

Preparation of Ultradispersed NiO and MoO₃ by Using of Low Molecular Weight Sol Stabilizers

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ABSTRACT

Ultradispersed and submicron NiO and MoO₃ powders with a particle size of 40 nm were synthesized by the modified sol-gel technique with using of hexamethylenetetramine and N,N-dimethyloctylamine as sol stabilizers. Obtained powders were characterized by XRD and TEM. It was shown that in depending on sol stabilizer and molar ratio stabilizer/metal it is possible to obtain the metal oxide powders with different morphology parameters and texture. The addition of acetylacetone in the reaction mixture led to particle size increasing. It is experimentally proved that the dispersion of metal oxide powders can be controlled accurate to 10-20 nm in this way.

Keywords: ultradispersed NiO and MoO₃, modified sol-gel technique, hexamethylenetetramine, N,N-dimethyloctylamine

1. INTRODUCTION

It is well known that high specific surface area and low temperature sintering of ultradispersed NiO and MoO₃ powders make them indispensable intermediates for fine-grained ceramics (Chow 1998), which in the next decade will be the most popular material in many industries: the creation of cathodes and anodes for the next generation of power supplies (Xiang 2002, Pejova 2000), catalysts (Chen 2011), photochromic and electrochromic materials, chemical energy accumulator used natural gas or hydrogen (Monk 2009), and multilayer ceramic capacitors (Xu 2003). The use of ultradispersed powders allows obtain materials with high density and high electrical conductivity, which is an important for the development of small-size high-speed electronic devices with wide range of functions and at the same time with low energy consumption. The physical and chemical approaches are used to prepare such powders, however, in the past decade they have become increasingly important because they can provide high reproducibility for the physicochemical properties with high yield.

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The sol-gel technique is distinguished among chemical methods due to its effectiveness, efficiency and ability to control the structure of the prepared powders (Ren 2007, Porta 1999, Lewellyn 1997, Jiao 2003).

Previously, we reported about the possibilities of wet method for the synthesis of mesoporous materials and nanostructured powders (Trusova 2012, Trusova 2012).

The purpose of this research is to develop the synthesis of highly dispersed NiO and MoO₃ powders by modified sol-gel technique using hexamethylenetetramine (HMTA) and N,N-dimethyloctylamine (DMOA) as sol stabilizers. The investigation of influence of the different sol stabilizers on the NiO and MoO₃ oxides morphology also was included in the purposes of the work. The conformity to the soft chemistry concept, environmental acceptability and cost effectiveness are advantages of the developed approach. Therefore the developed laboratory technology is a promising for the obtaining of ultradispersed powders with specified physical-chemical properties and a wide range of applications.

2. EXPERIMENTAL

Nanostructured NiO and MoO₃ powders were prepared by modified sol-gel technique. Nickel acetate and ammonium molybdate hydrates (Ni(Ac)₂·4H₂O and (NH₄)₆Mo₇O₂₄·4H₂O) were used as metal sources. Initial salts were dissolved in deionized water with stirring on a magnetic stirrer and heating to the temperature of 60-65°C. HMTA and DMOA were used for the sol stabilization, and acetylacetone (AcAc) was used as a complexing agent in the MoO₃ case. The stabilizer/metal molar ratio value was changed in the range from 1/3 to 4/1, and AcAc/Mo molar ratio value was 3/1 or 6/1.

Aqueous-organic phases were prepared by adding a complexing agent and sol stabilizer in the initial aqueous solutions of salts, mixed and heated at 60-65°C to the formation of colloid, which then was evaporated at 80-90°C to gel formation. The obtained gel was transferred to a porcelain or corundum crucible and calcined at 500°C in the furnace during 1h.

The obtained NiO and MoO₃ powders were characterized by using of methods TEM (LEO 912 ab Omega Carl Zeiss instruments), XRD (DRON-3M with Cu K α radiation, Russia), and elemental analysis (atomic emission spectrometer with inductively coupled plasma, Optima-5300). The crystalline phases were identified by matching the experimental patterns to the JCPDS powder diffraction file. The average crystallite size was calculated by the Rietveld method.

3. RESULTS AND DISCUSSION

A detailed study of the synthesis conditions was carried out. Accordingly to the elemental analysis, all obtained powders contained no more than 0.07 wt% of carbon. Table 1 shows synthesis conditions, phase compositions and morphology parameters of obtained NiO and MoO₃ powders according to XRD data. Fig. 1 shows the XRD patterns of NiO powders, obtained at different HMTA/Ni molar ratio values. It was

shown that this value has a significant influence on the powder dispersion. Thus, when the HMTA/Ni molar ratio value was equal 2/1 NiO average crystallite size was 48 nm. The change of this ratio to reverse led to the dispersion decrease: average NiO crystallite size grew more than 200 nm (compare samples 1 and 2, Table 1). However, the content of fully reduced nickel Ni⁰ impurities did not exceed 3 wt% in all cases.

Table 1. Syntheses conditions and XRD data for NiO и MoO₃ powders

	Metal source	Sol stabilizer	Sol stabilize r/ metal source, mol	XRD data		
				Phase composition	wt%	Crystallite size, nm
1	Ni(Ac) ₂ ·4H ₂ O	HMTA	2/1	NiO	99	48
				Ni	1	-
2	Ni(Ac) ₂ ·4H ₂ O	HMTA	1/3	NiO	97	>200
				Ni	3	-
3	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	HMTA	2/1	MoO ₃	100	82
4*	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	HMTA	2/1	MoO ₃	100	125
5**	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	HMTA	2/1	MoO ₃	100	112
6	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	DMOA	1/1	MoO ₃	100	133
7	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	DMOA	2/1	MoO ₃	100	84
8	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	DMOA	3/1	MoO ₃	100	103
9	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	DMOA	4/1	MoO ₃	100	106
10***	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	DMOA	2/1	MoO ₃	100	167

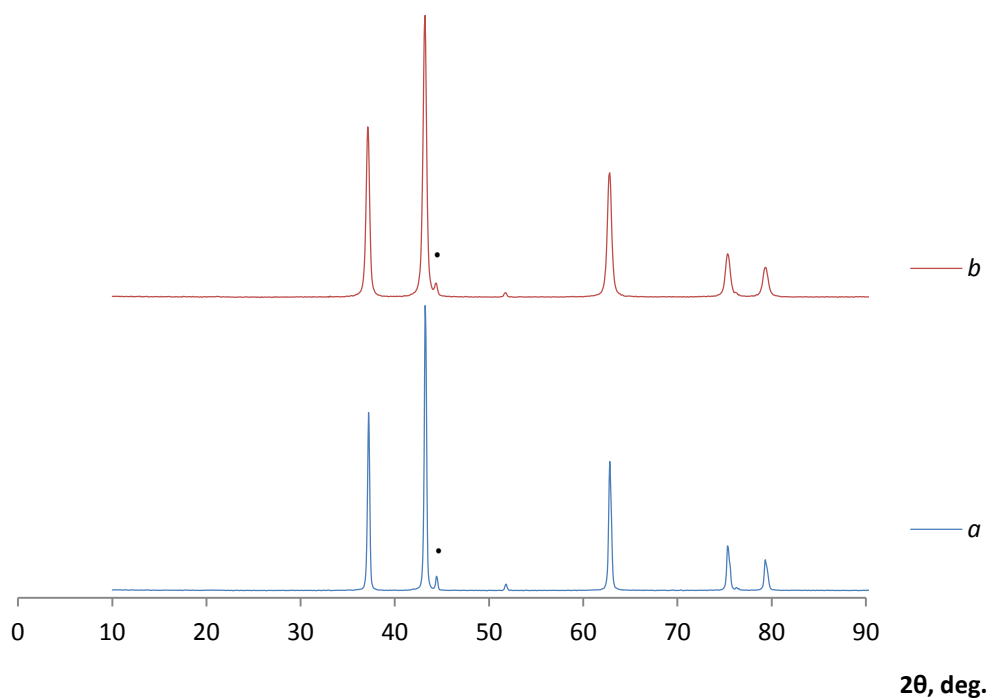
*AcAc/Mo=3/1, mol

**AcAc/Mo=6/1, mol

***7 days aged sol was used

When HMTA was used and the HMTA/Mo molar ratio value was equal to 2, the average crystallite size of MoO₃ was 82 nm, according to XRD data (sample 3, Table 1). Microphotos in Fig. 2 show that the MoO₃ powder (sample 3, Table 1) consisted of the rods with a side of cross-section of 20-50 nm and a length of 1 μm and more (indicated by white circles) as well as the agglomerates larger than 200 nm. At the same time, the highly crystallinity of MoO₃ powder was confirmed by XRD data (Fig. 3, X-ray diffraction pattern *a*), which suggests that the MoO₃ had a 100% orthorhombic syngony oP16 (JCPDS card 05-0508).

When AcAc was added to the reaction mixture at AcAc/Mo mole ratio value was equal to 3/1 or 6/1, MoO₃ crystallite agglomeration occurred reaching to 110-130 nm (samples 4 and 5, Table 1). Moreover, the amount of added AcAc had no significant effect on the powder dispersion, however, the impact on the powder texture was found. This is evidenced by the differences in the intensity ratio of reflections in the range of 23-28 degrees (X-ray diffraction patterns *b* and *c*, Fig. 3).



•Ni⁰

Fig. 1 XRD patterns of NiO powders: *a* – sample 1 and *b* – sample 2 (Table 1).

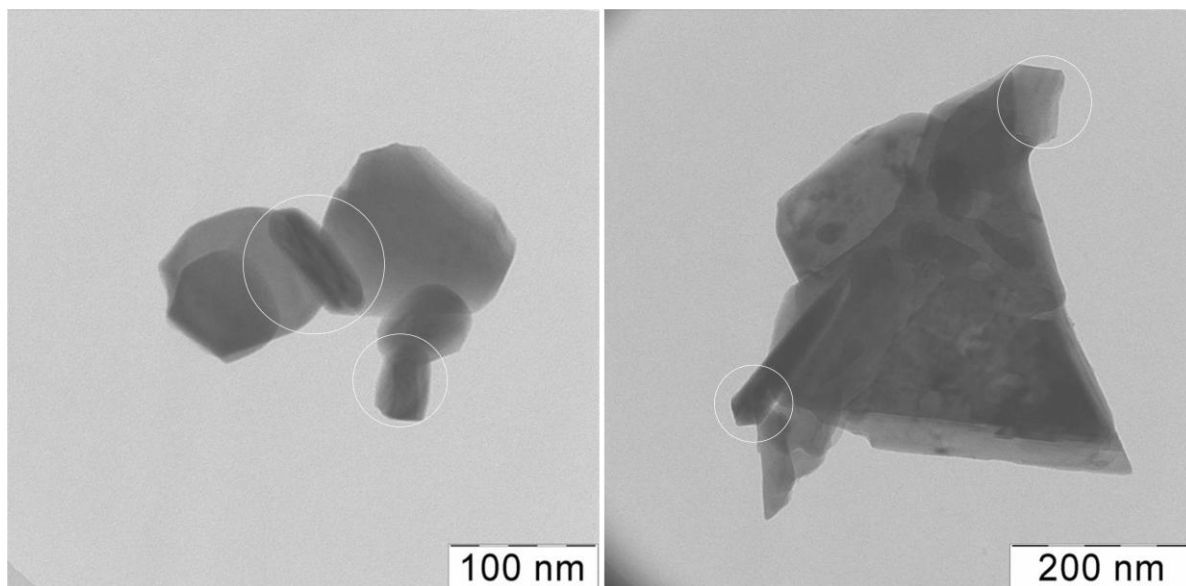


Fig. 2 TEM images of MoO₃ powder (sample 3, Table 1).
The nanorods are indicated by white circles.

Substitution of HMTA on DMOA (samples 6-10, Table 1) at the same molar ratio produces no significant change the dispersion (to compare samples 3 and 7, Table 1), but the texture changes also have been observed as can be seen from a comparison region of 23-28 degrees (to compare X-ray diffraction patterns *a* and *d*, Fig. 3). It is interesting that in the case of DMOA a change of molar ratio value 2/1 to increase or decrease led to enlargement of MoO₃ crystallite size to 100-140 nm (samples 6, 8 and 9, Table 1).

All described above powders were obtained by calcination of as-prepared sols. Also it was shown that the use of 7 days aged sols led to the formation of the coarse MoO₃ powder during the calcination at 500°C for 1h (Fig. 4). The TEM microphotos in Fig. 4 show the large blocks consisting of the rods with a length greater than 300 nm and a side of cross-section about 100 nm (to compare with Fig. 2). At the same time in accordance with XRD data, the average crystallite size of MoO₃ powder increased by almost 2 times when the aged sol was used (to compare samples 7 and 10, Table 1). Apparently, ageing of a sol at room temperature during 7 days resulted in significant enlargement of the colloid particles. So, subsequent calcination of aged sol at 500°C leads not only to the formation of the larger crystallites, but also to the association them to form the large-dimension blocks (Fig. 4).

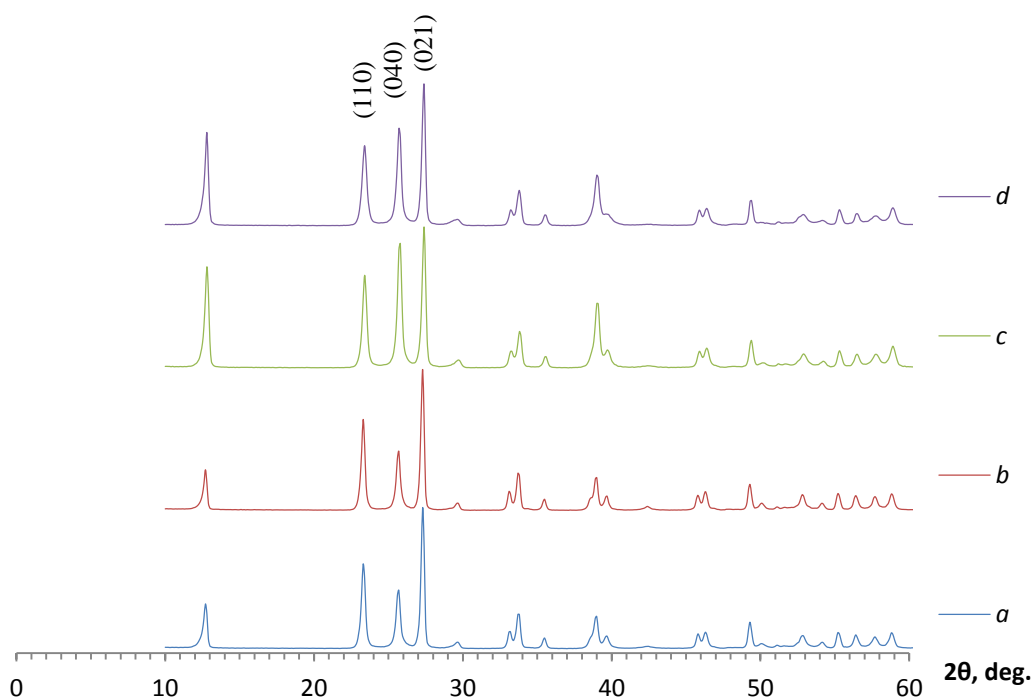


Fig. 3 XRD patterns of MoO₃ powders obtained: *a* – sample 3, *b* – sample 4, *c* – sample 5, *d* – sample 7 (Table 1)

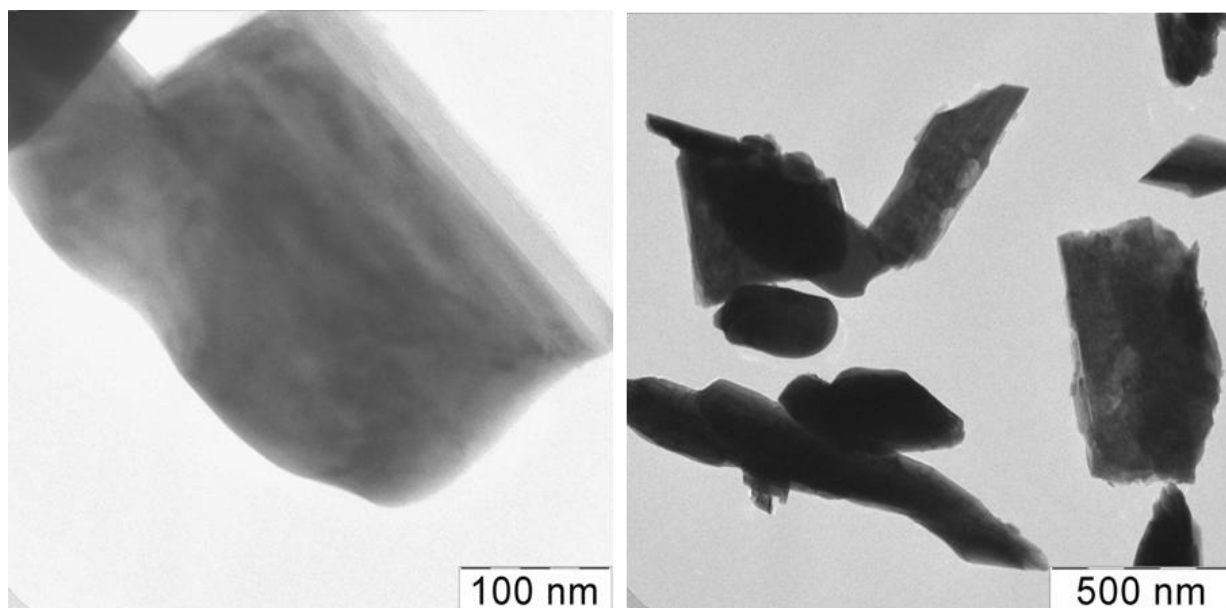


Fig. 4 TEM images of MoO₃ powder obtained from the aged sol (sample 10, Table 1).

3. CONCLUSIONS

Thus, ultradispersed and submicron NiO and MoO₃ powders with a particle size of 40 nm were synthesized by the modified sol-gel technique using of HMTA or DMOA and characterized by XRD and TEM. It has been shown that in depending on used sol stabilizer and molar ratio value stabilizer/metal it is possible to obtain the metal oxide powders with different morphology parameters and texture. It was shown that AcAc addition in the reaction mixture leads to particle size increasing. The proposed method allows control for the formation of sol structure at the molecular level and to obtain during their further calcination at 500°C NiO and MoO₃ ultradispersed powders with predetermined morphology and texture parameters. It is experimentally proved that the dispersion of metal oxide powders can be controlled accurate to 10-20 nm by developed way. The as-prepared sols need be used for the obtaining of ultradispersed MoO₃ powders. The developed laboratory approach to the synthesis of ultradispersed powders can be used to create a flexible technology to produce large quantities of ultradispersed powdery raw materials of wide purposes.

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