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Preparation of WO_3 Nanoparticles Using Cetyl Trimethyl Ammonium Bromide Supermolecular Template

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Abstract: Problem statement: WO_3 is one of the most interested metal oxides because of its application as catalysts, sensors, electrochromic devices, ceramic, solar cell, pigments and so on. More investigation is needed to find the good and low cost method for preparation of WO_3 nanoparticles with uniform morphology and narrow distribution using a surfactant mediated method. **Approach:** In this study, the synthesis of WO_3 nanoparticles was accomplished using a cationic surfactant (cetyl trimethyl ammonium bromide) as the organic supermolecular template and WCl_6 and NH_4OH as the inorganic precursor and counter ion source, respectively. The effects of reaction temperature and surfactant concentration in particle size of resultant WO_3 nanoparticles were investigated. **Results:** The different ranges of particle size and size distribution were obtained using different surfactant concentration and reaction temperature. The WO_3 particles in the nanometer range (3-15 nm) with uniform morphology and narrow distribution were obtained by optimization of reaction condition. X-ray diffraction, transmission electron microscopy, variable pressure scanning electron microscope, X-ray photoelectron spectroscopy and UV-Vis spectroscopy were used to characterize the final products. The nanomaterials WO_3 showed different pattern in UV-Vis spectroscopy compare to the bulk WO_3. **Conclusion:** A relatively simple and effective procedure for synthesis of WO_3 nanoparticles with mean size below 10 nm, narrow size distribution and high monodispersity using CTAB supramolecular template had been developed and optimized.

Key words: Nanostructures, WO_3, chemical synthesis, optical properties

INTRODUCTION

One of the most interesting properties of some materials is their ability in spontaneous assembling into higher order structures with distinctive chemical and physical properties. Cationic supermolecular surfactant Cetyl Trimethyl Ammonium Bromide (CTAB) can form CH_3-CH_3-CH_3-N structure and induce the sphere-rod transition of micelles in aqueous solution when some salts are added[1]. The ionic surface in ionic micelle (which also contains associated water of hydration) is called as the Stern layer. Surroundings this ionic mantle is a region containing both counter ions and oriented water molecules-the Gouy-Chapman layer (diffuse layer). Together the Stern and Gouy-Chapman layers are known as the electrical double layer. The structure of the Stern and Gouy-Chapman layers depends on the ionic strength of the solution. The supermolecular arrangement of surfactants which acts as the template is utilized to synthesize nanocrystal superlattice, nanotubes, nanorods, nanowires, spherical and mesostructure nanoparticles with different compositions, pore size and novel properties. They attract considerable attention because of their remarkably large surface area and narrow pore size distributions, which make them ideal candidates for catalysts, molecular sieves, gas sensors, etc. Surfactants play different roles in crystallization process. Surfactant molecules may act as a growth controller, as well as an agglomeration inhibitor. This is done by forming a covering film on the newly formed particles[2]. The surfactant-assisted method is an effective process to prepare size controllable nanocrystals and a simple, convenient and low cost

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route. Liu *et al*.[3] and Jana *et al*.[4] have prepared SnS nanowires and Ag nanorods in CTAB aqueous solution respectively. Mandal *et al*.[5] have reported synthesis of sphere- and rod-shaped superparamagnetic Ni-Pd and Ni-Pt nanoparticles. Wang *et al*.[6] and Ye *et al*.[7] have synthesized mesostructured and nanoribbons SnO_2 with CTAB solution respectively. Metal oxide nanoparticles with uniform shape and narrow size distribution are gaining increased technical importance. They are widely used in industrial applications as catalysts, sensors, electrochromic devices, ceramic, solar cell, pigments and so on. WO_3 is one of the most interested metal oxides because of its application in most of the fields mentioned before. In our previous study, WO_3 nanoparticles were synthesized using CTAB and sucrose ester microemulsions[8]. However, in this study, an investigation is done to find the good and low cost method for preparation of WO_3 nanoparticles with uniform morphology and narrow distribution using a surfactant mediated method. The influence of surfactant concentration and reaction temperature on the size is also investigated.

MATERIALS AND METHODS

A number of materials are used in this research. Hexadecyl trimethyl ammonium bromide (CTAB) (purity approx. 99%) was purchased from Sigma. Tungsten (VI) chloride (purity 99%) and ammonia solution (25% v/v) were purchased from Aldrich and BDH respectively. Deionized and double distilled water was used for micelle and solution preparation. All the chemicals and solvents were used as received without further purifications.

It is well known that many factors such as the sort, amount of additives, the concentration of surfactant, the value of pH and reaction temperature can influence the reaction pathway. The different concentrations of CTAB were prepared as mentioned in Table 1. After getting the clear solution, 10 mL of ammonia solution (25 wt%) was added to the CTAB solutions while stirring. After getting a homogenous solution, 0.117 mol of WCl_6 1000 mL^{-1} of CTAB solution was added with vigorous stirring by applying the different temperatures as mentioned in Table 1. After stirring for 4 h, the products were aged at ambient temperature for 72 h. The final product was filtered, washed with deionized water and absolute ethanol in order to remove surfactant, residual reactants and by products and then calcinated at 500°C for 2 h. The same condition and concentration of sample 2 and 3 were applied by using only water as reaction medium (without surfactant) for synthesis of sample 9 and 10, respectively. The study of morphology and composition of the calcinated WO_3 nanoparticles was performed by Variable Pressure Scanning Electron Microscope (VPSEM) (model Leo 1450VP, accelerating voltage at 30 kV) equipped with Energy-Dispersive X-ray analysis (EDX) and Transmission Electron Microscopy (TEM), (model Phillips, CM12) operated at 100 kV. The X-Ray Diffraction (XRD) measurements were performed using a Philips PANalytical x'pert PRO PW3040 X-ray diffractometer with running step = 0.03 in the range of 15-70 2θ, using a monochromatized Cu K radiation (λ = 0.154 nm). The XPS analyses were performed using a XSAM-HS KRATOS X-ray photoelectron spectroscopy. X-ray source type MgK was used with 10 mA current and 12 KV voltage to run XPS analysis for samples at 10^{-9} torr pressure. The pass energy was set at 160 eV for the survey spectra and at 40 eV for the high resolution spectra of all elements of interest. Data processing was performed using the Kratos software after Shirley baseline subtraction and using Schofield sensitivity factors corrected for instrumentation transmission function. The C_{1s} (285.0 eV) photoelectron peak was used as the reference to correct any charging effect. The UV-Vis absorption spectra of the samples were recorded in a Perkin-Elmer Lambda 35 spectrophotometer in the wavelength range 200-1000 nm using a 10 mm quartz cuvette. The measurements were done at room temperature around 25°C. The samples dispersed in 1-butanol using a sonicator (bath type) and UV-Vis spectra for those dispersions were measured.

Table 1: The conditions of reactions and results of some characterizations for synthesized WO_3

Sample	CTAB concentration	Reaction temperature	Particle size[1*] (nm)	crystal system [2*]	crystalline size[3*](nm)
Sample 1	0.05 M	28±3°C	-	-	-
Sample 2	0.05 M	28±3°C	23±1	Monoclinic	15
Sample 3	0.05 M	45±3°C	13±1	Monoclinic	14
Sample 4	0.05 M	75±3°C	22±1	-	-
Sample 5	0.05 M	95±3°C	17±1	Monoclinic	14
Sample 6	0.13 M	45±3°C	22±1	Monoclinic	16
Sample 7	0.027 M	45±3°C	8±1	Anorthic	-
Sample 8	0.067 M	45±3°C	14±1	Monoclinic	10
Sample 9	-	28±3°C	-	Orthorhombic	30
Sample 10	-	45±3°C	-	Orthorhombic	20

[1*]: The mean from TEM results with percentage consideration, [2*]: From XRD patterns, [3*]: The mean from Scherrer's equation using XRD data

RESULTS

The sample 1 and sample 2 were prepared with the same surfactant concentration and temperature. Sample 1 is synthesized without using ultrasonication while sample 2 is synthesized with using ultrasonication. The morphology and size of nanoparticles can be determined from TEM images. The TEM and mean size distribution of sample 7 were depicted in Fig. 1.

The XRD patterns for synthesized WO_3 after heating treatment at 500°C for 2 h were presented in Fig. 2 and 3. The crystalline domain size (D) for WO_3 nanoparticles obtained from XRD peaks based on Scherer's equation: $D = \lambda/(\Delta W \cos\theta)$, where λ is the wavelength of X-ray, θ is the Bragg's diffraction angle and ΔW is the true half-peak width of the XRD lines. The more details are tabulated in Table 1.

The surface composition of sample 3 and 7 were characterized by XPS analysis. The wide scanning XPS spectrum within the range of 0-1100 eV of the WO_3 nanoparticles only show the C impurity in the sample and confirm that the surfactant template CTAB is completely removed from the sample. The narrow scanning of W, C and O elements of the WO_3 nanoparticles is done to investigate their chemical states, which is depicted in Fig. 4.

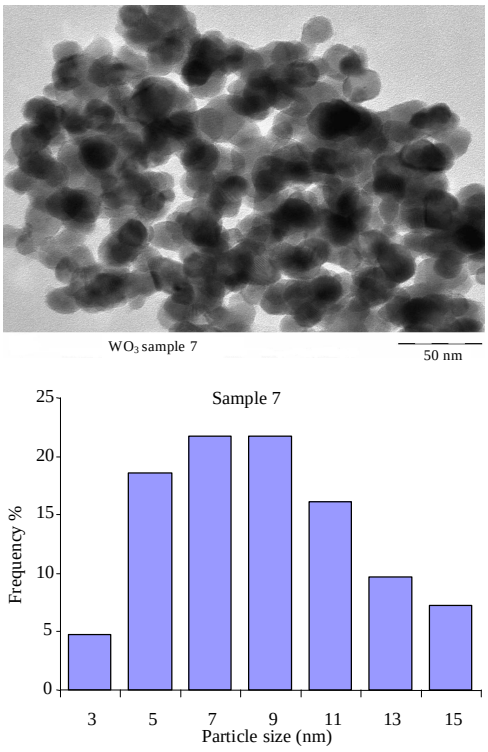

Fig. 1: The TEM image and particle size distribution (obtained from TEM) of WO_3 nanoparticle

The resultant C_{1s} peak in XPS, is from carbon contamination that is very usual and in fact, it is often used to calibrate peak position. The C impurity in this study is believed to originate from the surface contamination in the atmosphere and also the residual surfactants absorbed on the nanoparticles. The photoelectron peak of the W $_{4f}$ region in all of WO_3 samples shows a well-resolved double peak due to the $4f_{7/2}$ (BE = 35.9 eV) and $4f_{5/2}$ (BE = 38.0 eV) components (spin orbit splitting) and reveals the W^{+6} state. On the other hand, the O_{1s} band is deconvoluted in 3 components. The main peak is associated with the O^{2-} state, while another one is assumed to be resulted from different sources, probably coming from rooted OH groups or from ambient humidity. Subsequently the XPS resulted from these samples reveals the WO_3 composition of the synthesized samples[9]. Both XRD and XPS analyses show that WO_3 nanostructure is successfully produced via the present one-step synthetic route.

The UV-Vis spectra for WO_3 samples are depicted in Fig. 5. As shown in Fig. 5, the nano WO_3 gives more resolved peaks (corresponding to the band gap of the WO_3) compare to the bulk.

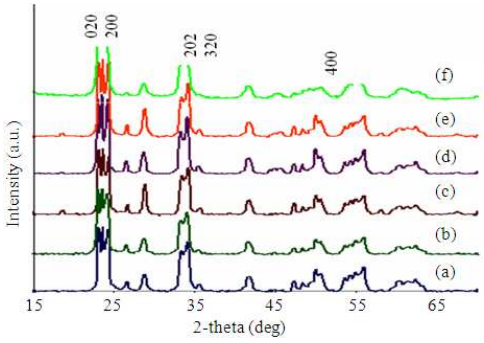

Fig. 2: The XRD patterns for WO_3 nanoparticles: (a) Sample 2; (b): Sample 3; (c): Sample 5; (d): Sample 6; (e): Sample 7; (f): Sample 8, respectively

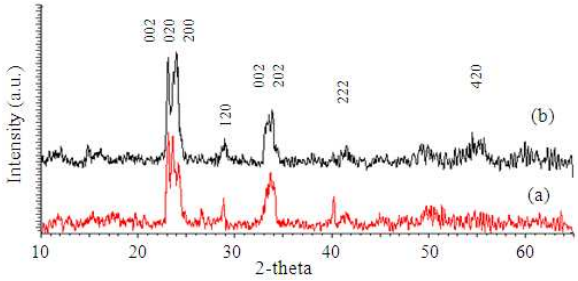

Fig. 3: XRD patterns for synthesized WO_3: (a) sample 9; (b) sample 10, respectively

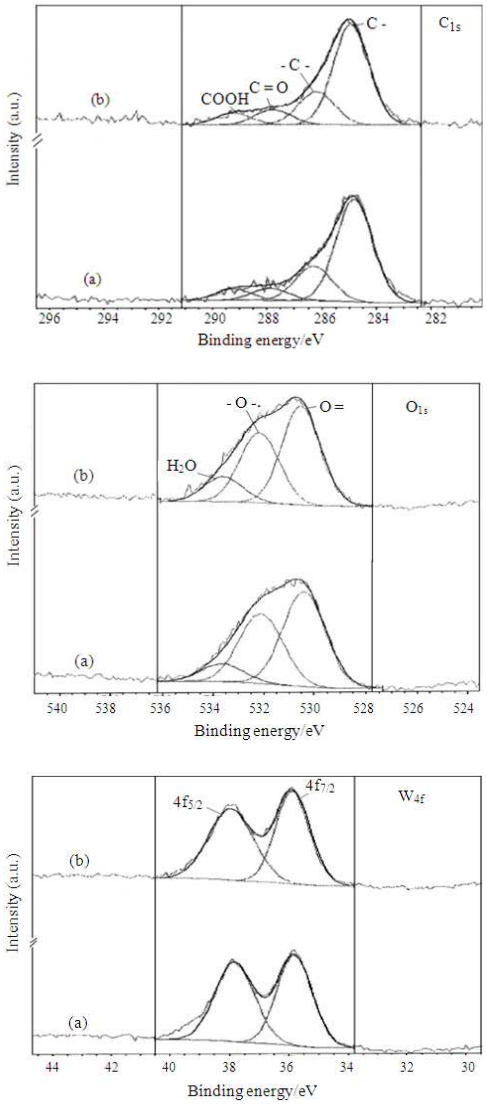

Fig. 4: Peak-fitted C_{1s}, O_{1s} and W_{4f} signals of (a): Sample 7; (b): Sample 3 nanoparticles, respectively

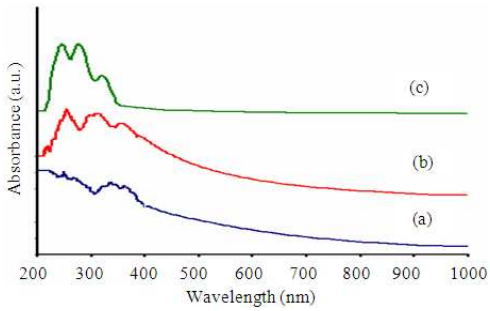

Fig. 5: UV-Vis spectra of WO_3 (a): Bulk; (b): Sample 10; (c): Sample 7, respectively

DISCUSSION

One of the main mechanical effects of ultrasonication is the disaggregation and deagglomeration of the particles.

The SEM results show that particles in sample 1 are more agglomerated compare to sample 2. So, we used ultrasonication after the addition of WCl_6 to the solution.

In this study, the concentration of CTAB in all solutions has been chosen to be higher than CMC (1.3 g L^{-1}) and above the CMC, surfactant molecules aggregate to make micelles. The shape of micelle depend on the surfactant concentration and the surrounding medium of surfactant. According to TEM images, in this study, we assume that micelles are in spherical shape. Micelle does not only provide favorable site for the growth of the particulate assemblies but also influences the formation progress including nucleation, growth, coagulation and flocculation and so on. The surfactant-assisted method is an effective process to prepare size controllable nanocrystals which is simple, convenient and low cost process. High concentrations of anionic nucleophiles (OH^- in this study) in the electric double layer of a cationic micelle (CTAB in this study) implies that the surfactant counter-ion (Br^- in this study) is readily transferred to the aqueous phase since the reaction must occur at this interface and since the micellar surface cannot be oversaturated by anions. Better to mention that the reaction between the two reagents can occur when they meet at the interface .The electric double layer serves as a diffusion barrier to the growth species, resulting in a diffusion-limited growth in the subsequent growth of nuclei. The diffusion-limited growth would reduce the size distribution of the initial nuclei, leading to monosized nanoparticles.

The reason for more resolved peaks compare to bulk in UV-VIS spectra for WO_3 samples is possibly because of the peaks overlapping which is consequent of peak broadened in bigger size. The same result is also reported by Sun *et al.*[10]. The shift of the absorption edge in nano WO_3 to higher energies compare to that of bulk WO_3 along with increase in particle size can be seen, indicating a widening of the energy gap caused by quantum size effects. It is well-known that, as a consequence of quantum confinement of the photogenerated electron- hole pairs, the UV-vis absorption spectra of semiconductor nanoparticles is size dependent. Particularly, the wavelength at the maximum exciton absorption (λ_{max}) decreases because of the decrease of the size of the nanoparticles. The decrement of particles size increases the optical band

gap energy of the nanoparticles, indicating the presence of quantum confinement effect, which is consistent with previous theoretical argument by Brus[11].

Karazhanov[12] showed an oxygen (anion) vacancy in WO_3 does not only generate a donor like state near the fundamental band gap, derived from the top valence bands, but also gives rise to an additional pair of defect states: A hyper-deep resonant state in the valence band and a high-lying resonant state in the conduction band, derived from s-like bonding and antibonding bands, respectively. We assume that the transition in mentioned bands offers a possible explanation for the observed peaks in UV-V is spectra of WO_3. Also, the absorption edges of nanocrystallites are sharp, indicating that the synthesized particles have relatively narrow size distributions. It is in good agreement with TEM results. The optical band gap value is determined by considering an indirect transition between the 2p electrons from the valence band of the oxygen and the 5d conduction bands of tungsten[13]. The results in this study are in good agreement with previous researches.

CONCLUSION

A relatively simple and effective procedure for synthesis of WO_3 nanoparticles with mean size below 10 nm, narrow size distribution and high monodispersity using CTAB supramolecular template has been developed and optimized. The results reveal that the CTAB supermolecular template is a good and low cost method for preparation of WO_3 nanoparticles in the size range of 3-15 nm with uniform morphology and narrow distribution, using 0.027M CTAB supermolecular solution without using organic solvent at the reaction temperature of 45±3°C. Synthesize of WO_3 without using CTAB template yields more agglomerated particles. The difference of prepared nanomaterials compare to bulk WO_3, in the term of optical properties, is contributed to quantum confinement effect.

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