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Effect of gel making agent on the morphology and particles sizes of chromium oxide nanostructures

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ABSTRACT

The paper presents deals with the effect of poly vinyl alcohol (PVA) amount as gel making agent of sol-gel combustion method on the morphology and the particles sizes of chromium oxide nanostructures (CONS). Chromium nitrate is dissolved in 1:1 water ethanol mixed solvent. Some different amounts are dissolved in the chromium nitrate solution under controlled temperature to make a sol. The solvent of the sol is evaporated under controlled temperature to obtain a high viscous material which called gel. The suitable pyrrolysis temperature of the gel is found by TGA/DTA analysis. The homogenous gel is slowly pyrrolized under 500 ºC by an electrical furnace to obtain a CONS sample. Five different samples are synthesized by using different amounts of PVA. The morphology, particles sizes and the composition of the CONS is characterized by SEM, TEM, XRD and DLS.

KEYWORDS

Sol-gel combustion method;
Chromium oxide;
Nanostructure;
PVA.

INTRODUCTION

Nanomaterials have small grain size (100nm or less) and large surface, often exhibited unique novel properties relative to those of the coarse-grained counterparts. Chromium (III) oxide nanostructures (CONS) with high surface areas have attracted considerable attention in the recent years. They exhibit useful and fantastic properties compared to the micrometer-sized materials. The chromium oxide nanoparticles have a wide variety of applications such as photonic and electronic devices and drug delivery[1,2], coating materials and wear resistance materials[3,4], hydrogen storage[5–7], catalysts[8–10], digital recording system[11], dye and pigment[12,13], advanced colorants[14], solar energy application[15]. Various methods have been reported to synthesize CONS such as sonochemical methods[16], mechanochemical reaction and subsequent heat treatment[17], laser induced deposition[18], hydrothermal[19], solid thermal decomposition[20], bio-method[21], combustion[22], nanocasting method[23], sol–gel[24], precipitation–gelation[25], and oxidation of chromium in oxygen[26].

Chromic oxide (Cr_2O_3) is an important refractory material due to its high melting temperature (~2300°C) and oxidation resistance; although its sinter-ability is very poor and requires special sintering condition to achieve high density. For such an application, the availability of nanosized powders would be desirable since they usually present high surface areas and may favor the sintering process[16]. In addition, this kind of powders is essential for preparing nanocrystalline ceramics, which may present improved properties (hardness, toughness, etc.) over the conventional ones. In catalysis, both chromium oxide and supported chromium have been used in many reactions such as ammonia decomposition[27], dehydrogenation[9], and oxidation of toluene[28]. Calcined catalysts, whether supported or unsupported, perform actively in redox reactions.

Chromium oxide nanoparticles with crystals sizes of 30–70 nm were prepared via hydrothermal synthesis[19,29]. Also, nanoporous chromium oxides were prepared by solid thermal decomposition using citric acid as template agent and the relation between the structure and the reaction conditions of chromium oxide was investigated[30]. In addition, chromium oxide nanocrystallites have been synthesized by thermal decomposition of solid precursors and evaluated as catalysts for ammonia decomposition[20].

Among the various methods used to prepare metal oxides, the sol–gel process has wide interests. The sol–gel method is believed to preserve the advantages of making nanoscale pore diameter, narrow pore size distribution, and superior homogeneity. Recently, El-Sheikh et al. has been reported a simple method to synthesize controlled size chromium oxide nanocrystals[31]. They prepared chromium oxide nanopowder via the reduction of $K_2Cr_2O_7$ by maleic acid at pH 7 and room temperature. The resulting solution was stirred for 24 h, and left for 15 days to form a green gel. The obtained gel was kept at room temperature for about 24 h, followed by heating at 110 °C for about 24 h. The dried samples were annealed at different times (3 to 12 h) and different calcination temperatures (300 to 600 °C). During the calcination process the green gel converted to black grey color. They investigate the effect of pH, reduction agent concentration, and calcinations time and calcinations temperature. Based on this report, preparation method is very time consuming (at least 96 h).

Previous, we developed a novel and fast PVA-based sol-gel method to synthesize metal oxide nanoparticles[32]. In this work, CONS is synthesized by sol-gel consumption method based on PVA as gel making agent. The total time of this synthesis is lower than 6 h.

Figure 1 : The synthesized green CONS

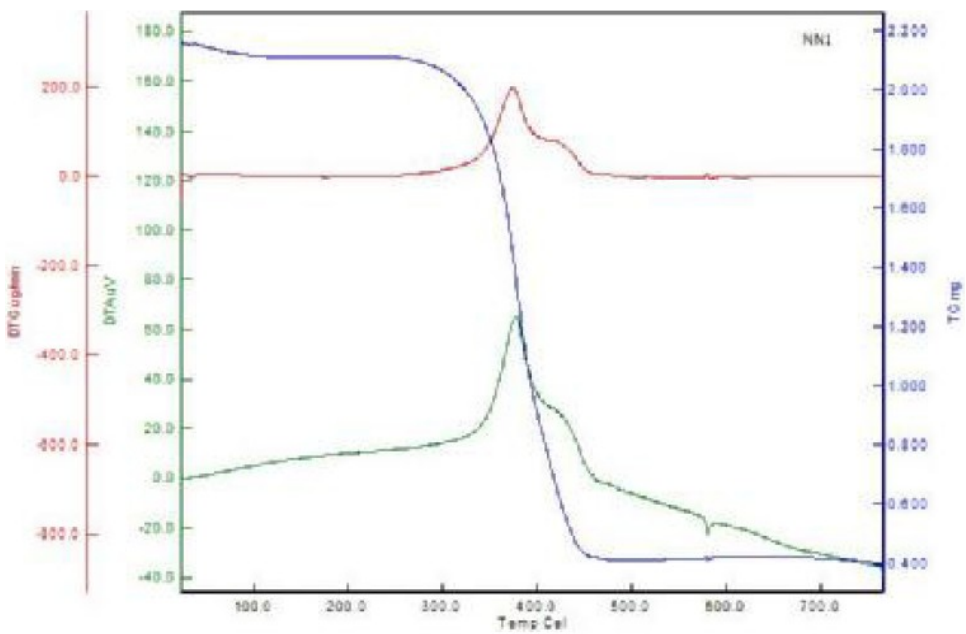

Figure 2 : TGA/DTA analysis of the un-pyrrolized gel consisting chromium nitrate

EXPERIMENTAL

All materials and reagents were purchased from Merk of Fluka. Double distilled water was used in all experiments. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were simultaneously performed using a thermogravimetric analyzer (TGA/DSC1, Mettler Toledo) for thermal studies. The morphologies, Particles sizes and the compositions of samples were characterized by the scanning electron microscopy (SEM, Zeiss, Sigma/VP, Germany). A transmission electron microscope (TEM, Zeiss EM900, 80 keV) was used to measure the size and shape of particles accurately. Size distribution diagram of the opti-

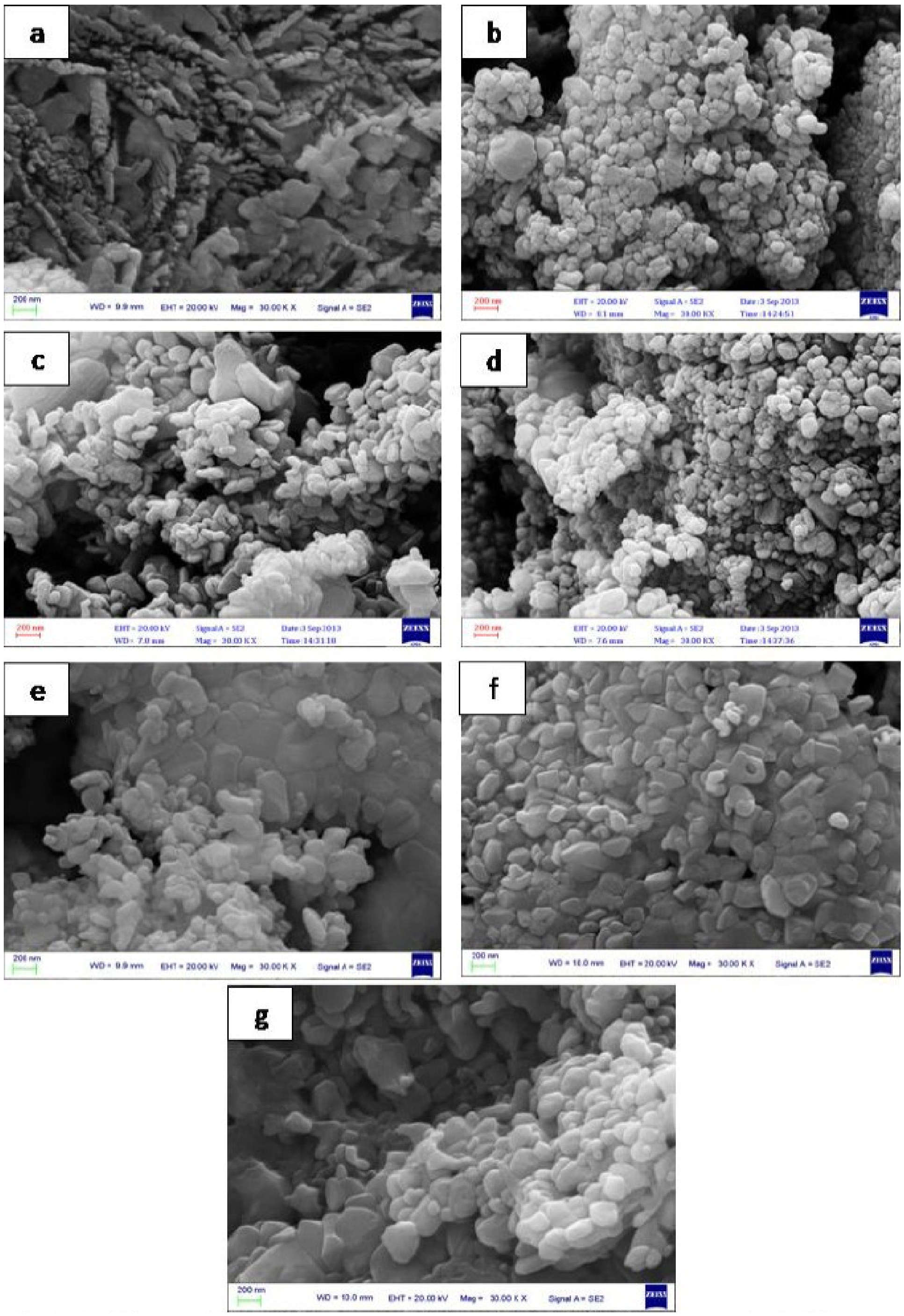

Figure 3 : SEM images of the CONSs samples which synthesized via different amounts of PVA (% wt); a= without PVA, b= 0.5, c= 1, d= 1.5, e= 2, f= 3 and g= 4

mized sample was obtained by DLS (Malvern, Zetasizer Nano ZS3600).

RESULTS AND DISCUSSION

In the proposed method, the gel network rigidity controls the morphology and particle size of the synthesized sample to make a uniform CONS. In the gel structure, chromium salt is homogeneously dispersed in the polymeric network. Because of gel network rigidity, the dispersed ions in the gel network can not alter their positions. Therefore, during the combustion of the gel's outer layers, the chromium salt of the burnt layers is calcined to yield Cr_2O_3 nanoparticles. Figure 1 shows the real image of the synthesized nanomaterial.

To obtain suitable temperature to increase the sample crystallinity, the un-pyrrolized gel was analyzed by TGA/DTA (Figure 2). Figure 2 shows that the gel pyrrolysis and chromium salt calcinations are simultaneously taken at about 400 ºC. The formed chromium oxide (Cr_2O_3) nanoparticles are stable at thermal range of 400 to 800 ºC. Therefore, to increase sample crystallinity, all samples were heated to 500 ºC for 3 h.

In this method, the PVA is main factor which control the morphology and particles sizes of the sample. To investigate the effect of PVA amount on the morphology and the particles sizes of CONS, seven samples with different amount of PVA content (0, 0.5, 1, 1.5, 2, 2.5, 3, and 4) in the sol were synthesized. Figure 3 shows the SEM images of the prepared CONSs. As it can be seen in Figure 3, PVA content can change the morphology and particles sizes of the samples. Based on the Figure 3, the 1.5% PVA is suitable value to synthesize uniform and smaller particles of CONS.

The synthesized sample via 1.5% PVA is identified by energy dispersive spectroscopy (EDS). Figure 4 shows the EDS peaks of the CONS. Based on the EDS peaks, the sample is only included chromium and oxygen atoms. With respect to the weight percentage of the Cr and O, the sample can be Cr_2O_3.

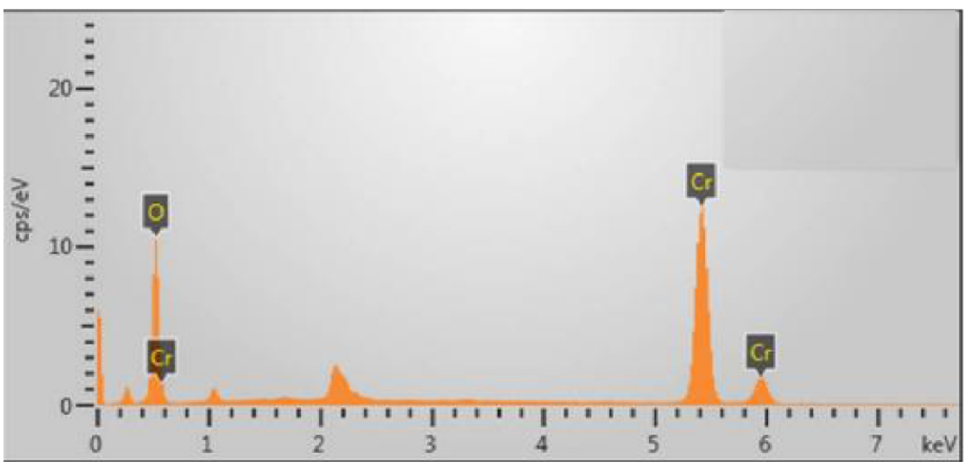

Figure 4 : XRD patterns for the synthesized CONS

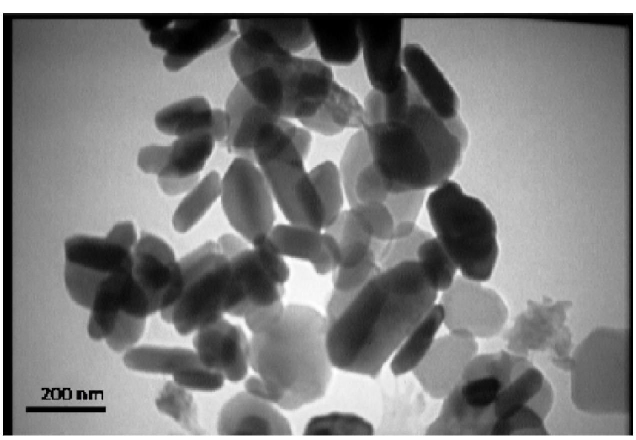

Figure 5 : TEM images of the synthesized CONS sample

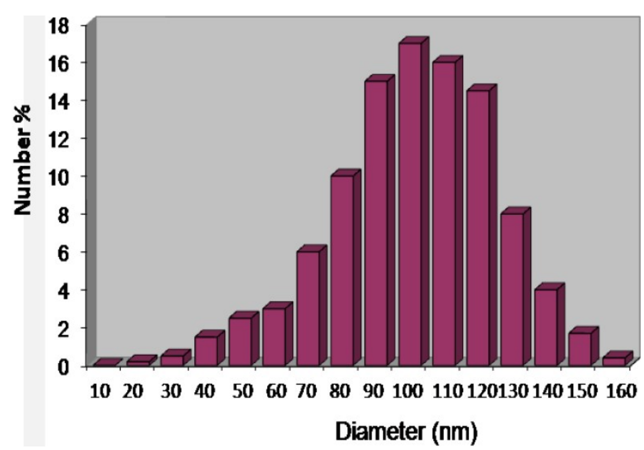

Figure 6 : Size distribution result for CONS analysis

The sample synthesized via optimum amount of PVA is studied by TEM (Figure 5). Based on the present images in Figure 5, the sample includes rice shape nanoparticles with 70 nm average diameters and 180 nm average lengths.

To exactly evaluate the sizes of sample particles, the CONS sample is analyzed by DLS (Figure 6). Based on the shown sizes distribution diagram, 80% of particles are in 80 to 130 nm range of size distribution. The average diameter presented in DLS is not agree with TEM image because, the particles are rice shape (diameter lower than length) so, DLS presents average amount for diameter and length.

CONCLUSIONS

PVA-based sol-gel combustion method can be used as a confident and controllable method to prepare chromium oxide (Cr_2O_3) nanoparticles. In this method, PVA is used as a suitable gel making agent in polymer-based sol-gel method. The amount of PVA in sol is main factor to control the morphology and particles sizes of chromium oxide nanoparticles.

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