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A Novel Approach for the Synthesis of Tungsten Trioxide Nanostructures

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Abstract. A novel and facile approach has been described for the synthesis of tungsten trioxide nanostructures by a simple reaction at very low temperature. The mechanism for the formation of various nanostructures has been discussed in detail. The resulting nanostructures have been comprehensively characterized by Field Emission Scanning Electron Microscopy (FESEM) coupled with EDX. The employed route is template free, easy, economical and requires a low temperature.

Keywords: Tungsten powder; Synthesis; Nanostructures; FESEM

Introduction

Transition metal oxides have been intensively studied for a long period of time because of their promising applications in chemistry. Among them, Tungsten trioxide (WO_3) has many technological applications. It is good electrochromic, optochromic and gasochromic material[1-3]. It has been used to construct infrared switching devices, writing-reading erasing optical devices, gas sensors for determination of hydrogen, ammonia, nitrogen and to produce humidity and temperature sensors[4,5]. Because of their band gap situated within the solar spectrum range tungsten oxides are one of the solar energy transforming materials leading to applications of catalytic activity and photoconductivity[6]. Of special interest is the preparation of nanostructured tungsten oxide since nanometric structures exhibit novel properties due to large number of surface atoms and or three dimensional confinement of electrons.

Various methods including pyrolysis, thermal decomposition, wet chemical process such as sol gel, colloidal and ion exchange method have been used to prepare WO_3 nanostructures[7-10]. Tree like structure have been observed by heating a tungsten foil, partly covered by SiO_2 in Ar atmosphere at 1600ºC whereas WO_2 nanowires have been reported by heating tungsten wire under N_2 at the same temperature[11,12]. Tungsten hot filaments have previously been used to prepare tungsten oxide nanostructures but studies on how to control the synthesis conditions to prepare different nanostructures are not yet clear[13].

Therefore, new methodologies are highly in demand for the preparation of tungsten trioxide nanostructures at low temperature. Hydrothermal techniques have found their place in several branches of science and technology. Owing to their special properties, particularly the high salvation power, high compressibility, and mass transport of these solvents, one can also expect the occurrence of many novel reactions. Encouraged by the recent results of ZnO nanorods prepared by a simple reaction of zinc metal and water in the temperature range down to room temperature, we have carried out the reaction of tungsten metal with water at very low temperature[14]. In this letter, we report a simple and facile method to produce nanoparticles, nanoplates and rectangular nanorods of tungsten oxide in the temperature range of 50-100ºC without any additives. The literature reports that researchers generally use amines and complex compounds employing high temperatures. The aim of the study is to provide the feasibility of the simple route for the preparation of tungsten oxide nanostructures. This method has been found convenient, economical and fast.

Experimental

The procedure employed by us for the synthesis of tungsten trioxide nanostructures including nanoparticles, nanoplates and nanorods is as follows. In a typical synthesis, 10 mg of W powder was taken in a vial containing 10 ml of distilled water (pH 6.5). After sonication, samples prepared have been kept at different temperatures ranging from 50 to 100ºC in an oven at different reaction times from 12-72h. Distilled water has been used throughout the experiment. Afterwards the mixture was centrifuged to reclaim the precipitated sample. Final product was vacuum dried. The detailed analysis of the products was carried out using high resolution FESEM (FEI NOVA NANOSEM) coupled with EDX were employed. The EDX measurement on the nanorods indicates that the rod is composed of W and O. X-ray diffraction patterns of the samples were recorded with Siemens D 5005 diffractometer using Cu Kα (λ =0.15141 nm) radiation.

Results and Discussion

Figure 1 shows various types of tungsten trioxide nanostructures obtained by reaction of tungsten metal powder with water at different temperatures and time. Nanostructures were not observed for a sample reacted for 6h at room temperature. Figure 1(a) shows the morphology of nanoparticles obtained after the reaction of tungsten metal with water at 50ºC and the reaction time was 12h. The nonoparticles are not entirely spherical in shape and have diameters varying between 100 to 300nm, with an average diameter of 200nm as can be seen from figure. Figure 1 (b) shows nanoplates prepared at 75ºC and the reaction time was extended to 24h. The nanoplates are having average dimension of 300nm wide and 200nm thick. These nanoparticles and nanoplates are similar to those reported by Sittisuntorm[15]. Figure 1 (c) and (d) shows the FESEM image of products obtained at 100ºC and the time of reaction was extended to 36h and 72h respectively. Rectangular naorods have been observed with average size of 400nm wide and 200nm in thick and length upto several micrometers. We have observed the presence of short noanords also. The effect of reaction time plays a marvelous role in the morphology of nanoparticles. The influence of reaction conditions on physical properties of synthesized nanoparticles as well as mechanism is yet to be investigated.

The EDX measurement on the nanoparticles, nanoplates and nanorods indicate that the rod is composed of W and O as shown in Fig. 2. The molecular ratio of W/O of the nanostructures, calculated from EDX and quantitative analysis data is close to that of bulk WO_3 crystal. The XRD pattern for the nanostructure shows a triclinic WO3 with no traces of WO2. The formation of pure tungsten trioxide nanostructures by heating the as prepared samples under air is also evidenced by change of colour for annealed samples. The chemical reaction for synthesizing nanostructures can be expressed as:

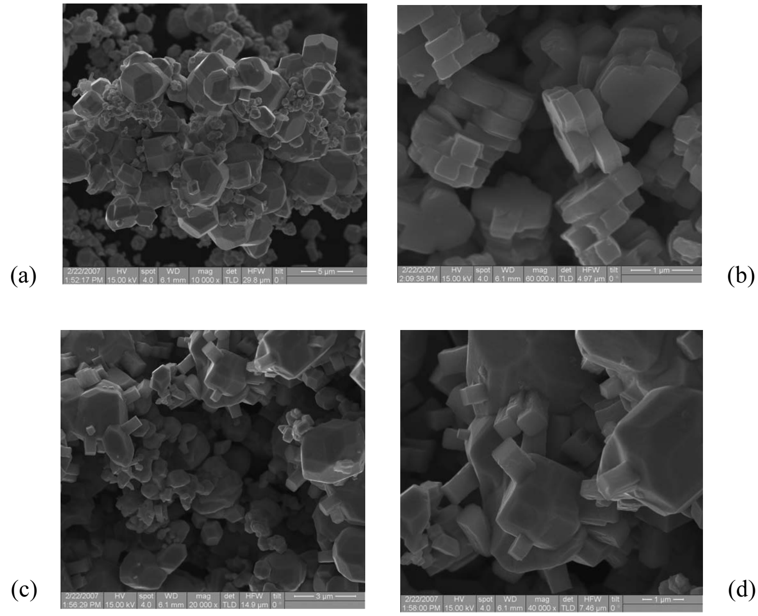

Fig. 1. FESEM images of nanoparticles, nanoplates and nanorods obtained by the reaction of W metal with water at different temperatures form 12-72h: (a) shows images of nanoparticles at 50ºC for 12h, (b) at 75ºC for 24h, (c) at 100ºC for 36h and (d) 100ºC for 72h.

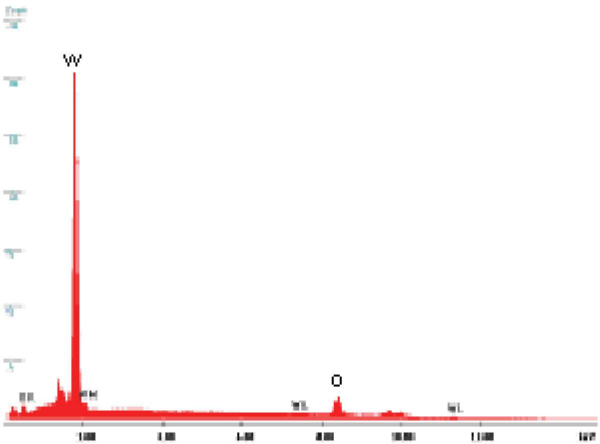

Fig. 2. The EDX analysis confirming the existence of all elements involved in sample preparation.

$$W(s) + 3H_2O\,(l) \rightarrow \quad WO_3\,(s) + 3H_2\,(g)$$

Here (s), (l) and (g) represent solid, liquid and gas respectively. The similar study has been reported earlier in case of iron oxide, where evolution of hydrogen has been documented[16]. The mechanism for the formation of various nanostructures can be explained as. Tungsten metal on reaction with water slowly gives out hydrogen (g) and the oxygen liberated reacts with metal to give oxides as shown in above reaction. Further, WO_3 layer formation on the rod surface, acting as a passivation layer, will inevitably reduce the dissolution rate of W substantially and thus prevent further growth of nanorods. This explains why the length and width of nanorods do not grow in an unlimited fashion, when an increased reaction time and temperature are used. Moreover, water at elevated temperatures play an essential role in the precursor material transformation because the vapour pressure is much higher and the state of water at elevated temperatures is different from that at room temperature. The solubility and the reactivity of the reactants also change at high pressures and high temperatures and high pressure is favorable for crystallizations.

Conclusion

In this report, we described a novel method for the syntheses of tungsten trioxide nanoparticles, nanoplates and nanorods from a simple W-H_2O reaction. FESEM examination reveals various types of nanostructures. Rectangular nanorods-like nanostructures are created at increased reaction time and temperature. This direct and efficient route, extendable to other metal or alloy oxide nanostructures has the potential to be further scaled up towards production of large quantities.

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طريقة جديدة لتحضير أكسيد التانكستان النانوي البنية

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المستخلص. لقد تم شرح وتوضيح الطريقة الجديدة والسهلة لتكوين البنى النانونية لأكسيد التنجستن عند درجة حـــرارة أقــل. وهــذه الطريقة سريعة واقتصادية، ولم يستخدم أي مواد محفزه لها. وقد تم مناقشة وتوضيح ميكانيكية تكوين أنواع مختلفة من البنى النانونبة.