Abdelkrim Al Khattabi, Marrakech,
Morocco

* Corresponding author : aline.rougier@icmcb.cnrs.fr

Keywords	Abstract
NiO thin films; Sol-gel; UV treatment ; Electrochromic properties.	Nickel oxide thin films were deposited by sol-gel combined with spin coating method. Herein, the influence of the concentration of the precursor, kind of solvents, stabilizers and type of final treatment (calcination and UV treatment) on the structural, morphological, and electrochromic properties of NiO thin films is reported. Enhanced electrochromic properties, corresponding to a modulation of the optical transmittance under an applied voltage, are established for NiO thin films prepared with methanol as solvent, Triton X-100 as stabilizer and treated by UV using a lamp with low power of 30 W for 5 h. These findings highlight the benefit of using UV treatment, as replacement of annealing step for enhanced NiO electrochromic properties.

1. Introduction

More recent attention has focused on the issues of energy efficiency that characterize the architecture of this century leading to the development of innovative glazing systems. This aims at reducing heat loss and controlling incoming solar radiation in order to minimize solar gain in summer and maximize it in winter. For this purpose, electrochromic system, able to control the amount of light and heat entering in the interior depending on the seasons, offers key solutions in the form of smart windows [1-3]. Among electrochromic materials, nickel oxide (NiO) has received significant attention due to its anodic coloration leading to neutral color devices when combined with WO₃ [4].

Electrochromic phenomenon is commonly described as a simultaneous injection/extraction of electrons and ions into/from electrochromic materials [5]. Indeed, it is generally accepted that the switch from a transparent to a brownish state in anodically colored NiO is related to the redox reactions from Ni²⁺ to Ni³⁺ states associated with either H⁺ or Li⁺ (de)insertion. Interestingly, in our group, in the past few years, coloration associated with electrochemical cycling in electrolyte without small cations was reported for non stoichiometric nickel oxide thin films, emphasizing the complexity of the EC mechanism [6]. The latter also results from the numerous techniques used to grow NiO thin films leading to films of various crystallinities, morphologies and compositions (i.e. Ni/O ratio) [7].

Up to now, NiO thin films have been deposited using RF sputtering [8], co-precipitation method [9], electrochemical deposition [10], spray pyrolysis [11-12], etc., but in the development of soft chemistry, sol-gel method was shown to be one of the most attractive techniques, owing to its simplicity, low cost, and possibility of thin films deposition on large area and flexible substrates at room temperature using UV light [13-15]. In addition, the morphology and structural properties of thin films deposited by sol-gel process are very sensitive towards the experimental conditions such as type and concentration of starting

materials, pH, nature of solvent, temperature, time of reaction, and drying processes that affect the rate of hydrolysis and condensation reactions.

In this paper, NiO thin films were prepared by sol-gel method combined with spin coating technique. The influence of the concentration of the precursor, solvents, stabilizers and the type of final treatment (calcination and UV treatment) on structural, morphological, and electrochromic properties of NiO thin films is discussed. This study sheds new light on the advantage of UV treatment for NiO thin films deposition suitable for a wide range of substrates, confirming our earlier results on the benefit of this room temperature treatment for nice electrochromic properties [16].

2. Experimental

2.1. Materials and methods

All the chemical reagents used were of analytical grade and used without further purification. Several parameters were varied in order to optimize the deposition conditions of NiO thin films by sol-gel via spin coating method. The flowchart of the protocol is shown in Fig. 1.

Nickel acetate ($\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$), triton X-100 ($\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$ ($n=9-10$)) or CTAB ($\text{C}_{19}\text{H}_{42}\text{BrN}$), and methanol (CH_3OH) or water (H_2O) were used as precursor, stabilizers and solvents, respectively.

The prepared sol solutions were mixed in required amounts and stirred at ambient temperature for 1 h, then at 70 °C for an additional hour and finally at ambient temperature for 4 h. ITO coated glass (commercialized by Solems with a resistance of 80 Ω/sq) was used as substrate. The obtained sol solutions with different nickel acetate concentrations using both stabilizers in two different solvents, namely water and methanol, were coated on substrates rotated with velocity of 4000 rpm for 30 s.

After deposition, each layer was dried at 175 °C for 20 min. For each thin film, this procedure was repeated 6 times, leading to thickness of hundred nanometers to few micrometers depending on the precursor concentration. The thickness of the films was measured by using Talley Step

Profilometer. As an example, for a nickel concentration of 0.3 M, the films thickness is about 470 nm \pm 50 nm.

As a final step, the as-grown films were exposed (i) at 300 °C for 2 h in air ambient or (ii) under a UV light for 1 h using a lamp of 160 W or 5 h using a lamp of 30 W.

2.2. Characterizations

The film structure was determined by X-ray diffraction using a PANAAalytical X'pert MPD diffractometer with Cu- k_{α} incident radiation. The morphology of the films was characterized by Scanning Electron Microscopy (SEM) (Hitachi Tabletop microscope TM-1000). Cyclic voltammograms (CVs) were recorded on a Biologic potentiostat using a three-electrode cell consisting of Glass/ITO/NiO as working electrode, a Pt sheet as counter electrode and a saturated calomel electrode as reference electrode ($E_{SCE}(V) = 0.234 \text{ mV/ENH}$). These electrodes were soaked in 1 M KOH electrolyte (purity (99.99%)). The optical transmittance measurements were carried on a Varian Cary UV-Visible NIR spectrometer.

3. Results and discussion

3.1. Influence of the precursor concentration, solvents and stabilizers nature

3.1.1. Structural analysis

Fig. 2 presents the X-ray diffractogram of NiO thin film, prepared in methanol using 0.5 M of precursor, triton X-100 as stabilizer and annealed at 300 °C for 2 h in air ambient. The XRD peaks observed at 2 theta values of 37.5 ° and 43 ° are associated with (111) and (200) reflections respectively, and are fully consistent with the cubic-structured crystalline NiO (S. G. : Fm-3m). The cell parameter of 4.188 Å agrees well with the one reported in the literature for NiO while it is slightly higher than the one of the bulk (4.167 Å) [17]. An average crystallite size of 55 Å was estimated using the Scherrer formula $L = 0.89 \lambda / \beta \cos \theta$; where L is the average crystallite size in nm, $\lambda = 0.154056 \text{ nm}$, β the full half-width and θ the diffraction angle.

3.1.2. Optical properties

The visual appearance of the as deposited films shows a slight brownish coloration of which intensity increases with molar concentration due either to a thickness effect and /or a slight departure from the NiO stoichiometry (i.e. presence of Ni³⁺ in Ni_{1-x}O thin films). The optical transmittances of the as-deposited thin films elaborated with different precursor concentrations 0.1 M, 0.3 M and 0.5 M and annealed at 300 °C for 2 h in air ambient are presented in Fig. 3a. In the as-deposited state, NiO thin films with 0.1 M and 0.3 M exhibit a rather high transparency, while the NiO film with 0.5 M is characterized by a low value of transmittance 30 % at 550 nm against 80 % and 78 % for NiO films with 0.1 M and 0.3 M, respectively [18].

In respect of the optical properties, the 0.3 M concentration was kept as precursor concentration for the choice of the solvent and stabilizer.

As shown in the Fig. 3b, whatever methanol or water as solvent, both as deposited NiO thin films present similar optical properties with a transmittance of about 72 % in the visible region. Therefore, due to better dissolution of nickel acetate in methanol associated with lower boiling point leading to higher homogeneity and smoother surface than water, methanol was kept as solvent [19].

The optical properties of NiO thin films can also be significantly adjusted through the addition of stabilizers. Thus, aiming at increasing the film porosity and consequently providing easy paths for electrolyte penetration further on when cycled in KOH, triton X-100 or CTAB-surfactant was added in the sols. The highest transmittance value is shown for triton X-100 as a stabilizer in methanol (transmittance of about 70 %) compared to those of CTAB and without stabilizer (Fig. 3c) [20]. All these thin layers were annealed at 300 °C for 2 h in air ambient.

3.2. *Influence of final treatment*

The benefit of UV treatment on the electrochromic properties of oxides was earlier demonstrated in our group [16] while, to our knowledge, earlier studies do not exist for NiO.

Thus, the common heat treatment at 300 °C was compared to two UV treatments using a lamp of 160 W for 1 h and one of 30 W for 5 h.

3.2.1. Structural analysis

The X-ray diffractograms of the films heat treated at 300 °C and UV treated (160 W/1h; and 30 W/5h) are shown in Fig. 4. The UV treatments lead to the disappearance of the (200) peak located around 43° suggesting a decrease of the film crystallinity in between the film heat treated at 300 °C as compared to the films treated by UV. This trend is confirmed on the 0.5 M thin film as shown in the inset of Fig. 4.

3.2.2. Electrochromic properties

The comparison of the cyclic voltammograms of the three previous films deposited on ITO glass substrates and cycled in Pt/1M KOH/NiO vs SCE, at a scan rate of 10 mV/s and in a voltage window of [-0.6 V; 0.6 V] shows significant differences. The behavior of the 300 °C annealed films is rather common with a CV shape consisting of two well defined peaks located at 0.4 V in anodic sweep and 0.25 V in cathodic sweep, illustrating a reversible faradic process and a Ni²⁺/Ni³⁺ redox reaction associated with the Ni(OH)₂/NiOOH phases [21] (Fig. 5a). Upon cycling the NiO film visually, switch from a transparent to a brownish state in oxidation as expected for its anodic character. The CVs shapes of the UV-treated films are quite different in particular in oxidation, for which the increase in current appears at lower potential than for the annealed films (Fig. 5b). The oxidation peak of the '30 W' is even no more visible as the current shows a sharp increase usually associated with the electrolyte degradation and oxygen formation due to the oxidation of water ($2\text{H}_2\text{O} = 4\text{e}^- + \text{O}_2 + 4\text{H}^+$).

Nevertheless, the presence of the reduction peak as well as the decrease in transmittance as described below (Fig. 6) confirms the film oxidation. For the 160 W films, the anodic peak is even quite large with the appearance of a second wave at higher voltage prior to the increase in

current density corresponding to the electrolyte decomposition. The *in-situ* measurements of the optical transmittance in the bleached (-0.5 V) and colored (0.5 V) states show a larger contrast; expressed at the ratio of the transmittance in the bleached state (T_b) vs the transmittance in the colored state (T_c) for the UV treated films (Fig. 6b). Indeed, the contrast, T_b/T_c , increases from unexpected very low value of 1.05, in respect of the nice CV, to 1.35 (160 W) and 1.51 (30 W). The difference in transmittance of 5 % for the film annealed at 300 °C increases to 20 % for the 160 W film and reaches its highest value of 30 % at 600 nm for the film treated with lower power, namely 30 W. Those results clearly demonstrate in our conditions, the benefit of UV treatment as compared to calcination.

The enhanced EC properties with UV treatment is further confirmed by the evolution of the transmittance that shows a similar change in transmittance of about 5 % for both oxidation and reduction for the annealed film, while the drop in transmittance is rather sharp and of about 15 to 20 % for the film treated by UV (Fig. 7). Upon reduction, the bleaching time is longer than the coloration time in oxidation, emphasizing faster kinetics from $\text{Ni}(\text{OH})_2$ to NiOOH .

The higher EC properties of the UV treated films are however associated with very limited cyclability. Indeed, as shown in Fig. 8 with the evolution of the capacity vs the cycle number, the capacity drops of about 50 % after only 7 cycles. The stabilization, appearing till 10 cycles, needs to be further confirmed. The poor cyclability is to be correlated to the poor surface morphology consisting of large cracks for the UV treated films while the one of the calcined film is much smoother (Fig. 9). Such morphology issue is currently being addressed as it limits the benefit of the UV treatment.

4. Conclusion

The present study was designed to deposit nickel oxide thin films by sol-gel combined with spin-coating method. Their characterization combining various techniques (XRD, SEM,

electrochemical and optical measurements) shows an enhancement of the electrochromic properties with UV treatment as the final step. The highest EC properties were established for NiO thin films prepared using methanol as solvent, triton X-100 as stabilizer and treated by UV using a lamp of 30 W for 5 h. Having established a protocol for un-doped NiO film, the influence of Li and phosphor doping on the physico-chemical and EC properties of NiO thin films are currently in progress, aiming at understanding the influence of the p-type character of NiO on its EC behavior.

Acknowledgments

The financial supports from the “Hubert Curien/TOUBKAL Program” (Project number: Toubkal/16/35-Campus France: 34730RJ) are gratefully acknowledged. The authors wish to thank Mathias Da Rocha, Alexandre Fargues (optical measurements), Sébastien Fourcade (spin-coating technique) and Nicolas Penin for helpful discussion.

References

- [1]. Marco Casini, Smart windows for energy efficiency of buildings, Proc. of the Second Intl. Conf. on Advances In Civil, Structural and Environmental Engineering- ACSEE, (2014).
- [2]. C.M. Lampert, Advanced in smart materials technologies – Window, Proc. Annual Technical Conference – Society of Vacuum Coaters, (2005) pp 675 -677, DOI: 10.1016/S1369-7021(04)00123-3
- [3]. C.G. Granqvist, Electrochromic for smart windows: Oxide-based thin films and devices, Thin Solid Films 564 (2014), 1-38, DOI: 10.1016/j.tsf.2014.02.002.
- [4]. M. Da Rocha, X. He, X. Diao, A. Rougier, Influence of cycling temperature on the electrochromic properties of WO₃ //NiO devices built with various thicknesses Solar Energy Materials and Solar Cell, (2017) in press, DOI: 10.1016/j.solmat.2017.05.070.
- [5]. S.K. Deb, Opportunities and challenges of electrochromic phenomena in transition metal oxides, Solar Energy Mater and Solar Cells 24 (1992) 327-338, DOI: 10.1016/0927-0248(92)90077-3.
- [6]. H. Moulki, C. Faure, M. Mihelčič, A.Š. Vuk, F. Švegl, B. Orel, G. Campet, M. Alfredsson, A.V. Chadwick, D. Gianolio, A. Rougier, Electrochromic performances of nonstoichiometric NiO thin films, Thin Solid Films, 553 (2014) 63-66, DOI: 10.1016/j.tsf.2013.10.154.

- [7]. M. Wang, Y. Thimont, I. Presmanes, X. Diao, A. Barnabé, The effect of the oxygen ratio control of DC reactive magnetron sputtering on as-deposited non stoichiometric NiO thin films, *Applied Surface Science* 419 (2017) 795-801, DOI: 10.1016/j.apsusc.2017.05.095.
- [8] S.C. Chen, C.K. Wen, T.Y. Kuo, W.C. Peng, H.C. Lin, Characterization and properties of NiO films produced by RF magnetron sputtering with oxygen ion source assistance, 572 (2014) 51-55, DOI: 10.1016/j.tsf.2014.07.062.
- [9]. A. Rahdar, M. Aliahmadb, Y. Azizib, NiO Nanoparticles: Synthesis and Characterization; *Journal of Nanostructure* 5 (2015) 145-151, DOI: 10.7508/JNS.2015.02.009.
- [10]. A.C. Sonavane, A.I. Inamdar, P.S. Shinde, H.P. Deshmukh, R.S. Patil, P.S. Patil, Efficient electrochromic nickel oxide thin films by electrodeposition, *Journal of Alloys and Compounds* 489 (2010) 667–673, DOI: 10.1016/j.jallcom.2009.09.146.
- [11]. L. Cattin, B.A. Reguig, A. Khelil, M. Morsli, K. Benchouk, J.C. Bernède, Properties of NiO thin films deposited by chemical spray pyrolysis using different precursor solutions, *Applied Surface Science* 254 (2008) 5814–5821, DOI: 10.1016/j.apsusc.2008.03.071.
- [12]. P.S. Patil, L.D. Kadam, Preparation and characterization of spray pyrolyzed nickel oxide (NiO) thin films, *Applied Surface Science* 199 (2002) 211–221, DOI: 10.1016/S0169-4332(02)00839-5
- [13]. Romana Cerc Korosec and Peter Bukovec, Sol-Gel prepared NiO thin films for electrochromic applications, *Acta Chim.Slov* 53 (2006) 136-147, DOI: 10.1.1.520.5813.
- [14]. G. Turgut, E.Sonmez, S.Duman, Determination of certain sol gel growth parameters of nickel oxide films, *Ceramics International* 41 (2015) 2976–2989, DOI: 10.1016/j.ceramint.2014.10.133
- [15]. J.L. Garcia-Miquel, Q. Zhang, S.J. Allen, A. Rougier, A. Blyr, H.O. Davies, A.C. Jones, T.J. Leedham, P.A. Williams, S.A. Impey, Nickel oxide sol–gel films from nickel diacetate for electrochromic applications, *Thin Solid Films* 424 (2003) 165–170, DOI: 10.1016/S0040-6090(02)01041-6.
- [16]. A. Danine, L. Cojocar, C. Faure, C. Olivier, T. Toupance, G. Campet, A. Rougier, Room temperature UV treated WO₃ thin films for electrochromic devices on paper substrate, *Electrochimica Acta* 129 (2014) 113-119, DOI: 10.1016/j.electacta.2014.02.028
- [17]. A. Mendoza-Galvan, M.A Vidales-Hurtado, A.M. Lopez-Beltran, Comparison of the optical and structural properties of nickel oxide-based thin films obtained by chemical bath and sputtering, *Thin Solid Films* 517 (2009) 3115-3120, DOI: 10.1016/j.tsf.2008.11.094
- [18]. Nabeel A. Bakr, Sabah A. Salman and Ahmed M. Shano, Effect of solution molarity on structural and optical properties of nickel oxide thin films prepared by chemical spray pyrolysis

technique, International Journal of Current Research 6 (2014) 9644-9652, DOI: 10.12785/ijtfst/040208

[19]. Nasrin Talebian, Sol-gel derived nanostructured nickel oxide films: Effect of solvent on crystallographic orientations, Solid State Sciences 27 (2014) 79-83, DOI: 10.1016/j.solidstatesciences.2013.11.010

[20]. M. Kooti, and L. Matouri, A facile and mild method for synthesis of nickel oxide nanoparticles in the presence of various surfactants, Journal of Material Sciences 2 (2014) 2347-2278.

[21]. I. Bouessay, A. Rougier and J.M. Tarascon, Electrochemically inactive nickel oxide as electrochromic material, Journal of Electrochemical Society 151 (2003) 145-152, DOI: 10.1149/1.1731584

Figure Captions :

Fig. 1. Experimental protocol for the synthesis of NiO thin films by sol-gel method combined with spin-coating technique.

Fig. 2. XRD pattern of NiO thin films prepared from $(\text{Ni}(\text{acetate})_2 \cdot 4\text{H}_2\text{O})$ (0.5M) in methanol, using triton X-100 as stabilizer.

Fig. 3. Optical transmittance of the as-deposited NiO thin films prepared by (a) different precursor concentrations 0.1 M; 0.3 M or 0.5 M, (b) with different solvents, and (c) without and with stabilizers. All films are annealed at 300°C for 2 hr in air ambient.

Fig. 4. XRD patterns of NiO thin films prepared with 0.3M $(\text{Ni}(\text{acetate})_2 \cdot 4\text{H}_2\text{O})$ in methanol, and triton X-100 as stabilizer treated by annealing process, UV light by a lamp of 160 W for 1 hr and UV light by a lamp of 30 W for 5 hr. In inset NiO thin films prepared with 0.5 M $(\text{Ni}(\text{acetate})_2 \cdot 4\text{H}_2\text{O})$ and similar conditions.

Fig. 5. CVs of Pt/KOH 1M/SCE/NiO vs SCE cell prepared with 0.3M $(\text{Ni}(\text{acetate})_2 \cdot 4\text{H}_2\text{O})$ in methanol and triton X-100 as stabilizer treated by (a) annealing process and (b) UV light by a lamp of 160 W for 1 hr and UV light by a lamp of 30 W for 5 hr (b). The cell was cycled with a sweep rate of 10mV/s.

Fig. 6. Optical transmittances of NiO thin films 0.3M $(\text{Ni}(\text{acetate})_2 \cdot 4\text{H}_2\text{O})$ in methanol as a solvent with triton X-100 as stabilizer and treated by (a) annealing process (NiO-M-annealing process), a (b) lamp of 160 W for 1 hr (NiO-UV-160W-1 h), or (c) a lamp of 30 W for 5 hr (NiO-U-30W-5 h), in colored and bleached states.

Fig. 7. *In-situ* measurement of NiO thin films prepared by 0.3 M of nickel acetate in methanol, triton X-100 as a stabilizer, and treated by annealing process (NiO-annealing process), UV treatment with a lamp of 30 W for 5 hr (NiO-UV-30W-5h). [-0.5V; 0.5V].

Fig. 8. Evolution of the capacity of NiO thin films treated by annealing process or by UV using a lamp of 30 W for 5 hr vs cycle number when cycled in Pt/KOM 1 M/SCE/NiO vs SCE cell.

Fig. 9. SEM images of NiO thin films prepared with 0.3M $(\text{Ni}(\text{acetate})_2 \cdot 4\text{H}_2\text{O})$ in methanol, and triton X-100 as stabilizer treated by annealing process (NiO-annealing process); UV light by a lamp of 160 W for 1 hr (NiO-UV-160W-1 h) and UV light by a lamp of 30 W for 5 hr (NiO-UV-30W-5 h).

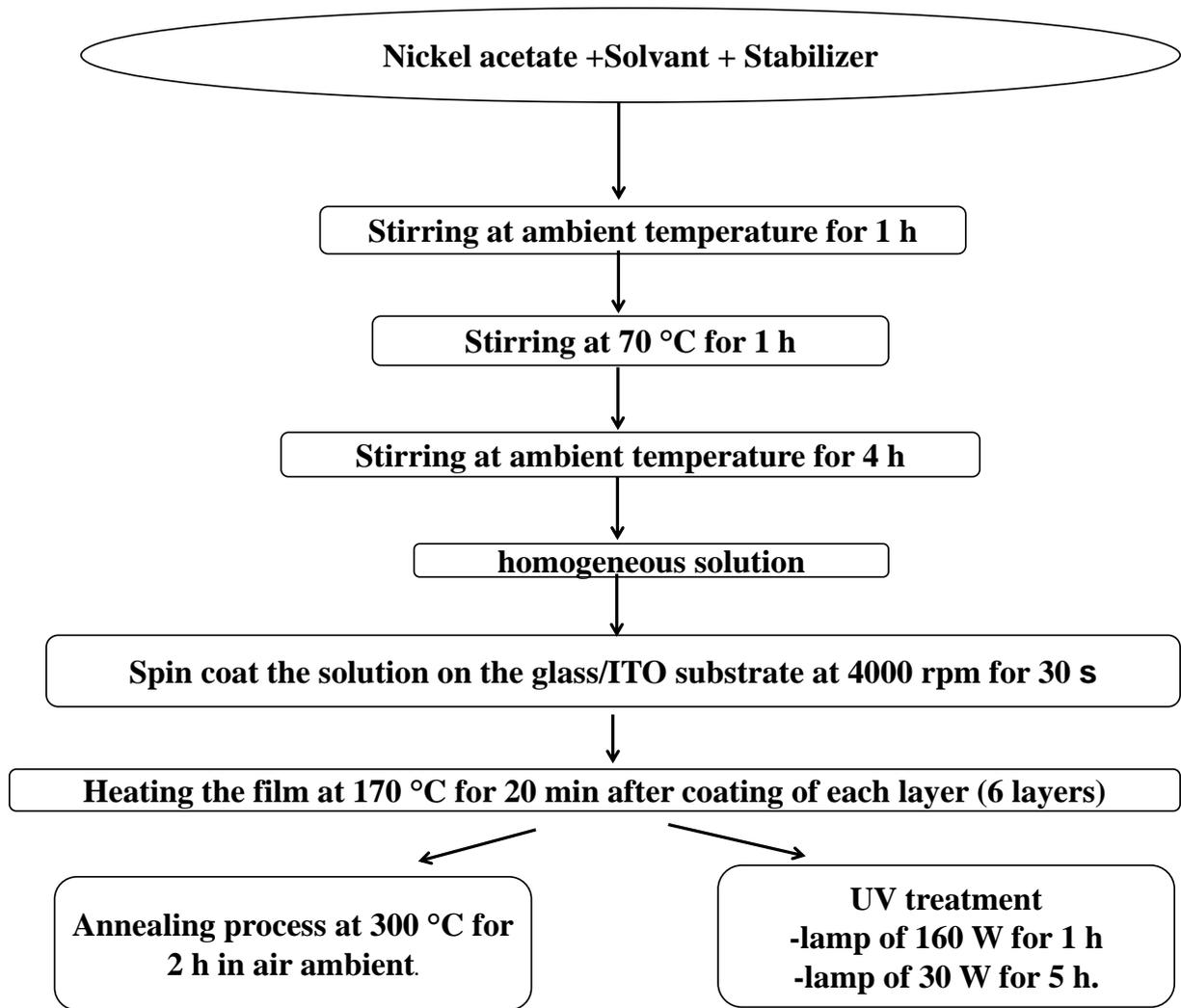


Figure 2 - K. Zrikem et al.

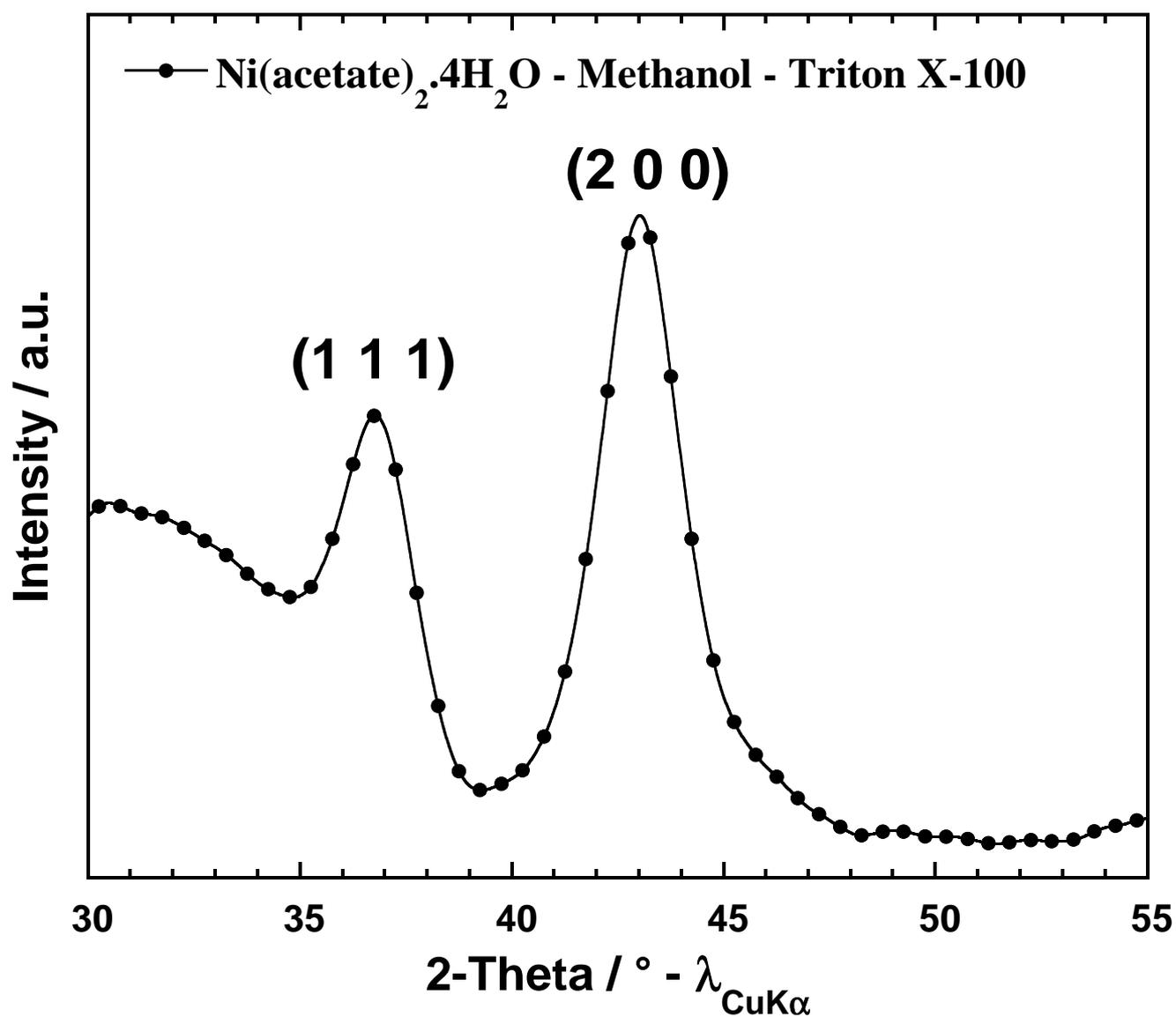


Figure 3a - K. Zrikem et al.

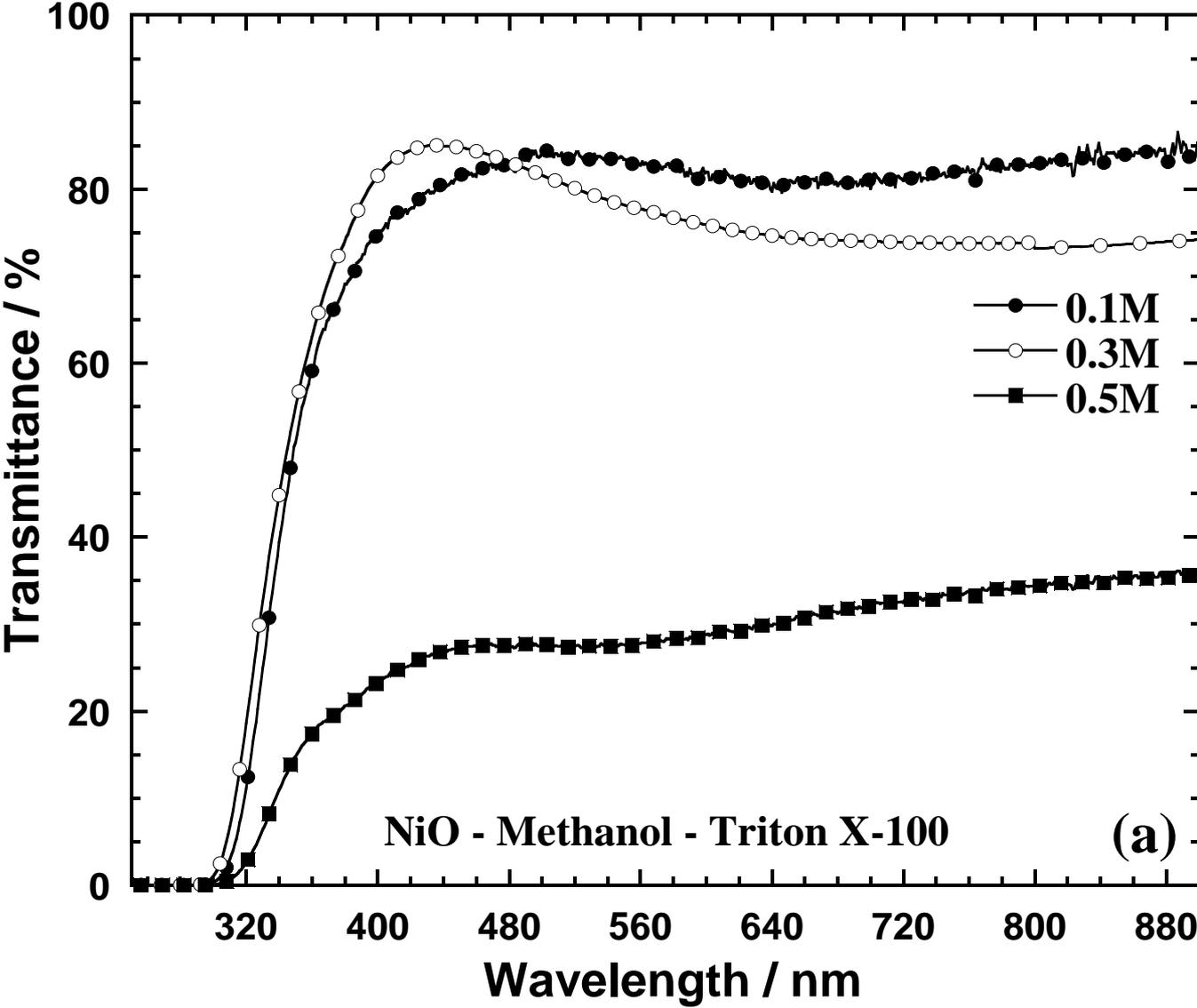
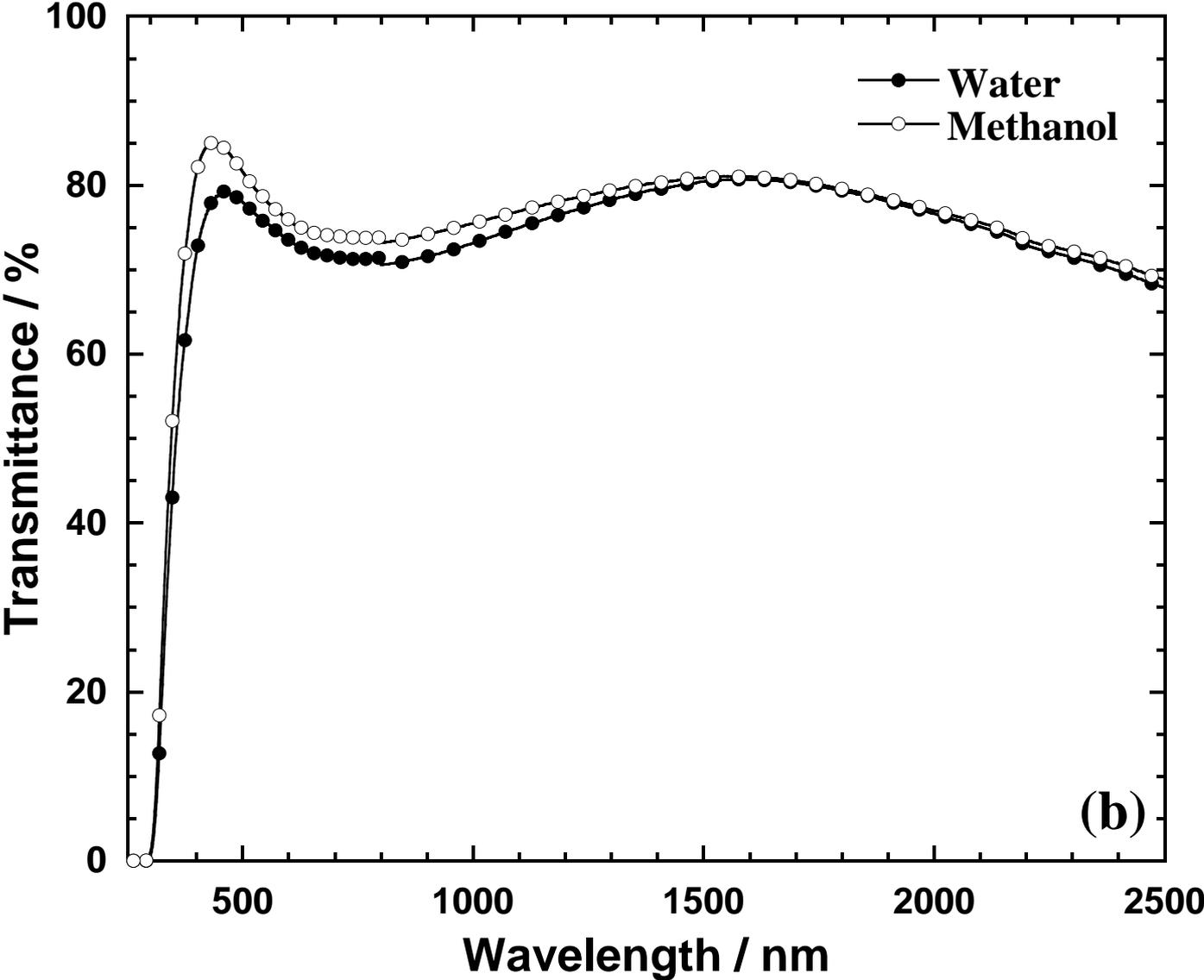
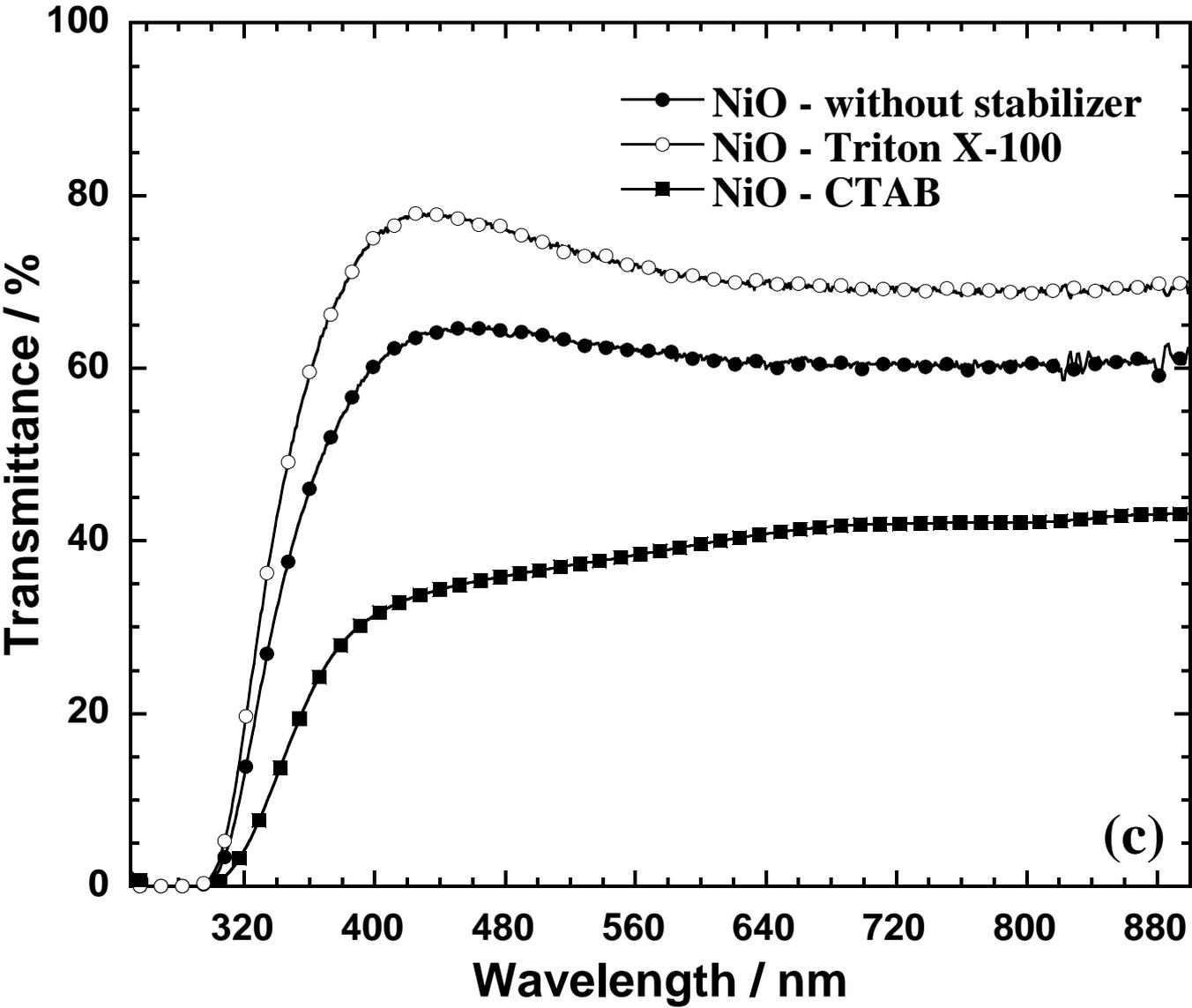


Figure 3b - K. Zrikem et al.



(b)

Figure 3c - K. Zrikem et al.



(c)

Figure 4 - K. Zrikem et al.

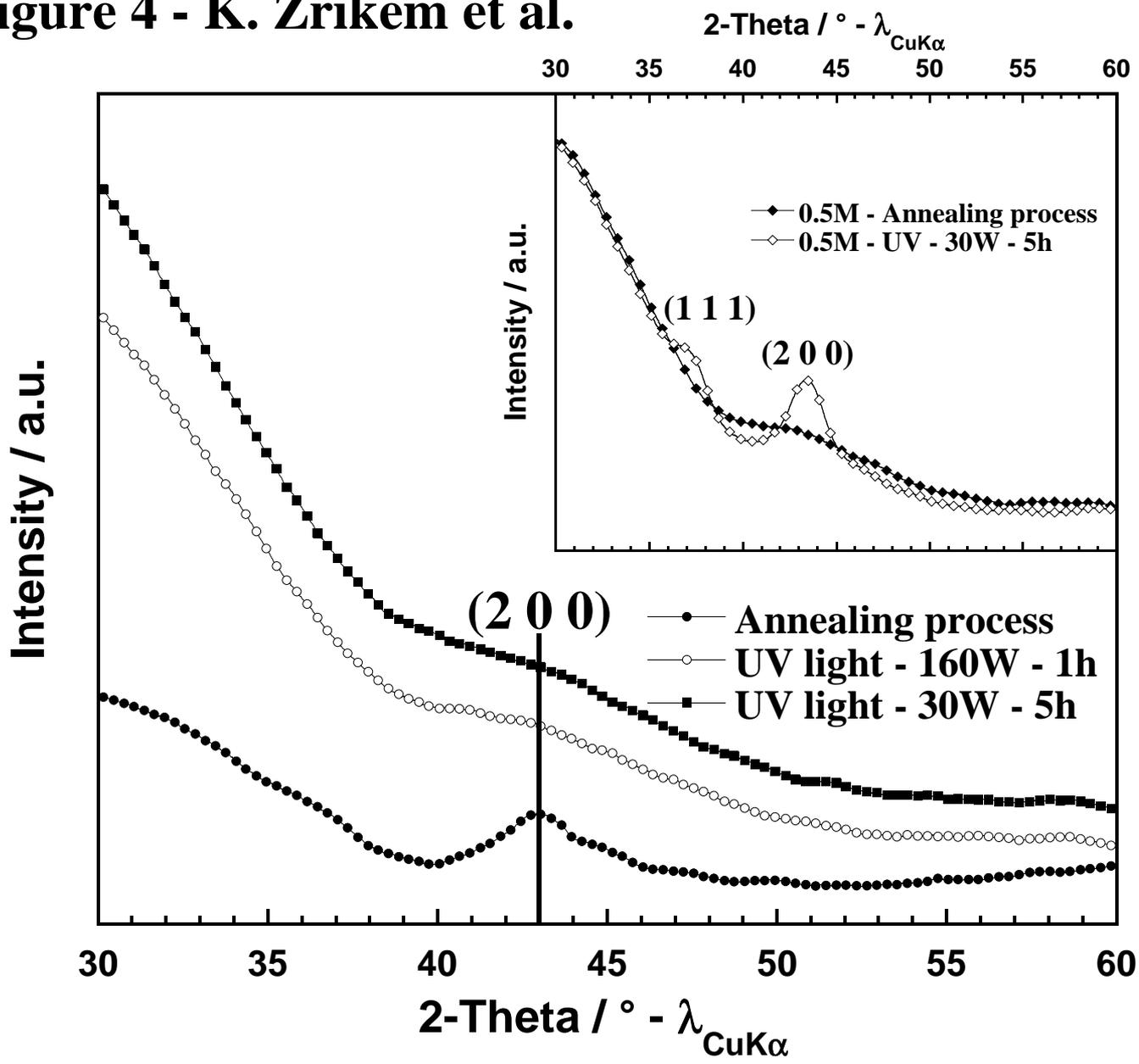


Figure 5a - K. Zrikem et al.

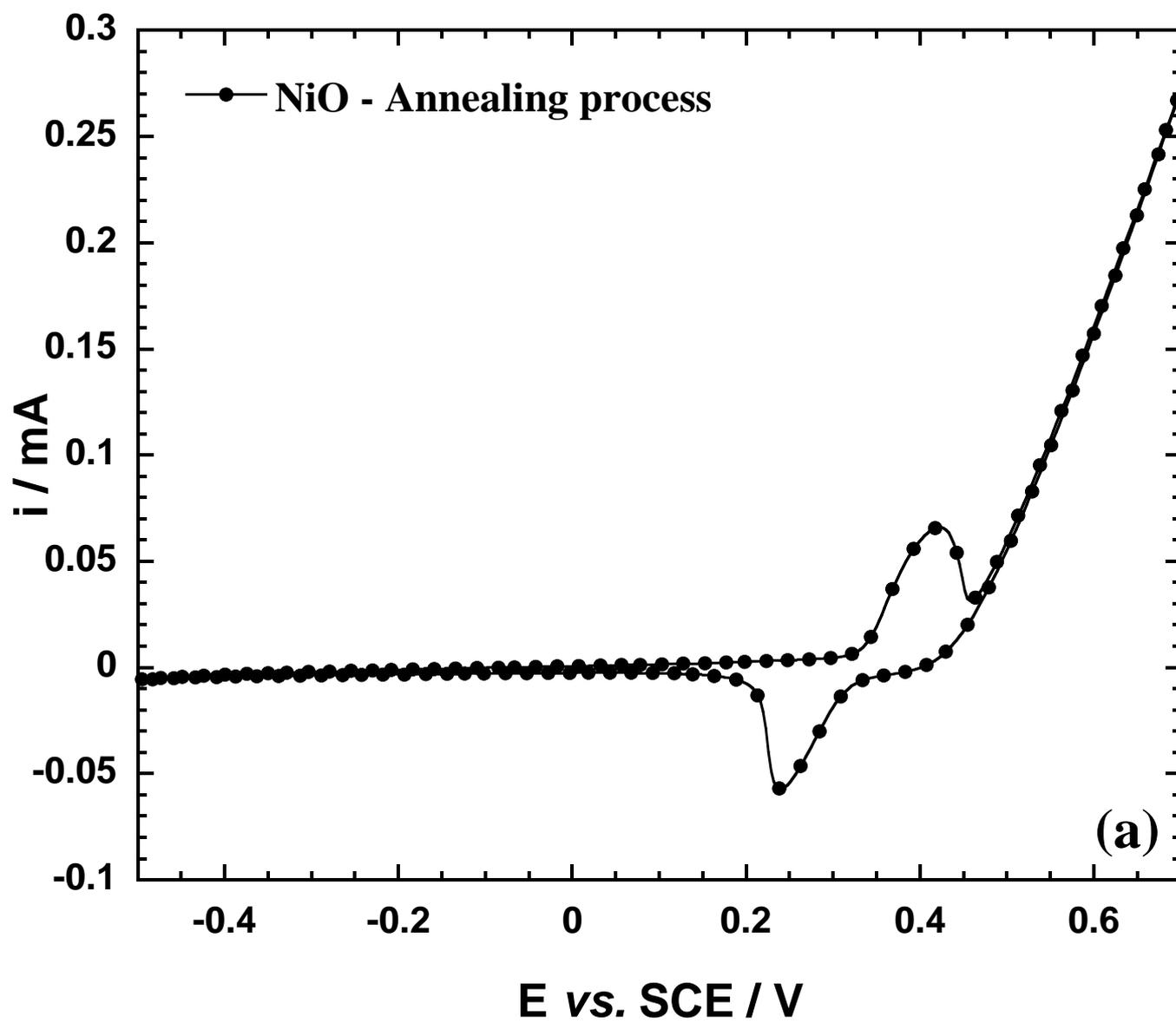


Figure 5b - K. Zrikem et al.

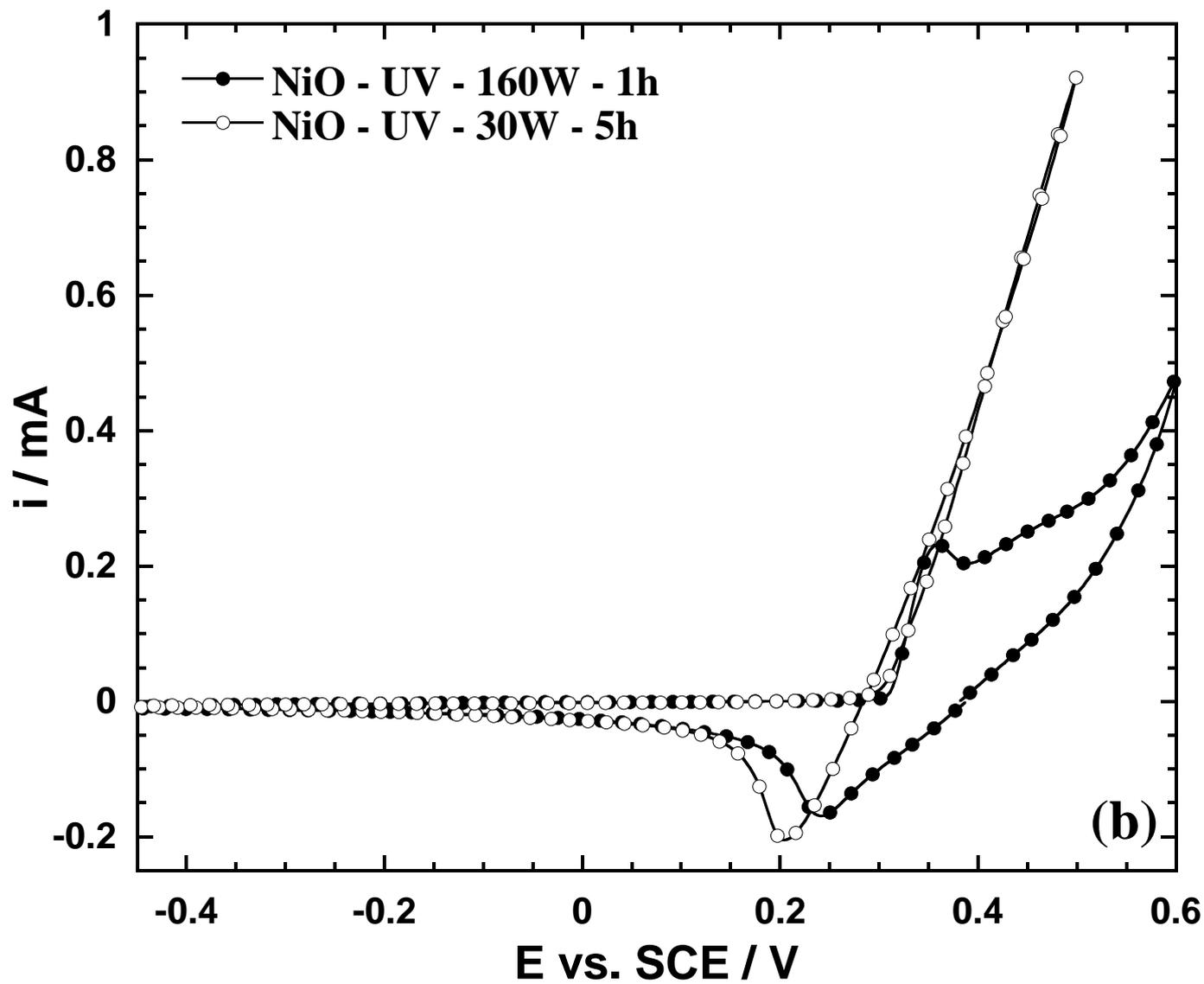


Figure 6a - K. Zrikem et al.

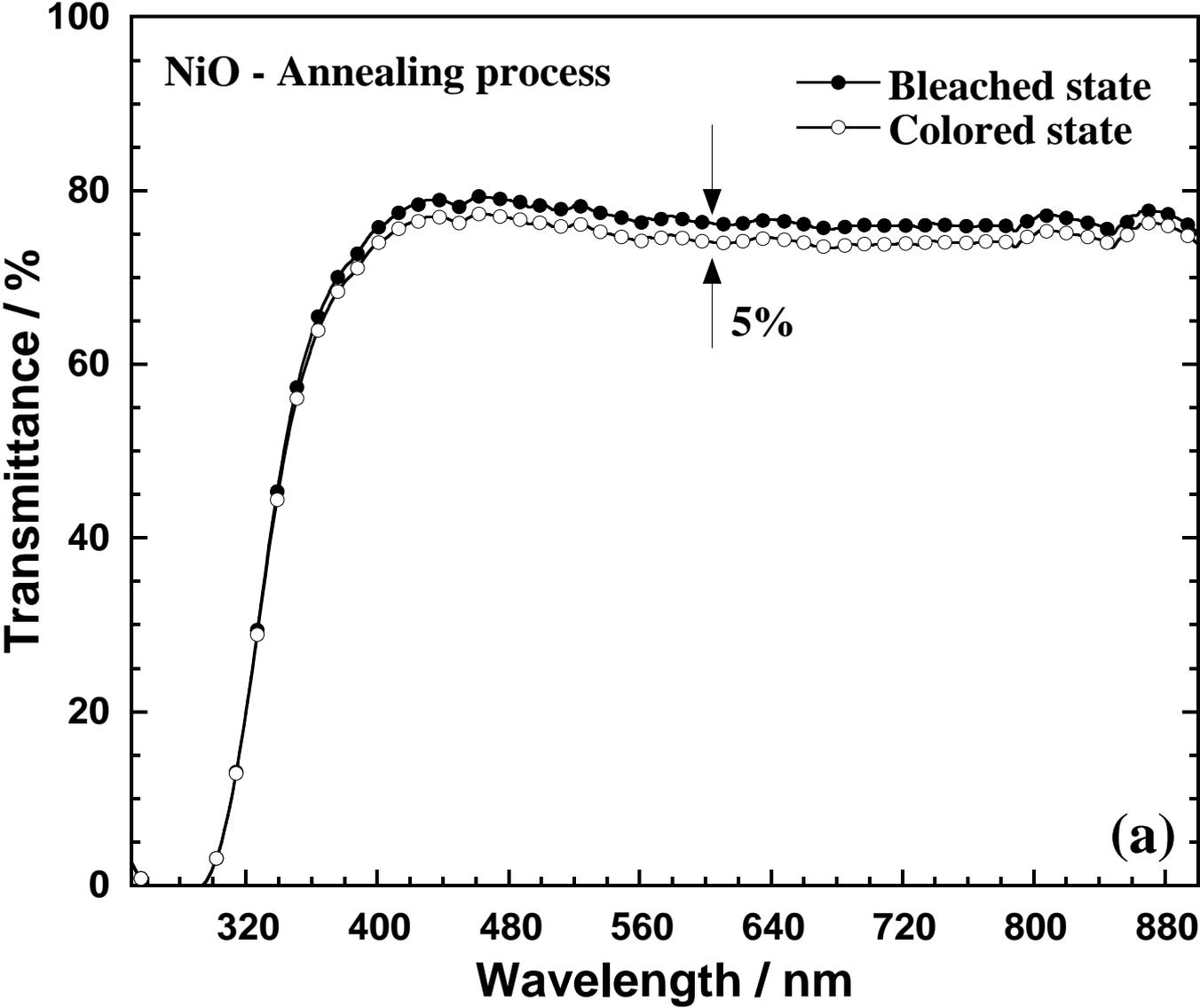


Figure 6b - K. Zrikem et al.

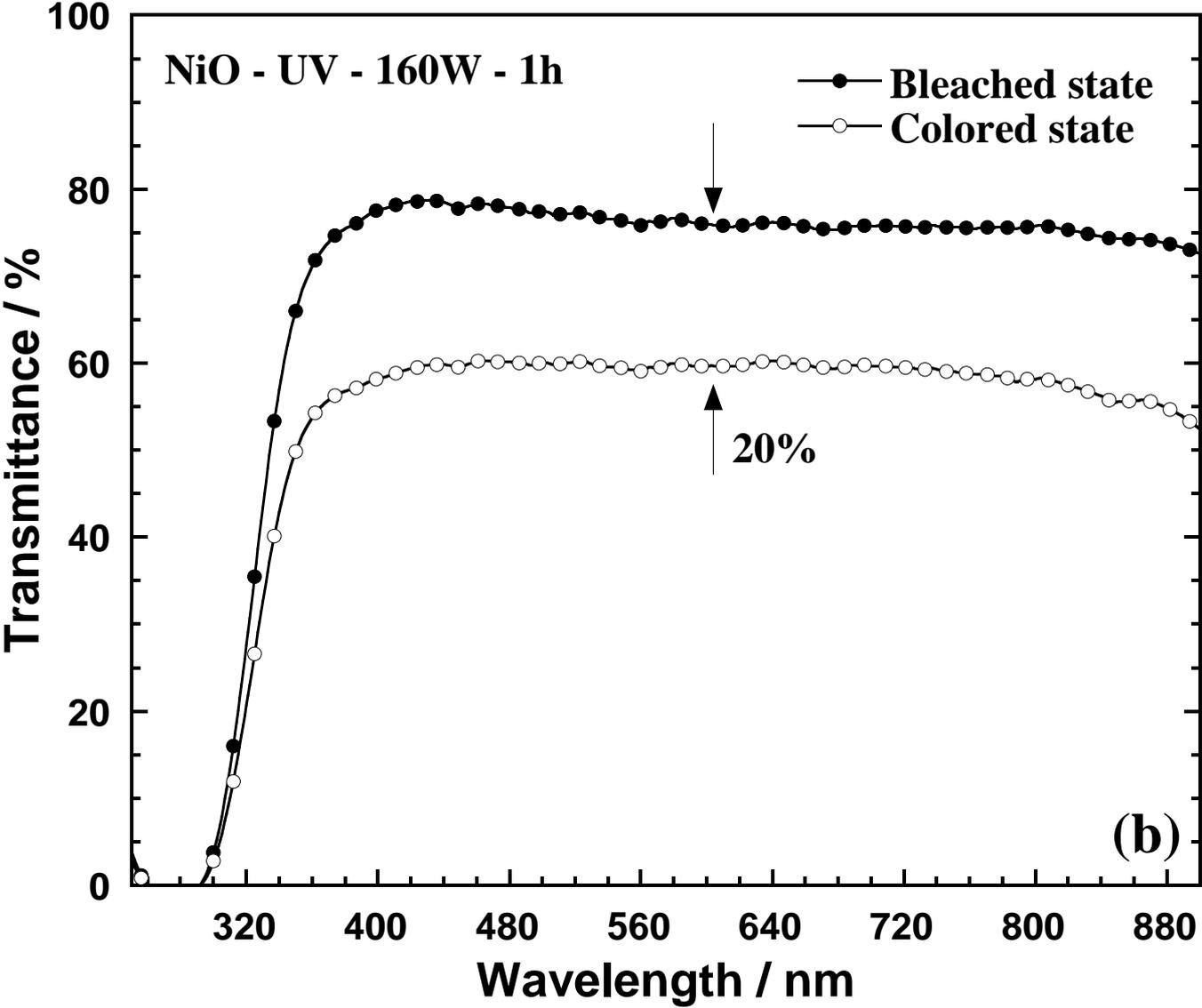


Figure 6c - K. Zrikem et al.

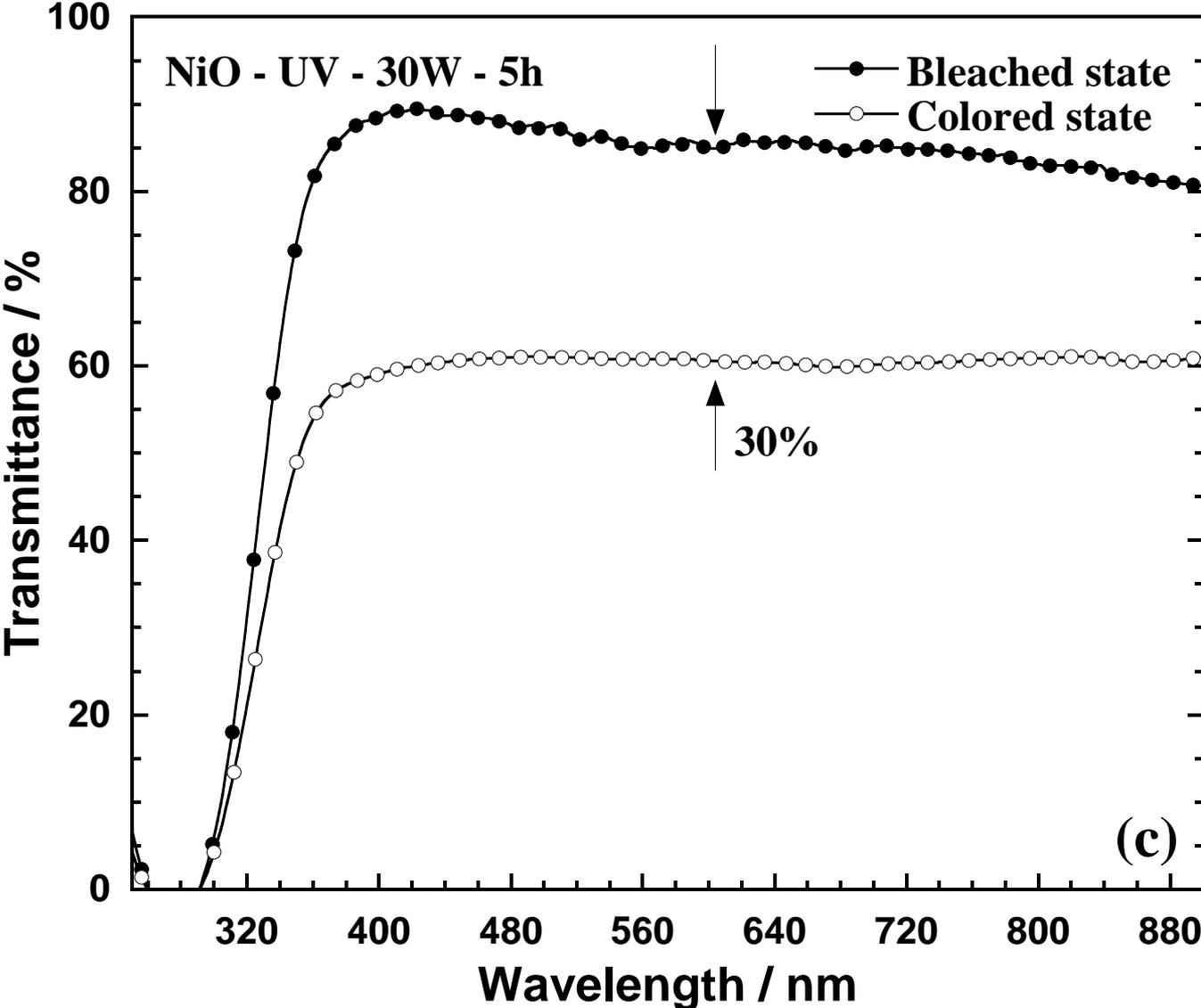


Figure 7 - K. Zrikem et al.

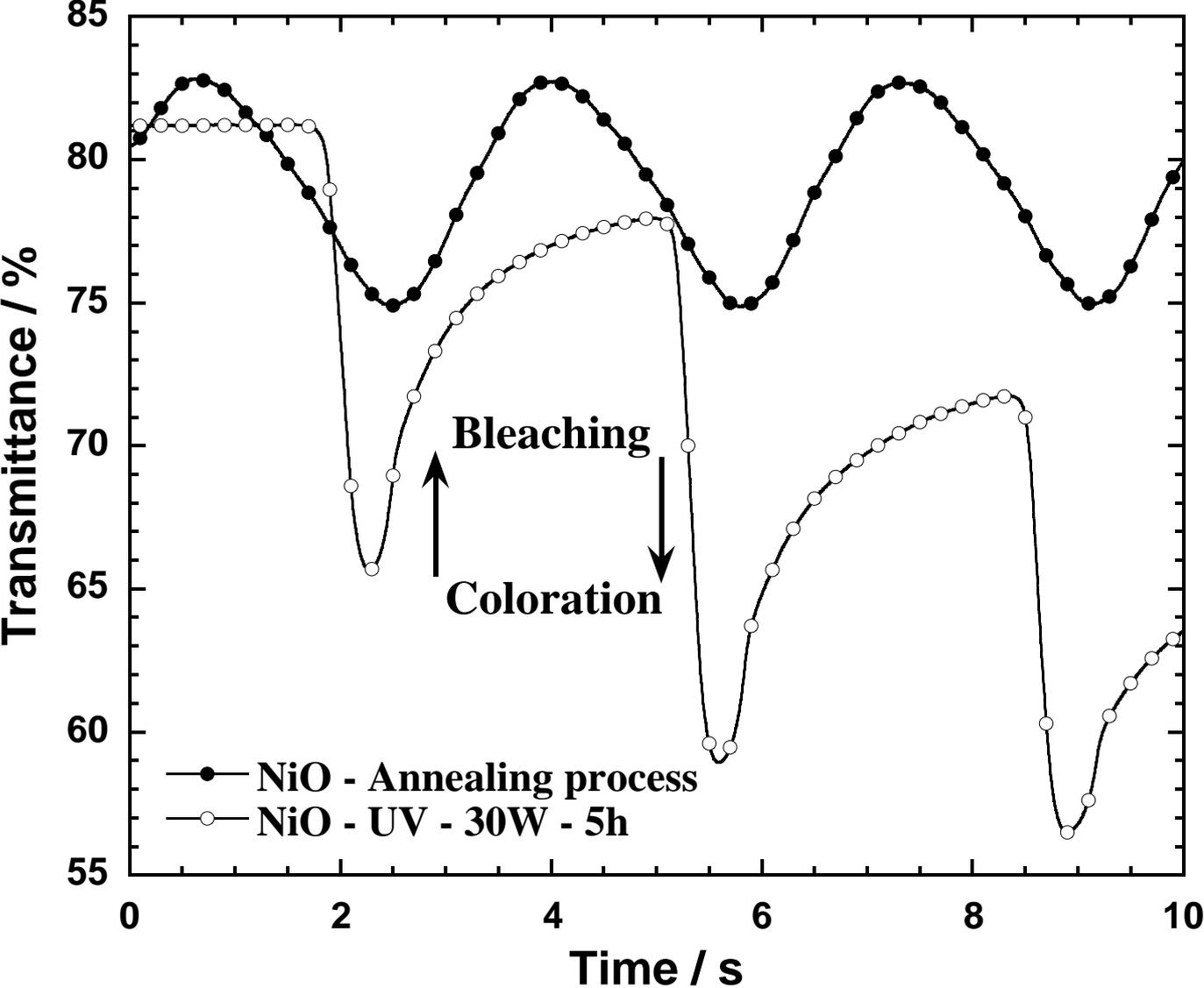


Figure 8 - K. Zrikem et al.

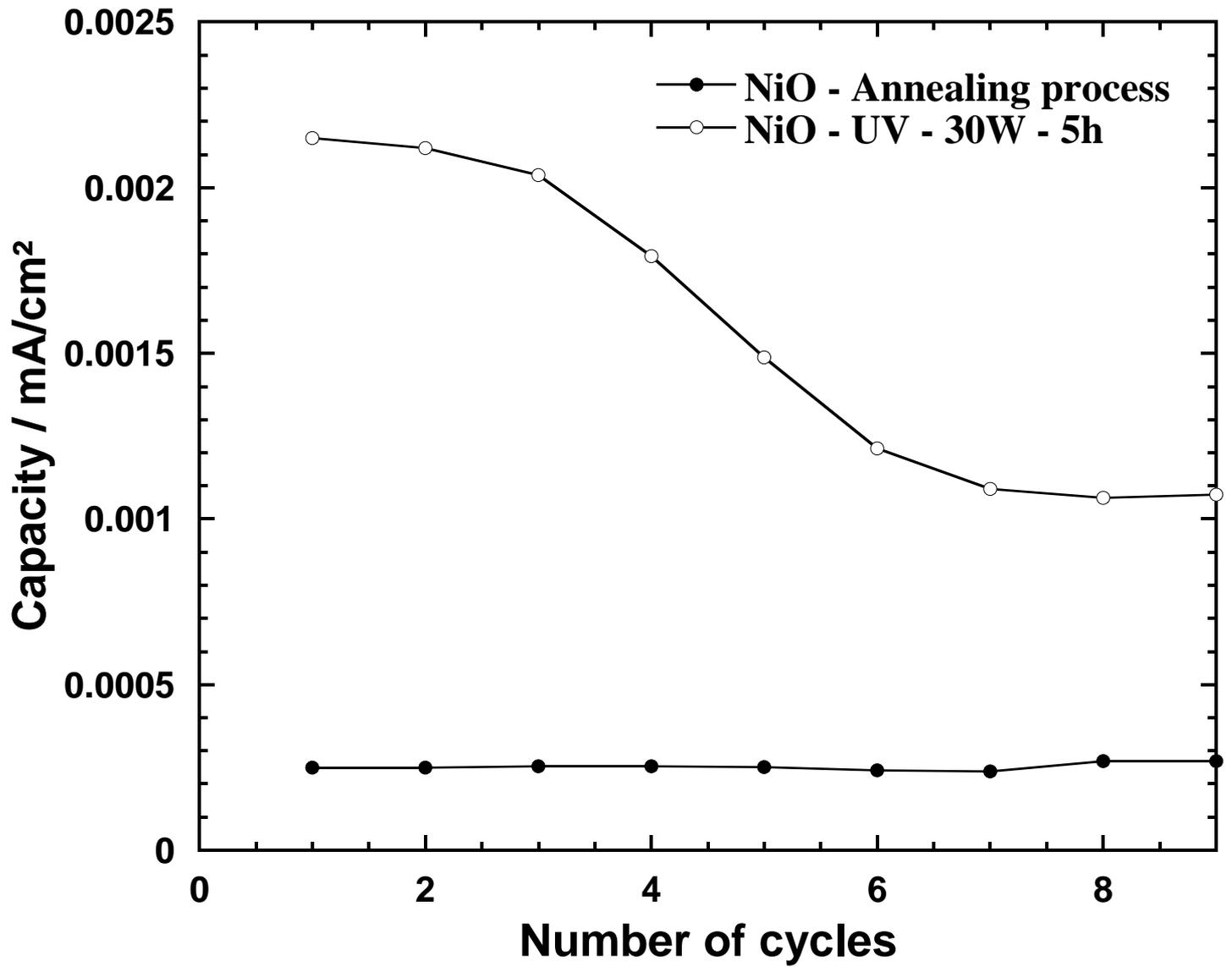


Figure 9 - K. Zrikem et al.

