

Micelle Directed Synthesis of Polyoxometalate Nanoparticles and Their Improved Catalytic Activity for the Aerobic Oxidation of Sulfides

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Nanoparticle-based materials are building blocks in many areas of nanotechnology, being utilized in applications such as sensors, information storage, and catalysis.¹ These applications require the ability to assemble molecules into a defined shape and size so that the unique nanoscale properties can be effectively exploited. Approaches for controlling nanoscale structures that are being used for catalytic applications include microemulsion-mediated nanoparticle synthesis² and the use of self-assembled polymer or surfactant microstructures as templates for nanostructured materials.³ These methods, and others, are widely applied for the assembly of inorganic nanoparticles, such as metal particles, metal oxide particles, metal particles coated with silica, and silica nanospheres.⁴ Polyoxometalates are usually polyanions of discrete structure and have been extensively investigated as acid and oxidation catalysts.⁵ An interesting challenge is to assemble such polyoxometalates, forming defined structures that may have interesting, novel properties.⁶ In this research, we wished to show that the control of the size, shape, and structure of polyoxometalate nanoparticles is interesting in itself and might be important because of a possible correlation between these parameters and their catalytic properties.

Since it is known that polyoxometalates of the Keggin-type with cesium counteranions are insoluble,⁷ we hypothesized that an appropriate surfactant, cesium dodecyl sulfate (CDS), could be used to prepare micelles in water upon which Keggin-type polyoxometalates (POM), such as $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, could be deposited and precipitated, yielding spherical polyoxometalate nanoparticles with a surfactant core and polyoxometalate surface (Scheme 1).

Accordingly, cesium dodecyl sulfate was prepared from sodium dodecyl sulfate (SDS) by dissolving 1 g of SDS in a minimum amount of water (~2 mL); the solution was acidified to pH ~ 0 with 5% HCl (a few drops), and then a saturated aqueous solution containing 750 mg of Cs_2CO_3 was added. The CDS precipitated from the solution and was collected and dried. The micelle directed synthesis of the polyoxometalate nanoparticles was carried out by addition of 200 μL of a 0.01 M solution of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and 800 μL of a 0.1 M solution of poly(vinylpyrrolidone) (PVP) to 500 μL of 0.01 M CDS. The molar ratio of CDS: $\text{H}_3\text{PMo}_{12}\text{O}_{40}$:PVP was 2.5:1:40. The PVP enabled the formation of single micelle sized particles by preventing particle aggregation during the precipitation of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ onto the micelle surface. After the nanoparticle formation (5 min in a sonicator bath), PVP was extracted from the micellar solution with chloroform (3 \times 2 mL).

The polyoxometalate nanoparticles were directly observed by cryo-transmission electron microscopy, as shown in Figure 1. From the image, mostly single 10–13 nm particles may be observed. It is noticeable that the particles have relatively low contrast because of the large abundance of carbon and oxygen atoms in the nanoparticle. Importantly, the particle size is roughly consistent with

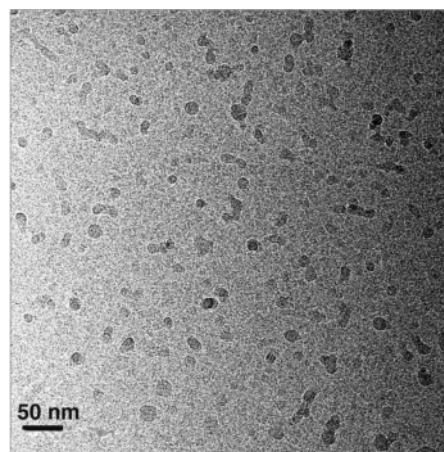
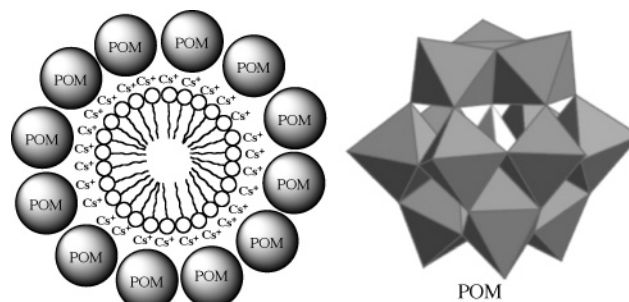


Figure 1. Cryo-TEM image of micelle directed polyoxometalate nanoparticles.

Scheme 1. Idealized Cartoon of the Cross Section of a CDS Micelle–POM Particle



the expected cross section diameter of such particles as may be computed (8 nm) from the idealized picture presented in Scheme 1. Some aggregation of particles may be observed in the solution. In samples where the stabilizing polymer was not removed, no aggregation was observed. Upon deposition of the solution onto surfaces, the particles tend to aggregate (Figure S1).

Beyond the correlation of the observed particle size with the idealized model, we were also interested in verifying the consistency of the idealized model with the distribution of the elements in the nanoparticles. A high-resolution transmission electron micrograph (HRTEM) of the polyoxometalate nanoparticles together with a mapping of the distribution of the oxygen, molybdenum, and cesium atoms using electron energy loss spectrometry (EELS) is presented in Figure 2. One may observe in the HRTEM particles of the size seen in the cryo-TEM image (see middle of image) and larger particles of up to 50 nm that are apparently a result of aggregation of smaller particles when the sample is dried under high vacuum needed for the HRTEM measurement. In all cases, the mapping of the elements shows that molybdenum, oxygen, and cesium all

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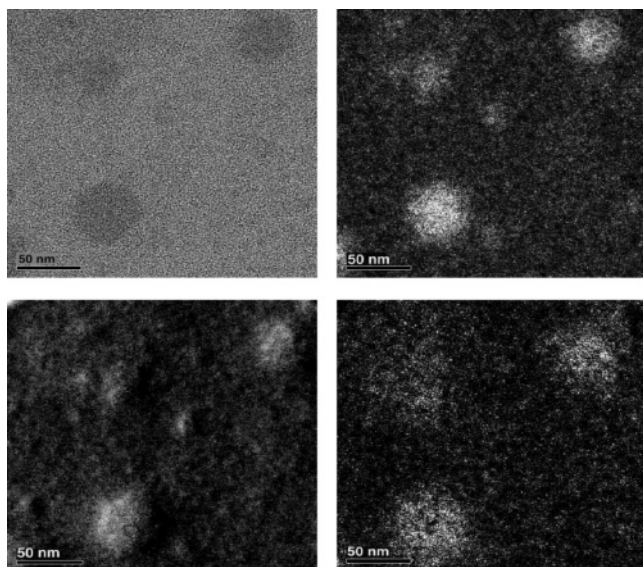


Figure 2. HRTEM image of CDS–POM nanoparticles. Top left: zero loss image. Top right: oxygen mapping image. Bottom left: molybdenum mapping image. Bottom right: cesium mapping image.

Table 1. Aerobic Oxidation of Sulfides Catalyzed by CDS/ $PV_2Mo_{10}O_{40}$ /PPG on Hydrophilic Silica^a

substrate	conversion, mol %	TON ^b	ratio SO/SO ₂
thioanisole	91	81	22/78
dibutylsulfide	100	89	26/74
diphenylsulfide	82	53	70/30
tetrahydrothiophene	95	95	0/100

^a Reaction conditions: 0.1 mmol sulfide, 2 μ mol $PV_2Mo_{10}O_{40}^{5-}$ as 10% CDS/ $PV_2Mo_{10}O_{40}$ /PPG on hydrophilic silica (CDS:H₃PMo₁₂O₄₀:PVP = 2.5:1:40), 0.5 mL of toluene, 2 atm O₂, 110 °C, 16 h (see SI for full details).

^b TON was computed assuming that the catalyst is involved in both sulfide to sulfoxide and sulfoxide to sulfone oxidation.

coincide within the nanoparticles, supporting our premise that we have indeed succeeded in synthesizing polyoxometalate nanoparticles using a micelle template. Note that, in general, the mapping for cesium is less effective and is hardly visible in the smallest particle in the center of the image. This is most likely due to the lower amount of cesium versus molybdenum and oxygen in the sample.

After having succeeded in preparing the desired micelle directed polyoxometalate nanoparticles, we wished to determine if the clustered assembly of polyoxometalates as prepared above showed superior catalytic activity for a typical heterogeneous reaction compared to a nonclustered polyoxometalate. For this purpose, we chose the relatively well-studied aerobic oxidation of sulfides to sulfoxides and sulfones catalyzed by $[PV_2Mo_{10}O_{40}]^{5-}$ as catalyst.⁸ Similar to the procedure described above, 200 μ L of a 0.01 M solution of H₃PV₂Mo₁₀O₄₀ and 800 μ L of a 0.1 M solution of polypropylene glycol (PPG, M_w = 750) were added to 500 μ L of 0.01 M CDS (CDS:H₃PV₂Mo₁₀O₄₀:PPG was 2.5:1:40). The micelle directed $[PV_2Mo_{10}O_{40}]^{5-}$ assemblies as well as H₃PV₂Mo₁₀O₄₀ alone for comparative control experiments were supported on hydrophilic silica (AEROSIL 380) at 10 wt % loading.⁹ Transmission electron micrographs of the CDS/ $PV_2Mo_{10}O_{40}$ assemblies in solution and supported on the hydrophilic silica were essentially the same as those of CDS/PMo₁₂O₄₀ described above. The results of the aerobic oxidation of several sulfides are presented in Table 1. The results demonstrate that the micelle directed nanoparticles of $[PV_2Mo_{10}O_{40}]^{5-}$ showed good catalytic activity for the oxidation of a series of sulfides, whereas H₃PV₂Mo₁₀O₄₀ on hydrophilic silica showed no

catalytic activity. Addition of PPG-750 to the control reaction (H₃-PV₂Mo₁₀O₄₀ on hydrophilic silica) did result in some catalytic activity, for example, 24 turnovers in the oxidation of dibutylsulfide compared to 89 turnovers for the CDS/ $PV_2Mo_{10}O_{40}$ /PPG. There is, however, a caveat in this control experiment because the addition of PPG to H₃PV₂Mo₁₀O₄₀ on hydrophilic silica may complex the polyoxometalate since ethers are well-known to complex acidic polyoxometalates, whereas no such complexation occurs for insoluble cesium salts of polyoxometalates as are present in the reactions catalyzed by CDS/ $PV_2Mo_{10}O_{40}$ /PPG on hydrophilic silica.

Micelle directed polyoxometalate nanoparticles have been synthesized and characterized by cryo-TEM and HRTEM techniques including the use of EELS imaging to map the distribution of the elements. In an aerobic oxidation of sulfides, the advantageous catalytic activity of the clustered polyoxometalate assemblies versus nonclustered assemblies was demonstrated.

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Supporting Information Available: Details of the experimental methods and additional transmission electron micrographs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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