Proceeding Paper

The Self-Organization of Nanoparticles in Molybdenum Blue Dispersions in the Presence of Organic Reducing Agents [†]

Maria Myachina *, Natalia Gavrilova, Daria Harlamova and Victor Nazarov

Department of Colloid Chemistry, D. Mendeleev University of Chemical Technology of Russia, Miusskaya sq., 9, 125047 Moscow, Russia; ngavrilova@muctr.ru (N.G.); dvharlamova@gmail.com (D.H.); nazarov@muctr.ru (V.N.)

* Correspondence: mmyachina@muctr.ru

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Abstract: Molybdenum blue dispersions were synthesized by reducing an acidic molybdate solution with glucose, hydroquinone and ascorbic acid. The role of the H/Mo molar ratio in the process of formation for molybdenum particles was established. For each reducing agent, the conditions for the formation of aggregative stable dispersion of nanoclusters with the maximum concentration of particles were determined. The dispersed phase was represented by toroidal molybdenum oxide nanoclusters, which was confirmed by the results of UV–Vis, FTIR, XPS spectroscopy, DLS and TEM.

Keywords: molybdenum blue; self-assembly; polyoxometalates; molybdenum oxide; sol-gel method

1. Introduction

Molybdates in aqueous solutions can form a variety of structures. Of greatest interest are the self-assembling molybdate nanostructures, one of which is molybdenum blue [1–3]. Molybdenum blue structures are oxygen-containing compounds of molybdenum of variable composition in which molybdenum is in oxidation states +5 and +6.

Molybdenum–oxygen clusters represent a large class of polyoxometalates (POM). The modern chemistry of polyoxometalates is very extensive and includes clusters of various chemical compositions, sizes and shapes [4–6]. Usually, the disperse phase of polyoxometalates represents giant clusters in the order of 1–3 nm, which are formed as a result of self-organization from the original building units [7].

Polyoxometalates exhibit remarkable physicochemical properties, structural versality and highly reactivity. These systems can be used as homogeneous and heterogeneous catalysts for drug delivery and for the synthesis of hybrid materials [2,3,8,9].

Since the synthesis of clusters of polyoxomolybdates is a process of self-assembly, the attention of researchers has been focused on the targeted synthesis of nanoscale structures from various initial building blocks and the identification of its structure.

There are various methods of obtaining molybdenum blue, and the most common is the reduction of molybdates in an acid solution. An either organic or organic compound can be used as the reducing agent [2–5].

Most works in the area of molybdenum–oxygen clusters are related to the production of aqueous systems of molybdates, their functionalization or their crystalline precipitation. Water systems containing molybdenum oxide clusters are often considered within the framework of the chemistry of complex compounds but not as objects of colloid chemistry [8,9].

One of the reasons for this approach is that molybdenum oxide clusters can undergo dissociation to form true solutions. Despite this, in many works devoted to molybdenum–oxygen clusters, such characteristics of disperse systems as the sign of the electrokinetic potential and the hydrodynamic radius were determined [5,10–12]. On the other hand, the behavior of these systems under certain conditions, including aggregation in the presence of some electrolytes, allows us to attribute molybdenum blue to disperse systems [13].

In [14–16] we found that the use of organic reducing agents such as glucose, hydroquinone and ascorbic acid made it possible to obtain colloidal systems. The selection of conditions—the contents of reducing agent and acid—makes it possible to create a chemical stable and resistant to sedimentation systems.

A study of the processes leading to the formation of particles in stable colloidal systems would lead to a more complete understanding of the synthesis of molybdenum blue as a colloidal system. The goals of this work were to obtain stable dispersions of molybdenum blue using organic reducing agents and investigate the process of self-assembly.

2. Materials and Methods

Dispersions of molybdenum blue nanoparticles were synthesized using the reagents ammonium heptamolybdate $((NH_4)_6Mo_7O_{24} \cdot 4H_2O$, reagent grade), crystalline glucose $(C_6H_{12}O_6,)$, hydroquinone $(C_6H_6O_2)$, ascorbic acid $(C_6H_8O_2)$ and hydrochloric acid (HCl). All reagents were purchased by CT Lantan (Moscow, Russia) and were of reagent grade.

A HI-8314 pH/mV meter (Hanna Instruments, Vöhringen, Germany) with a combined electrode was used for measuring pH.

UV–Vis spectra were obtained by scanning spectrophotometer Leki SS2110 UV (MEDIORA OY, Helsinki, Finland) in quartz cells.

The hydrodynamic radii were calculated from the results of dynamic light scattering using a Photocor Compact-Z analyzer (OOO Photocor, Moscow, Russia). The signal was accumulated during 30 min (laser power of 20 mW and laser wavelength of 658 nm).

The sizes and shapes of the particles were determined by LEO 912AM Omega Carl Zeiss transmission electron microscope.

IR spectra were recorded by Nicolet 380 IR Fourier spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) in KBr pellets (range 350 to 4000 cm^{-1}).

3. Results

3.1. Properties of Molybdenum Blue Properties

According to the literature, the nanoclusters of molybdenum blue are formed as a result of the self-organization (self-assembly) of molybdenum complexes. For the process of self-organization, the presence of certain complexes of Mo^{5+} and Mo^{6+} is required. For the obtaining of Mo^{5+} complexes, it is necessary to carry out a partial reduction of the molybdate ions in solutions. In this case, the self-assembly process is possible only at a certain dispersion pH (pH < 2). The polycondensation of molybdate ions is observed at this pH with further organization into giant molybdenum oxide clusters (nanoparticles of molybdenum blue).

For the synthesis of dispersions of molybdenum oxide nanoclusters (hereinafter referred to as molybdenum blue), the optimal molar ratios of the reagents should be determined: reducing agent/Mo (R/Mo); acid/Mo (H/Mo). Additionally, it is necessary to establish the pH value at which molybdenum blue hydrosols with long-lasting stability are formed. In this work, glucose, hydroquinone and ascorbic acid were used as the reducing agents.

Earlier [14–16], we found that the aggregative stable molybdenum blue dispersions are formed at a certain R/Mo ratio, while for each reducing agent there is an optimal ratio. For example, when using glucose, the required ratio of R/Mo is 7/1; for hydroquinone, 4/1; and 1/1 for ascorbic acid. Under these conditions the maximum number of molybdenum

oxide clusters is formed. These parameters were used in this work for the synthesis of stable dispersions.

The interactions of ammonium heptamolybdate with reducing agents in the above ratios led to the formation of dispersions of molybdenum blue with chemical and aggregative stability. The fact of their formation was confirmed by the appearance of an intense blue color and a change in the optical spectrum of electronic absorption. In Figure 1 UV–Vis spectra are given for dispersions synthesized using glucose, hydroquinone and ascorbic acid.
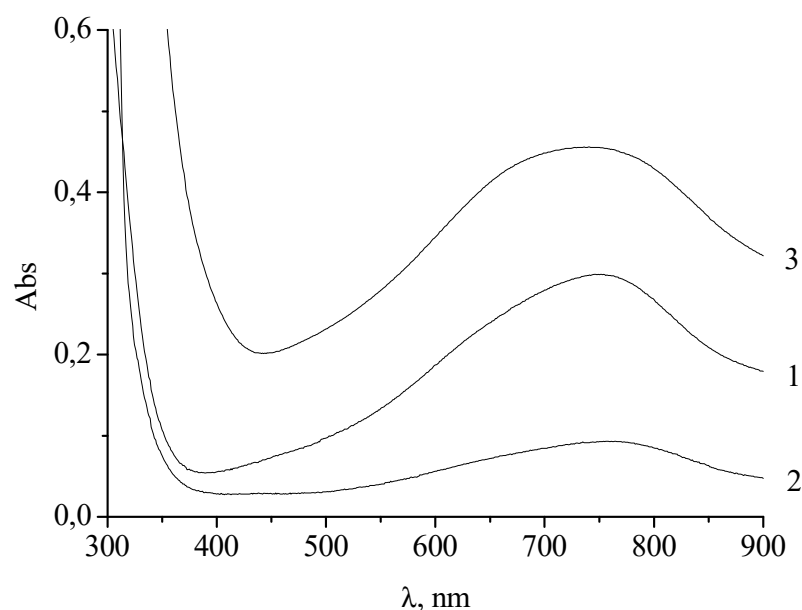

Figure 1. The UV–Vis spectrum of dispersion of molybdenum oxide clusters synthesized using various reducing agents: glucose (1), hydroquinone (2), ascorbic acid (3).

According to the literature, the self-assembly of molybdenum blue nanoparticles proceeds over time [17]. To establish the effect of the H/Mo molar ratio on the rate of the self-assembly of molybdenum blue particles, a series of samples were prepared with a constant R/Mo ratio and different acid contents. The absorbance at the wavelength corresponding to the absorption maximum (λ = 745 nm) was used as a controlled parameter. The time plots of the absorbance for various values of H/Mo are shown in Figure 2.

The formation of molybdenum blue particles occurred on the first day after mixing the reagents. These results were also confirmed by dynamic light scattering data (see Figure 3).

Over time, for systems prepared with glucose and hydroquinone, an increase in the optical density, and hence the number of particles of molybdenum blue, was observed. The rate of formation depends on the molar ratio of H/Mo. There is a range of values in which the rate of formation is higher. For glucose this range was 0.5–0.8 with a maximum of particles of molybdenum blue being observed at H/Mo = 0.5. At values of H/Mo less than 0.5, molybdenum blue formation did not occur. For hydroquinone, this range was 1.0–5.0, and the maximum was observed at H/Mo = 1.5.

Molybdenum blues synthesized under these conditions retained their aggregative stability for a long time.
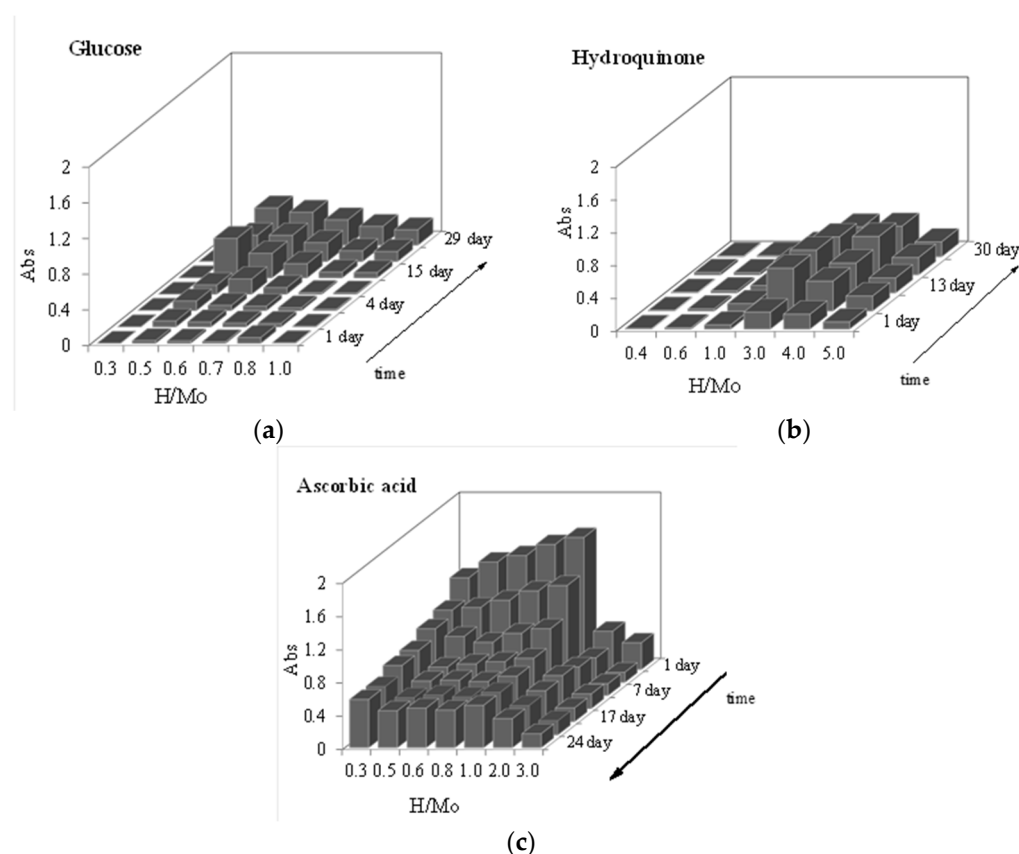
Figure 2. The dependence of the optical density of samples of molybdenum blue on time and molar ratio H/Mo, synthesized by using glucose (R/Mo = 7/1) (**a**), hydroquinone (R/Mo = 4/1) (**b**) and ascorbic acid (R/Mo = 1/1) (**c**).

A different situation was observed in systems synthesized with ascorbic acid. Particle formation occurred on the first day for the entire range H/ Mo ratios. The largest number of clusters was formed when H/Mo = 1. However, over time the optical density decreased to a certain value, whereas the character of the spectrum did not change (the absorption maximum was 745 nm). Such behavior can be explained by the reaction taking a long time to establish an equilibrium between the nanoclusters formed and the building blocks.

Based on DLS measurement, the particle-size distribution in the molybdenum blue dispersion was established. The predominant radius of the particles (R_h = 1.5 nm) obtained from DLS did not change during the study period.

TEM images were used to determine the particle size of the molybdenum blue. Figure 3 shows TEM images of molybdenum blue particles synthesized using glucose. The dispersed phase of the molybdenum blue is represented by particles with diameters not exceeding 5 nm.

The image of the particles does not have high contrast; the electron diffraction patterns lack clear reflections, which indicates a low degree of crystallization of the particles. Regardless of the reducing agent used, molybdenum blue nanoparticles were close in shape to spheres; the presence of toroidal particles is difficult to establish at this resolution.

According to the particle size distribution, the particles of molybdenum blue have a narrow size distribution: the predominant diameter is about 3 nm.
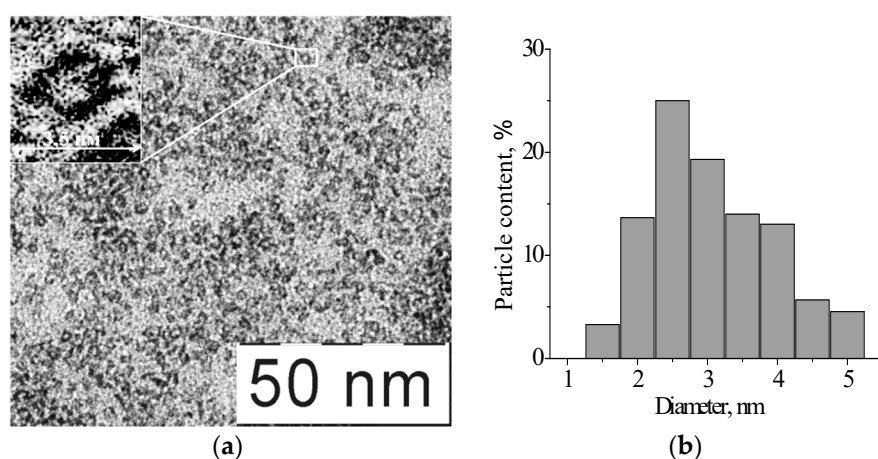
Figure 3. TEM images of particles (**a**) and the particle size distribution (**b**) of molybdenum blue synthesized by using glucose.

3.2. Characterization of Nanoparticles

UV–Vis and FTIR spectroscopy were used to characterize molybdenum blue particles and their structure [18,19]. The UV–Vis spectra of molybdenum blue particles synthesized using various reducing agents are presented in Figure 4.
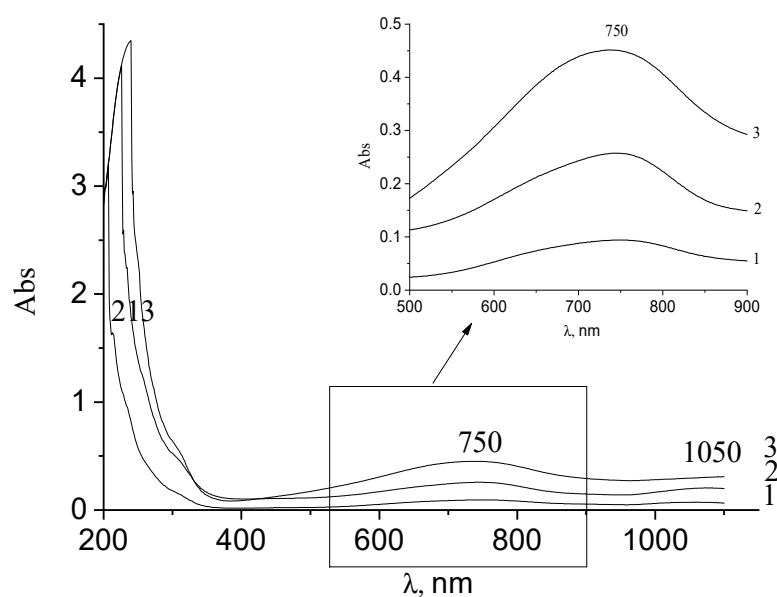
Figure 4. The electronic absorption spectra of molybdenum oxide clusters isolated from dispersions synthesized using various reducing agents: glucose (1), hydroquinone (2), ascorbic acid (3).

The electronic absorption spectra contain wide absorption bands around 213, 750 and 1050 nm. The observed bands, according to the literature [18], are typical for the molybdenum blue dispersions which contain tori nanoclusters (Mo_{138}, Mo_{150}, Mo_{154}, Mo_{176}).

The cluster structure can be determined using IR spectroscopy. The number of absorption bands is typical for Mo_{154-x} toroidal nanoclusters [18,19].

XPS spectroscopy was chosen for analysis of reduced molybdenum Mo^V in the analyzed samples. XPS spectroscopy confirmed the presence of reduced molybdenum Mo^{5+} in the structure of molybdenum oxide nanoclusters. The percentage of reduced molybdenum Mo^{5+} synthesized using glucose or hydroquinone was about 12%; with the use of

ascorbic acid—29%. These values are in a good agreement with the literature data on the reduction degree of molybdenum in tori-like nanoclusters.

4. Discussion

Methods for the synthesis of aggregative stable molybdenum blue hydrosols in the presence of organic reducing agents (glucose, hydroquinone and ascorbic acid) have been developed.

The role of the H/Mo molar ratio in the formation of molybdenum particles was established. For each reducing agent, the conditions (molar ratios of H/Mo, pH value) for the formation of aggregative stable dispersions of nanoclusters with the maximum concentration of particles were determined.

Based on the UV–Vis, FTIR, XPS spectroscopy, DLS and TEM data, it was shown that the particles of the dispersed phase are represented by a nanocluster of a toroidal shape.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/IOCN2020-07895/s1.

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