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Improving Electrochromic Properties of WO_3 Thin Film with Gold Nanoparticle Additive

K. A. Rahmanzade[a], A. Nikfarjam[b*], M. Ameri[c], E. Mansoori[c]

[a] *Ayatollah Amoli Branch, Islamic Azad university, Amol, Iran*
[b] *Faculty of New Sciences & Technologies, University of Tehran, Tehran, Iran*
[c] *Department of Electrical and Computer, Islamic Azad University, Science and Research Branch*

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In this research, WO_3 and Au-WO_3 thin films were prepared at different temperatures using the sol gel method. The effect of gold nanoparticles (GNPs) on the electrochromic properties of WO_3 was also studied. 2.5 nm GNP was synthesized through sodium citrate reduction of gold chloride in an aqueous solution. These films were characterized by XRD, SEM, TEM, and spectrophotometer analyses. The films annealed at 200˚C were amorphous and crystallized at high temperatures. According to the scanning electron microscopy (SEM) image, the films annealed at 200˚C were dense. Moreover, the particles were uniformly distributed on them. Spectrophotometer analysis of WO_3 thin films annealed at 200˚C showed high electrochromic properties (transmission modulation (ΔT) and response time were 72% and3.25s for 80% coloring, respectively). Spectrophotometer analysis of Au-WO_3 thin films annealed at 200˚C showed that their coloration properties increased (ΔT = 78%) and response duration decreased (1.65s) when gold nanoparticles were added. This enhancement is attributed to the increased conductivity caused by the addition of gold nanoparticles as well as the surface plasmon resonance based absorption of GNPs.

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1. INTRODUCTION

Today, researchers are interested in materials that are effective in improving optical witch performance. An electrochromic device which can be used as an optical switch is colorized through low DC voltage [1]. These electrochromic materials can be colorized by applying electric fields and decolorized by reversing the field [2]. Electrochromic phenomenon was called electrochromism for the first time by Platt in 1961 [3]. Deb et al. presented the first proto type electrochromic device in 1969 [4]. During the electrochromic process, electrons and ions go into or exit from the electrochromic material when voltage is applied [5], which results in new optical absorption bands in the electrochromic active materials [6].

*Corresponding Author's Email: *a.nikfarjam@ut.ac.ir* (A. Nikfarjam)

The structure of a standard electrochromic device is composed of five layers placed between two substrates which are usually made of glass or polyester and covered with transparent conductive film. The inner part is composed of anionic conductor, an electrochromic film, and an ion storage film [7].

The best known electrochromic metal oxide materials, colorized anodically or cathodically, are TiO_2, Nb_2O_5, MnO_x, CuO_x, and WO_3 [8]. Darkening due to ion adsorption is called cathodic coloration, and the ion disposal process causes anodic coloration [9].
Among the electrochromic materials, tungsten trioxide (WO_3) is more interesting because of its good coloration efficiency, acceptable reversibility, good life time, high-quality look, low constant time, affordable price, and nontoxic property [10, 11].

A basic understanding of the electrochromic coloration mechanism in disordered WO_3 is provided by the inter -valence charge transfer or small-polar on

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absorption theories. A WO_3 semiconductor is colorized due to a double injection of ions and electrons [12]. Coloration and bleaching reactions of WO_3 take place as follows [13]:

$WO_3 + x\ Li^+ + xe^- \leftrightarrow Li_x\ WO_3$

Electrochromic devices have many applications such as smart window for architectural glazing, automobile sun-roofs, building sun-roofs, light regulation, optical switch, etc [14-16].

Gold nanostructures are frequently applied because of their size-dependent effects such as high optical absorbance due to surface plasmon resonance [17, 18]. Moreover, GNPs as metal nanostructures are conductive materials that have a significant effect on charge transferring. Therefore, GNPs with excellent stabilities can modify the electrochromic and electrochemical properties of WO_3 thin films.

In a previous research, Park et al. (2005) studied the influence of GNPs on the electrochromic properties of WO_3 prepared by the sputtering deposition method and calculated the Au-WO_3 and WO_3 response times at ~ 5s and over 20s, respectively. In the current study, response times of only 1.65s and 3.25s for Au-WO_3 and WO_3 respectively, were obtained with the application of a simpler and cheaper method (sol-gel and spin coating) [19] and the effect of GNPs on the transmission modulation (ΔT) data of Au-WO_3 films (ΔT= 70% at λ= 800nm) was reported by Deng et al. [20], who fabricated Au-WO_3 thin films using the sol-gel method. In the current study, ΔT was 78% at λ= 800nm. Results showed that ΔT in this work was better than that of Deng et al. (using a similar method) [20].

The aim of the present work is to investigate the structural and optical properties of thin WO_3 and Au-WO_3 thin films produced by sol-gel method as a function of the growing conditions-most notably the substrate temperature and GNPs concentration.

2. EXPERIMENTAL PROCEDURE

The WO_3 precursor sols were prepared using the sol gel method according to Kudo [21]. Five grams of tungsten metal powder was dissolved in 20 ml aqueous solution of hydrogen peroxide and stirred continuously for a few hours until a yellow solution of peroxtungstic acid was obtained. Since this dissolution is a strong exothermic material, the reaction flask was cooled by cryostat in order to prevent the reactant from spurting. The excess hydrogen peroxide was removed by heating the solution at 60˚C for an hour. Then, it was mixed with 20 ml anhydrous ethanol yielding pale yellow-color sols and warmed again at 80˚C for 15min. The sols appeared as colloidal suspension and were aged for 24h before deposition.

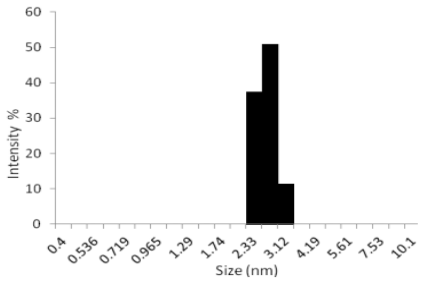

Figure 1. GNPs size distribution through DLS technique.

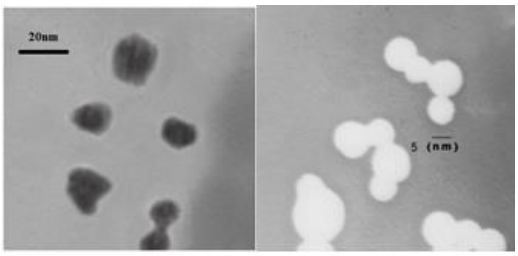

Figure 2. TEM image of (a) WO_3 (b) GNPs solution.

The GNP solution was synthesized through the sodium citrate reduction of gold chloride in an aqueous solution. GNPs encapsulated in 4-methylbenzenethiol was synthesized through the following procedure:

1) 10 ml 0.0288 mol $HAuCl_4.3H_2O$ aqueous solution was poured into a flask;
2) 20.6 ml 0.0358 mol $N(C_8H_{17})_4Br$ (toluene) was added to the flask;
3) The mixture was stirred for 15 minutes;
4) 23.8 ml 0.0139 mol 4-methylbenzenethiol ($HS-C_6H_4-CH_3$) (toluene) was added to the flask;
5) 8.25 ml 0.3836 mol $NaBH_4$ (aqueous) was added;
6) The solution was stirred for 3 hours until the black/brown organic and aqueous phases separated;
7) The solution volume was increased with ethanol;
8) The solution was frozen overnight to separate GNPs from it;
9) Black precipitates were filtered with a 0.2µm PTFE filter.

3. RESULTS AN DISCUSSION

The size of the prepared GNP, measured using the DLS technique, is 2.4 to 4.4 nm with Gaussian size distribution (Figure 1).

The size of the nanoparticles was investigated with microscopic analysis. The TEM images (Philips EM208, 100KV) of WO_3 and GNP solutions are shown in Figures 2 (a) and (b), respectively.According to the TEM results, the size of WO_3 and GNPs are 10 to 20 and 3-5 nm, respectively. The spin coating method at 2500 rpm for 25 s was used to depose thin films on indium thin oxide (ITO) glass, as a substrate. The

number of depositions was three, and the deposed glasses were baked at different temperatures. Figure 3 shows the x-ray diffraction (XRD) (STADI MP, 40KV, 30mA) of the WO_3 thin films at annealing temperatures of 200, 300 and 400˚C and Au-WO_3 (with a concentration of 1:50) at 400˚C. As seen in this figure, the film annealed at 200˚C was completely amorphous. Generally, amorphous tungsten oxide films are used instead of crystalline films for electrochromic applications.

It is difficult for ions to go into/or exit from crystalline films due to their dense structures, which results in lower response times of the electrochromic device.

The XRD of GNPs is shown in Figure 4. The XRD pattern of WO_3 films annealed at400˚C (Figure 3(c)) showed five sharp diffraction peaks of 2θ= 23.12˚, 24.36˚, 33.84˚, 47.08˚, and 49.88˚, indicating the presence of crystalline phases in the sample. The XRD diffraction pattern of Au-WO_3 films annealed at 400˚C, shown in Figure 3(d), shows two Au diffraction peaks of 2θ= 38.1˚ and 64.5˚.

The nanostructure of the WO_3 thin films deposited on an ITO electrode surface was investigated by scanning electron microscopy (SEM) (LEO-440I), and the findings are shown in Figure 5. The morphological structure of WO_3 thin films annealed at 200˚C was dense. Particles were distributed uniformly in the films and became larger as the temperature increased.

The electrochromic properties of WO_3 were determined in a cell with the configuration of WO_3 or Au-WO_3 film coated on ITO / $LiClO_4$ (0.1 M) / ITO glass. The cell potential switched between -1.5 to +1 voltage. The transmittance was measured by UV-visible spectrophotometer (Ocean Optics). Figures 6 and 7 illustrate the transmittance of bleached and colorized electrochromic devices, respectively. It was fabricated by nanostructure WO_3 films baked at temperatures of 200, 300 and 400˚C in the wavelength range of 300-900 nm. According to Figure 6, maximum transmittance was about 85% for the sample annealed at 200˚C. Annealing at 400˚C resulted in crystallization; therefore, densification of the film resulted in a drastic reduction in transparency.

Samples annealed at 200˚C show maximum transmission at a wavelength of 400 nm, having a good blue color. The samples' transmittances decreased as the annealing temperature increased. When the films were hardened by increasing temperatures, the ions were diffused fused to WO_3 layers, and then the coloration efficiency decreased.

Figure 8 shows the transmittance spectra of WO_3 and Au-WO_3 (at a concentration of 1:50) films annealed at 200˚C (optimum temperature) in both bleached and colored states. In Figure 8(b), it is clear that the transparency is reduced in Au-WO_3 film. The presence of gold nanoparticles and their surface plasmon resonance effects result in light scattering and light absorption, respectively. Therefore, the transparency of the Au-WO_3 film is reduced, as shown in Figure 8(b). The transmittances of WO_3 and Au-WO_3 show larger differences at lower wavelengths (410 nm), partially due to the SPR absorption of GNPs. This is why a noticeable red shift is seen in the transmittance spectra of the bleached Au-WO_3.

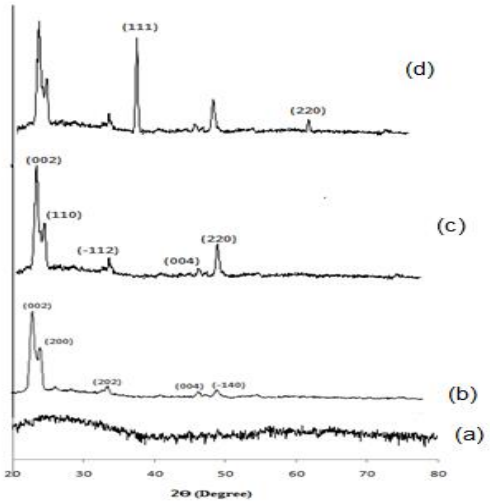

Figure 3. XRD pattern of WO_3 thin films annealed at (a) 200 (b) 300 (c) 400˚C (d) Au-WO_3.

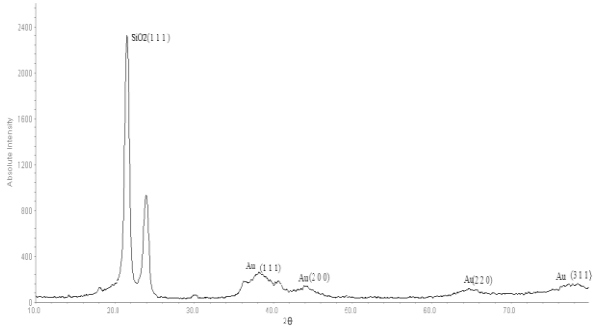

Figure 4. XRD pattern of GNPs.

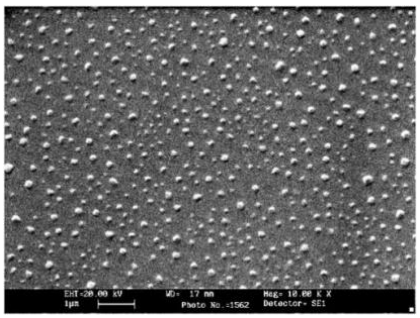

Figure 5. SEM image of WO_3 films annealed at 200˚C.

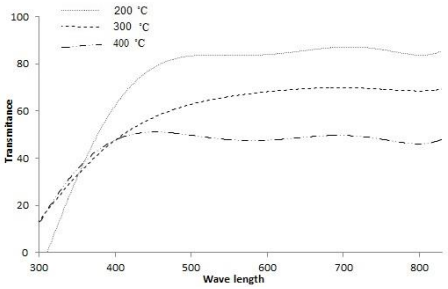

Figure 6. Transmission spectra of WO_3 films annealed in the bleached state.

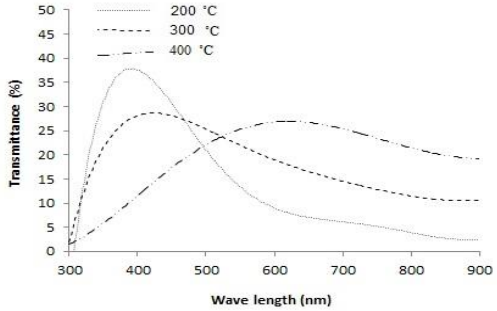

Figure 7. Transmission spectra of WO_3 films annealed in the colored State.

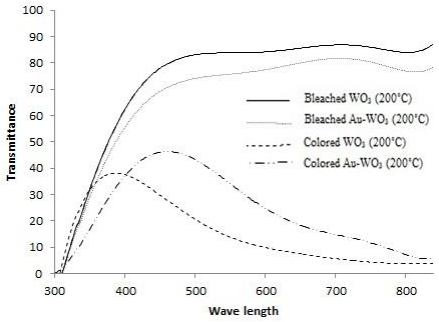

Figure 8. Transmission spectra of WO_3 and Au-WO_3 film in bleached and colored state.

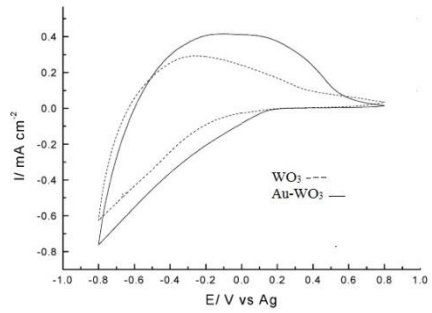

Figure 9. Cyclic voltammograms for WO_3 (dotted line) and Au-WO_3 (solid line); 0.1 M $LiClO_4$ at a potential scan rate of 50 mV/s.

TABLE 1. Transmission modulation for Au-WO_3 and WO_3 layers.

Film specification	ΔT % at λ = 450 [nm]	ΔT % at λ = 600 [nm]	ΔT % at λ = 800 [nm]
Au-WO_3	24	75	78
WO_3	48	52	72

TABLE 2. Switching times of WO_3 and Au-WO_3 films.

	Switching times (s)			
Film specification	50% coloring	50% bleaching	80% coloring	80% bleaching
Au-WO_3	1.27	0.73	1.65	1.52
WO_3	2.2	1.45	3.25	3

The transmission modulation (ΔT) data of the WO_3 and Au-WO_3 films are compared in Table 1. The switching times of WO_3 and Au-WO_3 films are summarized in Table 2 for 50 and 80% coloring and bleaching states. According to the table, the Au-WO_3 film showed a lower response time in comparison to that of WO_3 film in both coloring and bleaching states. Their response times were 1.65s and 1.52s, respectively, for 80% coloring and bleaching states. In identical injection charges, Au-WO_3 films showed higher conductivity resulting in improved electrochromic performance. Electrochromic properties (coloration ↔ bleaching) of the WO_3 and Au-WO_3 films were studied by cyclic voltammetry (obtained by sweeping the potential in the range from -1 V to +1 V) using a classical three-electrode potentiostatic cell system as depicted in Figure 9.

The cell system consists of a WO_3 and Au-WO_3 coated sample as working electrode, a platinum rod as counter electrode and Ag/AgCl as reference electrode. Anhydrous $LiClO_4$ (0.1 M) was used as electrolyte.

Initially, the two samples were almost transparent; when a more negative potential was applied, an increase in the cathodic current and a blue color can be observed, which is associated with WO_3 oxide reduction and simultaneous Li^+ insertion. The coloration process of the electrochromic films is usually described as a function of simultaneous injection of cations and electrons inside the oxide network. Plot of photo detector output (mV) vs. time (s) during coloration– bleaching experiments is depicted in Figure 10.The WO_3 coating exhibited more than 400 cycles (coloration ↔bleaching) in nonaqueous electrolyte. It was observed that although the reversibility of the cycle remained good, the intensity of the coloration decreased with the number of cycles. This was possibly due to the structural deformation of the WO_3 films for its long time exposure to the electrolytic solution.

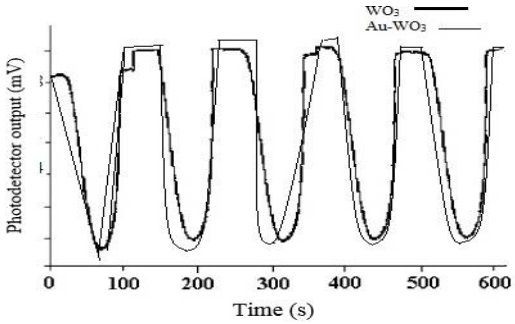

Figure 10. Plot of photo detector output (mV) vs. time (s) during coloration– bleaching experiments.

4. CONCLUSION

In this study, nanostructures of WO_3 and Au-WO_3 were prepared with the sol-gel method. Thin films of both WO_3 and Au-WO_3 were prepared using the spin coating technique. The XRD pattern of samples indicate that WO_3 thin films annealed at 200˚C became amorphous and crystallized as temperatures increased. According to the TEM images, WO_3 and GNPs were 17-35 nm and 3-5 nm, respectively, with almost spherical shapes. The results show that the transmission spectra of WO_3films baked at 200˚C had the most transparency and the best coloration. Electrochromic results indicate that the presence of gold nanoparticles caused electrochromic performance to improve and response time to decrease. This enhancement is attributed to the increase in conductivity by the gold nanoparticles and surface plasmon resonance based absorption of GNPs.

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6. REFERENCES

1. Lee, K.D., "Preparation and electrochromic properties of WO_3 coating deposited by the sol–gel method", ***Solar Energy Materials and Solar Cells***, Vol. 57, No. 1, (1999), 21-30.
2. Deepa, M., Saxena, T., Singh, D., Sood, K. and Agnihotry, S., "Spin coated versus dip coated electrochromic tungsten oxide films: Structure, morphology, optical and electrochemical properties", ***ElectrochimicaActa***, Vol. 51, No. 10, (2006), 1974-1989.
3. Logacheva, V., Lukin, A., Tikhonova, Y.A., Lynov, A., Pribytkov, D. and Khoviv, A., "Phase composition and optical properties of thin films based on lanthanum and tungsten oxides", ***Inorganic Materials***, Vol. 44, No. 10, (2008), 1125-1129.
4. Kim, C.-Y., Lee, M., Huh, S.-H. and Kim, E.-K., "Wo3 thin film coating from h2o-controlled peroxotungstic acid and its electrochromic properties", ***Journal of Sol-gel Science and Technology***, Vol. 53, No. 2, (2010), 176-183.
5. De Wijs, G. and De Groot, R., "Amorphous wo 3: A first-principles approach", ***ElectrochimicaActa***, Vol. 46, No. 13 , (2001), 1989-1993.
6. Cremonesi, A., Bersani, D., Lottici, P., Djaoued, Y. and Ashrit, P., "WO_3 thin films by sol–gel for electrochromic applications", ***Journal of Non-crystalline Solids***, Vol. 345, (2004), 500-504.
7. Ozkan, E., Lee, S.-H., Tracy ,C.E., Pitts, J.R. and Deb, S.K., "Comparison of electrochromic amorphous and crystalline tungsten oxide films", ***Solar Energy Materials and Solar Cells***, Vol. 79, No. 4, (2003), 439-448.
8. Gotic, M., Ivanda, M., Popovic, S. and Music, S., "Synthesis of tungsten trioxide hydrates and their structural properties", ***Materials Science and Engineering: B***, Vol. 77, No. 2, (2000), 193-201.
9. Badilescu, S. and Ashrit, P., "Study of sol–gel prepared nanostructured WO_3 thin films and composites for electrochromic applications", ***Solid State Ionics***, Vol. 158, No. 1, (2003), 187-197.
10. Pecquenard, B., Lecacheux, H., Castro-Garcia, S. and Livage, J., "Electrochromic properties of peroxopolytungstic acid thin films", ***Journal of Sol-gel Science and Technology***, Vol ,13 . No. 1-3, (1998), 923-927.
11. Heckner, K.-H. and Kraft, A., "Similarities between electrochromic windows and thin film batteries", ***Solid State Ionics***, Vol. 152, (2002), 899-905.
12. Sun, M., Xu, N., Cao, Y., Yao, J. and Wang, E., "Preparation , microstructure and photochromism of a new nanocrystallineWO_3 film", ***Journal of Materials Science Letters***, Vol. 19, No. 16, (2000), 1407-1409.
13. Somani, P.R. and Radhakrishnan, S., "Electrochromic materials and devices: Present and future", ***MaterialsChemistry and Physics***, Vol. 77, No. 1, (2003), 117-133.
14. Papaefthimiou, S., Leftheriotis, G. and Yianoulis, P., "Advanced electrochromic devices based on wo 3 thin films", ***ElectrochimicaActa***, Vol. 46, No. 13, (2001), 2145-2150.
15. Biswas, P.K., Pramanik, N., Mahapatra, M., Ganguli, D. and Livage, J., "Optical and electrochromic properties of sol–gel WO_3 films on conducting glass", ***Materials Letters***, Vol. 57, No. 28, (2003), 4429-4432.
16. Yao, J., Yang, Y. and Loo, B., "Enhancement of photochromism and electrochromism in MoO3/Au and MoO3/Pt thin films", ***The Journal of Physical Chemistry B***, Vol. 102, No. 11, (1998), 1856-1860.
17. He, T., Ma, Y., Cao, Y., Yang, W. and Yao, J., "Enhanced electrochromism of wo 3 thin film by gold nanoparticles", ***Journal of Electroanalytical Chemistry***, Vol. 514, No. 1, (2001), 129-132.
18. Nagai, J., McMeeking, G.D. and Saitoh, Y., "Durability of electrochromic glazing", ***Solar Energy Materials and Solar Cells***, Vol. 56, No. 3, (1999), 309-319.
19. Park, K.-W., "Electrochromic properties of Au–WO_3nanocomposite thin-film electrode", ***ElectrochimicaActa***, Vol. 50, No. 24, (2005), 4690-4693.
20. Deng, J., Gu, M. and Di, J., "Electrochromic properties of wo 3 thin film onto gold nanoparticles modified indium tin oxideelectrodes", ***Applied Surface Science***, Vol. 257, No. 13, (2011), 5903-5907.
21. Patra, A., Auddy, K., Ganguli, D., Livage, J. and Biswas, P.K., "Sol–gel electrochromic wo 3 coatings on glass", ***Materials Letters***, Vol. 58, No. 6, (2004), 1059-1063.

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[a] *Ayatollah Amoli Branch, Islamic Azad university, Amol, Iran.*
[b] *Faculty of New Sciences & Technologies, University of Tehran, Tehran, Iran.*
[c] *Department of Electrical and Computer, Islamic Azad University, Science and Research Branch*

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چکیده

در این تحقیق فیلم نازکWO_3 و $Au\text{-}WO_3$با استفاده از روش سل–ژل در دماهای مختلف ساخته و اثر نانوذرات طلا بر خاصیت الکتروکرومیک WO_3آن مورد مطالعه قرار گرفت. نانوذرات طلا با اندازه 2/5nm با استفاده از روش احیای سیترات سدیم در یک محلول آبی تهیه وبررسی شد. فیلم‌ها با استفاده از آنالیزهایXRD، SEM، TEM و اسپکتروفتومتری مشخصه‌یابی شدند. نتایج آنالیز XRD نشان داد که فیلم حرارت داده شده در200°Cآمورف است و با افزایش دما کریستالی می‌شود. آنالیز SEM نشان می‌دهد که فیلم حرارت داده شده در 200°C کاملاً چگال است و ذرات به طور یکنواخت در آن توزیع شده‌اند. آنالیز اسپکتروفتومتری فیلم نازک WO_3 که در 200°C حرارت داده شده، بالاترین خصوصیات الکتروکرومیک را نشان می‌دهد(72٪=ΔTو پاسخ زمانی 3/25s ثانیه بعداز 80٪رنگی شدن). آنالیز اسپکتروفتومتری فیلم نازک $Au\text{-}WO_3$حرارت داده شده در 200°C نشان می‌دهد که خاصیت رنگی شدن WO_3بعد از اضافه کردن نانوذرات طلا افزایش(78٪=ΔT) و پاسخ زمانی آن نیز کاهش یافته است(1/65s). این افزایش به دلیل بالا رفتن هدایت الکتریکی WO_3و اثر جذب بر پایه نوسان پلاسمون سطحی بعد از افزودن نانوذرات طلا می‌باشد.

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