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Research Article

PEG Assisted Hydrothermal Synthesis of Hexagonal WO_3 Nanoparticles

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Abstract

Tungsten oxide (WO_3) displays superior semiconductor properties which renders it attractive for utilization in the electrochromic devices, gas sensors and photocatalytic applications. Preparation of WO_3 nanostructures including particles, plates, wires, rods, tube and spheres with controlled morphology and crystal structure for the future application is gaining attention. It has been known that crystal structure and size, specific surface area, pore volume and particle size distribution of WO_3 have a significant effect on chemical activity. As a result, it is necessary to investigate systematically the effects of preparing conditions in synthesis of well-controlled morphology and crystal structure. In the present study, hexagonal WO_3 nano sized powders have been synthesized via hydrothermal method by controlling the weight ratio of substrate and addition of poly ethylene glycol (MW: 1500, PEG-1500) as surfactant agent. The characterization of WO_3 samples is complemented with N_2 sorption, particle morphology and crystalline properties are investigated by volumetric surface analysis, scanning electron microscopy (SEM) and X-ray diffraction (XRD). It has been shown that WO_3 samples can be achieved by adding or not PEG-1500 as the agent in hydrothermal process at 200 °C for 24 h under well controlled conditions. The growth direction of the tungsten oxide nanostructures is determined along (002) axis with 63.02 nm crystal size. SEM analyses results indicate that by addition of PEG-1500, hexagonal and mesoporous nanoparticles of WO_3 are formed instead of rods. Moreover, most effective reduction temperatures of the final WO_3 nano particles under hydrogen gas have been studied by using temperature programmed reduction (TPR). Characteristics of nano-sized metallic tungsten (W) obtained after the reduction process are investigated by XRD and SEM techniques.

Keywords: Tungsten oxide, Hexagonal, Mesoporous, H_2-TPR

Hegzagonal WO_3 nano parçacılarının PEG Destekli Hidrotermal Sentezi

Öz

Üstün yarı iletken özelliklere sahip olan tungsten oksit (WO_3) elektrokromik cihazlarda, gaz sensörlerinde ve fotokatalitik uygulamalarda ile dikkat çekmektedir. Gelecekteki kullanım alanları için kontrollü morfoloji ve kristal yapıya sahip parçacık, levha, tel, çubuk, tüp ve küre olmak üzere WO_3 nano yapısının hazırlanması önemlidir. Kristal yapısı ve boyutunun, spesifik gözenek alanı, gözenek hacmi ve parçacık boyut dağılımı WO_3'ün kimyasal aktivitesi üzerine önemli etkiye sahip olduğu bilinmektedir. Sonuç olarak, iyi kontrol edilmiş bir morfolojide ve kristal yapıda sentezlenebilmesi için üretim koşullarının etkilerinin sistematik olarak araştırılması

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gerekmektedir. Bu çalışmada, hegzagonal WO_3 nano boyutlu parçacıklar, substrat içeriğinin ağırlık oranı ve poli etilen glikol (MA:1500, PEG-1500) yüzey aktif kimyasalının eklenmesi ile kontrollü bir hidrotermal yöntem ile sentezlenmiştir. N_2 sorpsiyon, partikül morfolojisi ve kristal yapı özellikleri ile tanımlanan WO_3 örneklerinin karakteristiği; hacimsel yüzey analizi, taramalı elektron mikroskobu (SEM) ve X-ışını kırınımı (XRD) ile incelenmiştir. WO_3 örnekleri iyi kontrol edilen koşullar altında 200° C ve 24 saat boyunca hidrotermal yöntem ile PEG-1500'ün ajan olarak eklenmesi veya eklenmemesi koşullarında üretildiği gösterilmiştir. Tungsten oksit nano yapılarının 63.02 nm kristal boyutu ile (002) ekseni boyunca büyüme gerçekleştiği belirlenmiştir. SEM analizi sonuçlarına göre çubuk yapısı yerine hegzagonal ve mezopor WO_3 nano partiküllerinin oluştuğu tespit edilmiştir. Bununla beraber son ürün WO_3 nano partiküllerini hidrojen gazı altındaki en etkili indirgenme sıcaklıkları sıcaklık programlı indirme (TPR) analizi ile incelenmiştir. İndirgenme sonrası elde edilen nano boyutlu metalik tungsten (W) özellikleri ise XRD ve SEM teknikleri ile araştırılmıştır.

Anahtar Kelimeler: Tungsten oksit, Hegzagonal, Mezopor, H_2-TPR

1. Introduction

In the recent years nano structured WO_3 has been investigated as a potential material of electrochromic and optic devices, gas sensors, and catalysts (Huirache-Acuña, Paraguay-Delgado, Albiter, Lara-Romero, & Martínez-Sánchez, 2009; Abe, Takami, Murakami, & Ohtani, 2008). Nano sized WO_3 has been synthesized by different preparation methods such as electro spinning, annealing, physical vapor deposition, pyrolysis, sol-gel (Nogueira, Cavaleiro, Rocha, Trindade, & de Jesus, 2004; Lu, Liu, Zhang, Wang, & Wei, 2006; Díaz, Pinzón, & Méndez, 2009; Mwakikunga, Sideras-Haddad, Forbes, & Arendse, 2008; Li, Bando, Golberg, & Kurashima, 2003). Besides these methods, hydrothermal method is proposed for obtaining WO_3 at nano scale as a much more economical method not requiring expensive experimental set up compared to the above methods. However, this method requires long reaction times ranging from several hours to several days in order to obtain oxide structure. WO_3 exhibits polymorphism, and hexagonal and monoclinic phases of WO_3 attract more attention for potential application. Moreover, most of the electrochromic applications of WO_3 have been focused on amorphous films. Colored state amorphous WO_3 films show 50% transmittance in the visible light region which is not enough for practical applications (Meda, Breitkopf, Haas, & Kirss, 2002). The morphology and the crystalline properties of WO_3 can be controlled by chamber pressure and the oxygen content (Zheng, Zhang, & Guo, 2013).

Therefore it is necessary to develop one dimensional nano structures for electrochemical devices (Lu, Hon, Kuan, & Leu, 2014), which possess exceptional physicochemical properties depending on their shape and size (Boudiba et al, 2013). Hexagonal tungsten oxide shows a unique tunnel structure and it can easily change from colorless to dark blue under electrical voltage (Zhang, Wang, Xia, Gu, & Tu, 2011). The hexagonal phase, commonly obtained via hydrothermal application methods is more suitable for gas sensor applications, while monoclinic phase generally obtained at room temperature due to its thermodynamic stability, is more suitable for photocatalytic application (Peng, Ke, Xiao, Wang, Hu, & Zan, 2012 ; Qu, & Wlodarski, 2000; Martínez, Martínez-De La Cruz, & Cuéllar, 2011; Sánchez-Martínez, Martínez-De La Cruz, & López-Cuéllar, 2013). For this reason, researchers have focused on various methods in order to prepare WO_3 in well-known crystalline structures (Hernandez-Uresti, Sánchez-Martínez, Martínez-De La Cruz, Sepúlveda-Guzmán, & Torres-Martínez, 2014). It was reported synthesis of WO_3 nano rods using the simple hydrothermal method. WO_3 nano rods can be synthesized large quantities even at low temperatures conditions (Therese, Li, Kolb, & Tremel, 2005). It was prepared mesopourous WO_3 nano structures with hexagonal phase by using a two step-hydrothermal method. They mentioned that formation of WO_3 depended on the acidic medium inside the autoclave (Huirache-Acuña et al., 2009). Hydrothermal synthesis of hexagonal WO_3 from ammonium para tunsgtade was also carried out. Their phenomena indicated that hydrothermal treatment favors to formation of hexagonal WO_3 (Li, Cao, Wang, Yang, & Rao, 2006). It was synthesized monoclinic WO_3 from sodium tungstate at 300°C in 3 steps by a low temperature and low pressure hydrothermal process (Ahmadi, Younesi, & Guinel, 2014).

A uniform WO_3 nanorods for electrochromic devices was prepared by hydrothermal synthesis. The effects of various pH values and the addition of NaCl on the preparation of nanorods were investigated. It was showed that NaCl was a good capping agent for controlling the shape of WO_3 nanostructures and it was recommended to synthesize the crystalline hexagonal WO_3 nanorods at pH 2.0 with 5.4 wt % NaCl content (Lu, Hon, Kuan, & Leu, 2014). Modified the hydrothermal process by assisting with microwave to synthesize WO_3 nanoparticles with both hexagonal and monoclinic structures were also reported. The process was conducted without the use of any additives and was followed by different thermal treatments. It was show that the highest specific surface area was obtained compared to commercial WO_3 (Hernandez-Uresti et al., 2014). PEG is a non-ionic polymeric surfactants and also has hydrophobic –CH_2–CH_2– and hydrophilic –O– in the long chains. Thus, PEG dissolves very well in water and ensures complete elongation of the polymer chains. The oxygen atom in the PEG has the ability to coordinate with the metal ions. This extended sequence of the polymer chain provides a new organization of metal atoms along the backbone of the polymer, which provides a variety of assembly paths for 1D growth of final products (Shi, Li, Yang, Chen, Yuan, Zhang, & Sun 2007; Feng, Zhang, Guo, & Wang 2010).

In the present work, hexagonal mesoporous WO_3 nanoparticles were prepared via poly ethylene glycol (MW: 1500, PEG-1500) assisted hydrothermal method. The samples were characterized, and their H_2 reducing properties were evaluated for formation of metallic tungsten (W). It was found that PEG-1500 can influence the morphology of the WO_3 during hydrothermal conditions. The nano scaled WO_3 particles have a potential application as catalysts, gas sensors, and also raw material for nano sized powder metallic W synthesis. To best of our knowledge, systematically investigated of WO3 nanoparticles synthesis in which ammonium tungsten oxide hydrate as a precursors with PEG-1500 surfactant agent and especially its hydrogen reduction properties has not been reported before.

2. Experimental

WO_3 nano particles were synthesized by using PEG assisted hydrothermal method. All the chemicals were of analytical grade and were used directly. In the present study the precursor was firstly prepared by ammonium tungsten oxide hydrate ($(NH_4)_6.W_{12}.O_{39}.xH_20$) solution (0.02 M) mixing with ammonium nitrate ($NH_4.NO_3$) and/or ammonium sulfate ($NH_4.SO_2$) for controlling the formation of WO_3 particles. PEG-1500 per tungsten ion was added to precursor solution for controlling particles formation. The pre solutions with and without PEG-1500 were transferred into 100 ml Teflon-lined stainless steel autoclave. Hydrothermal reaction was performed at 200°C for 24 hours. After the reaction was completed, the resulting solid was separated by filtering, was washed with distilled water, and ethanol for several times in order to remove the ions, and then finally was dried at 150°C in air for 15 h.

The crystal structure of the samples were characterized by X-ray diffractometer (XRD, Philips Panalytical X'Pert-Pro, CuKα radiation). The surface morphology and microstructure of the samples examined by scanning electron microscope (SEM, Zeiss, EVO LS 10). The sorption isotherms were obtained by the adsorption of N_2 at 77 K in a Micromeritcs ASAP 2020 Physisorption Instrument. The specific surface area and pore volume of the samples were calculated by the Brunauer–Emmett–Teller (BET) and Barret-Joyner-Halenda (BJH) methods, respectively. A hydrogen temperature programmed reduction (TPR) experiment was also carried out in a stainless steel reactor coupled with the quadrupole mass spectrometer (Hiden Analytical QGA). A 200 mg final WO_3 sample was loaded into reactor and heated up to 1000 °C with 3°C/min heating rate and a reducing gas mixture (5% H_2 in nitrogen, total flow rate 400 $ml.min^{-1}$) was supplied. In the present study five different WO_3 samples with different physicochemical properties were obtained as a result of the precursor composition (Table 1). XRD pattern, N_2 sorption graphs, SEM micrographs were analyzed and discussed in detail.

Table 1. Weight ratio of substrates for hydrothermal synthesis

Sample	$(NH_4)_6.W_{12}.O_{39}.xH_20$	$NH_4.SO_2$	$NH_4.NO_3$	PEG-1500 *
W-1	1.0	1.0	-	-
W-2	1.0	0.5	0.5	-
W-3	1.0	0.5	0.5	0.75
W-4	1.0	1.0	-	0.75
W-5	1.0	-	1.0	0.75

* per amount of total tungsten content.

3. Results and Discussion

Crystal phases of the products were analyzed and confirmed by XRD technique. Figure 1 shows the XRD patterns obtained for the samples (W1-W5) prepared by hydrothermal method with different weight ratios of substrate. As shown in Fig. 1, sharp diffraction peaks in all the samples associated with the hexagonal phase of WO_3 (JCPDS 01-085-2460) and no other peaks indexed with impurity phases were found. The results indicated that well-crystallized WO_3 samples were successfully synthesized under different substrate ratios. Moreover, crystallite sizes were calculated by Scherrer equation for more intense and representative reflections as (100), (002) and (200) (Table 2).

XRD results indicated that by using different substrate ratios, same WO_3 crystalline phases can be obtained under hydrothermal conditions. However, the intensities of the diffraction peaks are different and (100), (002) and (200) crystal planes are much higher than those of other detected peaks. Evidently, weight ratio of substrate into the precursor solutions plays a key role in controlling the orientation of the synthesized WO_3 powders. The presence of ammonium nitrate in the solutions can affect the direction of planes in the crystal structure. The intensity of the (200) diffraction peak greatly increases when only ammonium sulfate was used in solution suggesting that the WO_3 rods grow along (200) direction according to the patters of W-1 and W-2 samples. Typically in hydrothermal synthesis, precursor solution ingredients and their concentration is related with the H+ ions are one of the important parameters onto crystal structure (Zheng, Zhang, & Guo, 2013). Wang et al. underlined that the uniform WO_3 nano rod was formed by controlled H^+ ions in aqueous solution. H+ ions served as one of the reactants and affect the acidity. The acidity of the precursor impacted the crystal growth of WO_3 that include nucleus formation and subsequent growth (Wang, Khoo, Lee, & Ma, 2009). In addition to this, the type of sulfates precursors added into the solution such Rb_2SO_4 and K_2SO_4 have strong impact onto the morphology and crystallite size of WO_3 nanoparticles (Gu, Zhai, Gao, Sheng, Wang, Fu, Ma & Yao, 2006). In hydrothermal process, when mineralizer or auxiliary reagent was not used, only monoclinic WO_3 nanoparticles were formed, while the p-aminobenzoic acid was introduced orthogonal $WO_3 \cdot 0.33H_2O$ nanorods were obtained (Liu, Su, Yang, & Ma, 2019).

It was determined that by addition of PEG-1500, the intensities of diffraction peaks of (100) plane have gradually weakened. Intensities of the peaks of the (002) plane were improved by degrees and there was no significant change in the peak intensities of the (200) plane. As a result, the W-5 nano particles arrays grew along (002) plane. These results can be confirmed by crystallite sizes determined by Scherrer equation in Table 2 (Huirache-Acuña et al., 2009; Zheng, Zhang, & Guo, 2013; Su, Xiao, Li, Jian, Sun, & Wang, 2010).

Table 2. Crystallite size of hexagonal WO_3 samples

Sample	(hkl)		
	100	**002**	**200**
W-1	85.58	63.01	42.33
W-2	41.37	42.32	63.01
W-3	62.17	63.00	42.32
W-4	49.51	63.00	50.65
W-5	49.51	63.02	42.33

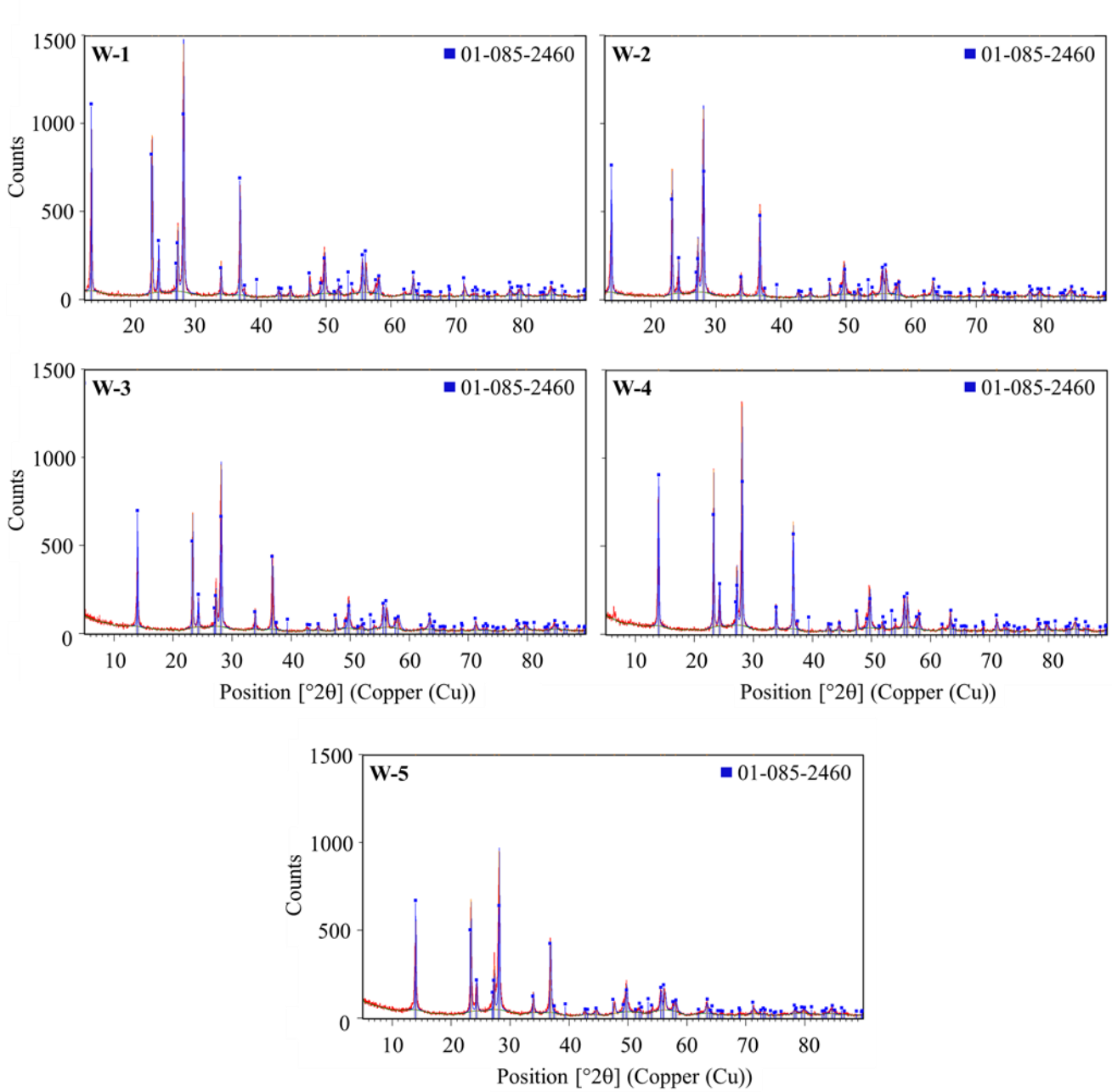

Figure 1. XRD patterns of WO_3 samples synthesized by hydrothermal method

Figure 2 shows the morphology of WO_3 samples. As can be seen from the images, the morphology of WO_3 strongly depended on the substrate ratios in reaction medium, especially in the presence of PEG-1500. The SEM images for the W-1 and W-2 samples, which were synthesized without PEG-1500 addition, showed a rod-flake like morphology. On the other hand, upon the addition of PEG-1500 into the substrate solution, particles shaped in rod-flake like morphology changed into particles having shapes as shown in W-3, W-4 and W-5.

Furthermore, homogeneity in the morphology of the particles were achieved only with the PEG-1500 added ammonium nitrate solution. These samples consist of aggregated particles with irregular shapes due to high surface energy owing to their nanosizes. (Huirache-Acuña et al., 2009). Agglomerates, formed by smaller particles with diameters with sizes of nearly 200 nm were observed in the W-5 powders. It was recommended to eliminate the grain boundaries by sintering to increase the average particle size (Hernandez-Uresti et al., 2014). According to the XRD results, hexagonal WO_3 should exist in the samples. From the SEM images, hexagonal structures were not clearly seen due to resolution, and for further studies, HR-TEM analyses will be performed.

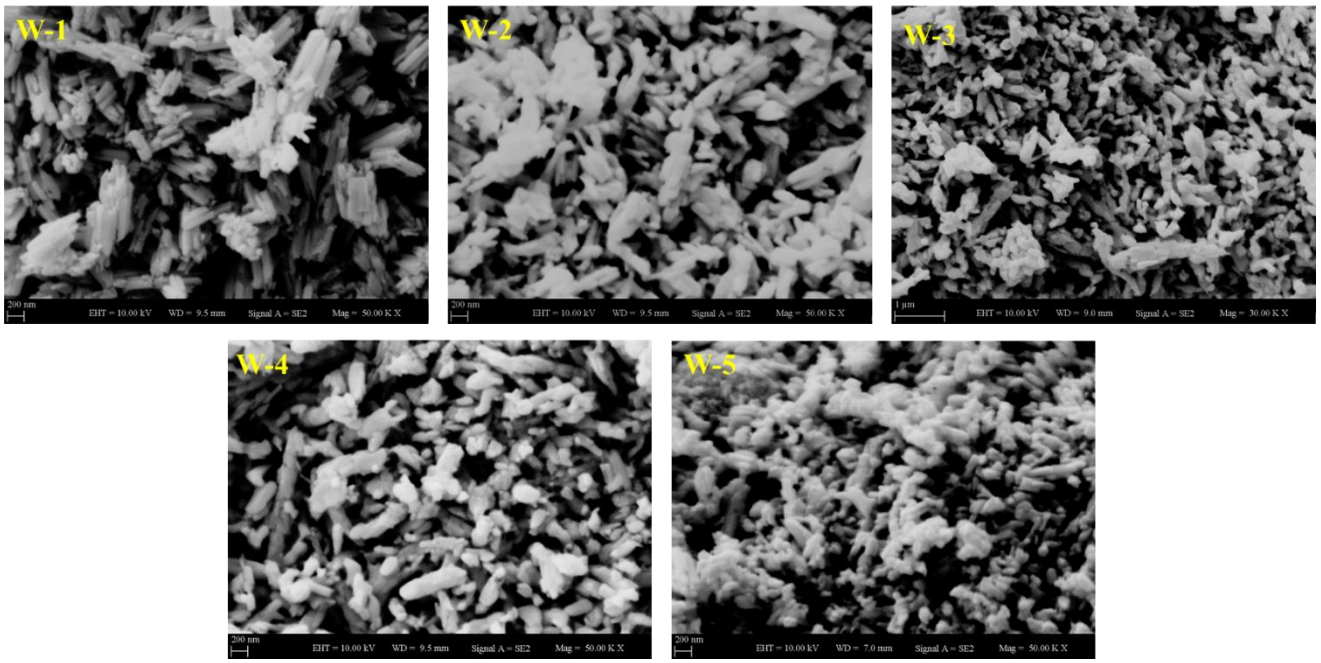

Figure 2. SEM images (X50000) of WO_3 samples synthesized by hydrothermal method

Figure 3 illustrates the ratio of pore volume/S_{BET} and the insets show the N_2 adsorption–desorption curves of W1-W5 samples. According to the IUPAC Classification, sorption isotherms correspond to type IV. Adsorption and desorption step characteristics show that all the synthesized WO_3 samples are mesoporous. The S_{BET} values of powders were in the order of W-5 (8.81 m^2/g) > W-1 (7.85 m^2/g) > W-2 (7.23 m^2/g) > W-3 (6.62 m^2/g) > W-4 (5.86 m^2/g). More importantly, it was reported that S_{BET} values and pore properties of powders were related to morphology and they affected the chemical activity of the surface. Pore volume/S_{BET} ratio at higher values related with smaller crystal size which contributed to chemical activity of the surface. As can be seen, PEG-assisted hydrothermally synthesized mesoporous WO_3 exhibits higher pore volume/S_{BET} ratio.

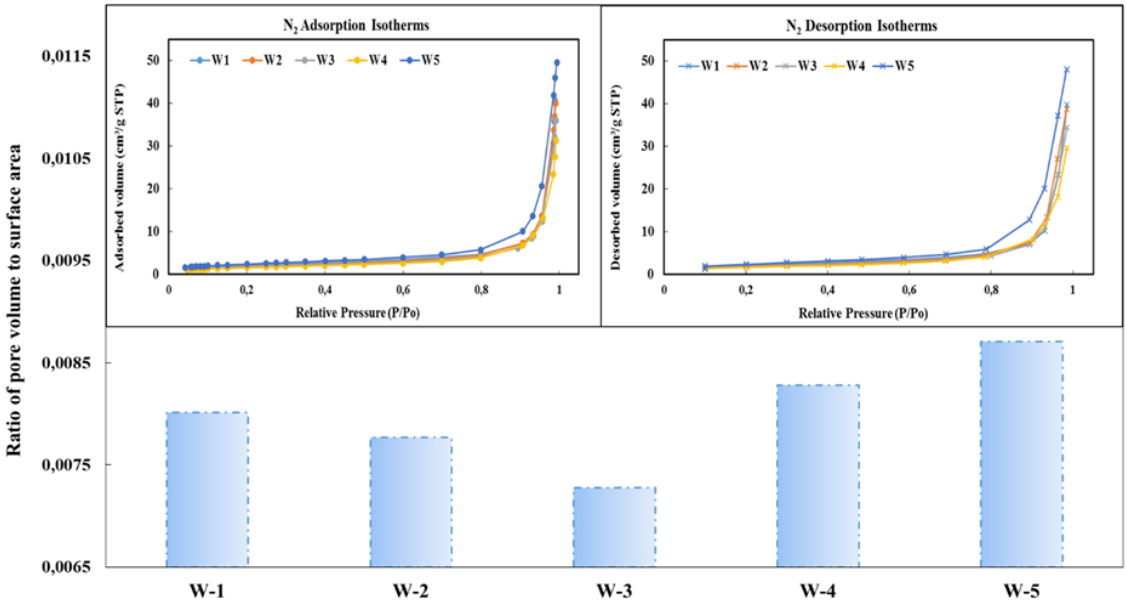

Figure 3. N_2 adsorption and desorption isotherms of WO_3 samples synthesized by hydrothermal method

Our findings suggest that the PEG addition is important for the formation of mesoporous WO_3 nanoparticles with improved properties similar to the results reported in the literature. It was reported the formation and growth of urchin-nanostructures by the addition of PEG. It was mentioned that polycrystalline and uniform microspheres were obtained by PEG addition (Keyson, Volanti, Cavalcante, Simões, Varela, & Longo, 2008). It was investigated PEG assisted $CoFe_2O_4$ nanoparticle synthesis and adsorption properties. They underlined that PEG addition affected the lattice structure and increased the adsorption capacity of the material. With the addition of PEG, a remarkable decrease of particle size is achieved, and the shape of the particles is spherical with a uniform distribution (Wu, Wang, Li, Khaimanov, Tsidaeva, & Lahoubi, 2016). Investigation of the synthesis and magnetic properties of $CoFe_2O_4$ nanoparticles by using PEG as surfactant additive was also performed. It was shown that the addition of PEG can elevate the crystallinity of samples and increases the size of product. Also, the value of magnetic saturation increased due to change of the product morphology (Chen, & Gao, 2007). In order to investigate the hydrogen reduction properties, W-5 was selected due to its outstanding properties: a mean particle diameter around 200 nm, 0.087 highest pore volume/surface area ratio and approximately 8.81 m^2/g specific surface.

The TPR analysis was used to find hydrogen reduction conditions associated with reduction of WO_3 species to metallic W. Figure 4a shows three main peaks of WO_3 with shoulders at 545°C, at 682°C, and 844 °C. 545°C associated with $WO_3 \rightarrow W_{20}O_{58}$, at 682°C corresponding to $W_{20}O_{58} \rightarrow WO_2$, and at 844°C indicated $WO_2 \rightarrow W$ (Ghoreishi, Yarmo, Nordin, & Samsudin, 2013). According to TPR results of W-5 sample has undergone reduction at temperature 844°C with nonisothermal reduction procedure. Following reduction, the sample W-5-TPR was also characterized by XRD and SEM. Figure 4.b shows the XRD pattern of W5-TPR compared with W-5 sample. It was clearly seen that WO_3 was totally reduced to cubic W metal (JCPDS: 98-065-3433). In addition to this WO_3 phase was not detected after the reduction step and it can be concluded that reduction behavior follows in three consecutives steps from WO_3 to W. Crystal size of metallic W was also calculated using Scherrer equation and was found 61 nm based on (011) and (112) planes. The morphology of the obtained metallic cubic W are shown in Figure 4.c. The image represents uniformed nano-sized particles with 135 nm average size.

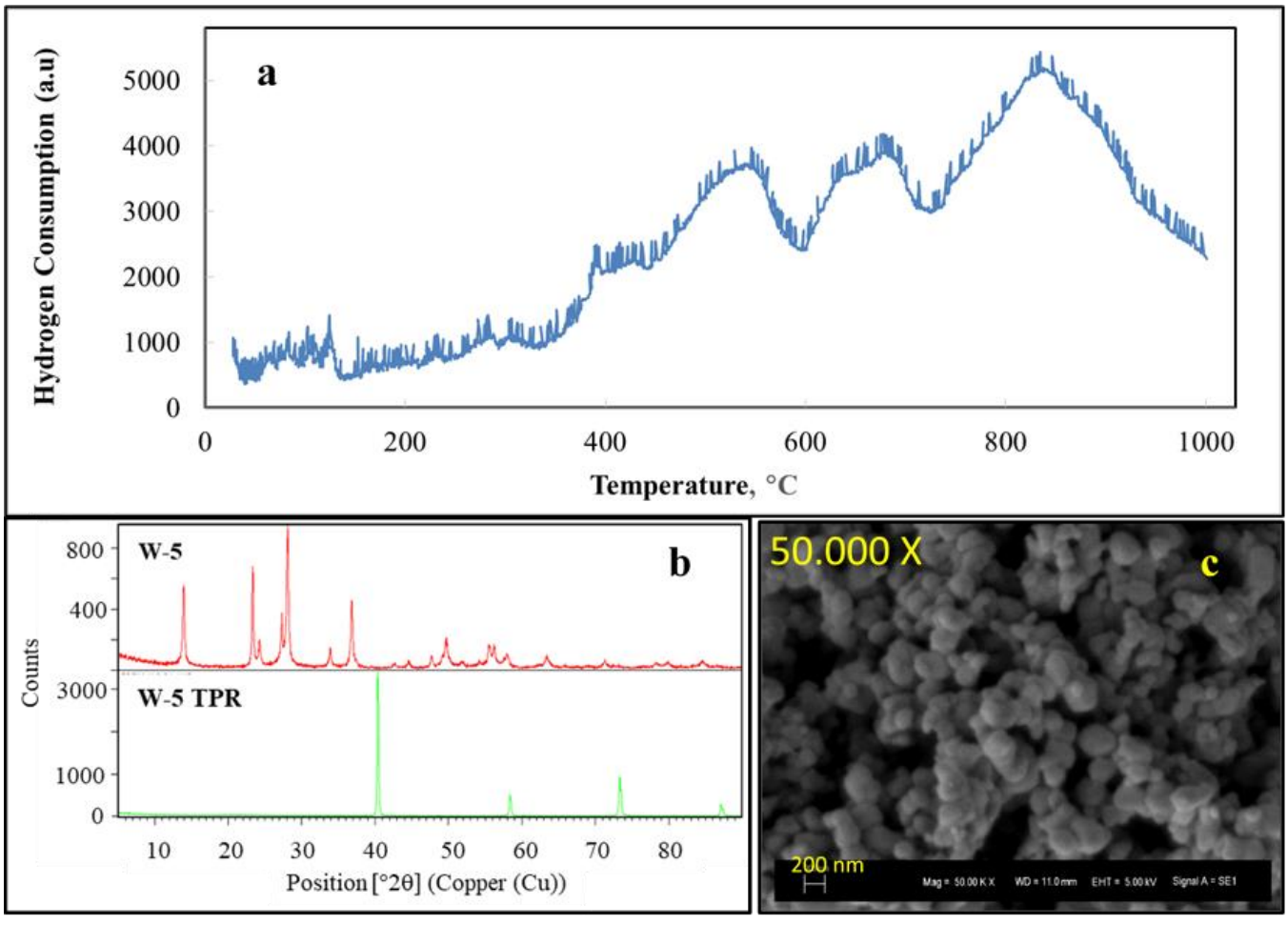

Figure 4. N_2 adsorption and desorption isotherms of WO_3 samples synthesized by hydrothermal method

4. Conclusion

WO_3 nanoparticles with hexagonal phase and mesoporosity were synthesized by PEG assisted hydrothermal method which resulted in nanoparticles with improved surface properties instead of nano rods. It was recommend that to used nitrate precursor instead of sulfate used with ammonium tungsten oxide hydrate as tungsten source at the molar ratio=1:1 assisted by PEG-1500 in hydrothermal method conducted at 200 °C for 24 h. Hexagonal-structured WO_3 was prepared and according to the crystal phase analysis results, it was observed that the growth direction of the tungsten oxide was along (002) with 63.02 nm crystal size. Hexagonal-structured particles exhibited the highest pore volume/S_{BET} ratio (0.0087) related with the highest chemical activity. The obtained WO_3 was completely converted to W phase with found 61 nm crystals at reduction temperature 844 ºC under hydrogen atmosphere. These results corroborate the possibility of obtained WO_3 for potential application in metallic W production.

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