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# Synthesis and Characterization of Neodymium nanoparticles

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## Abstract

The study of nanoparticles is currently an area of great interest because they exhibit new and improved properties compared to their bulk material. These properties make them very valuable in numerous applications in areas such as optics, biomedicine, and electronics. Our laboratory has been focused on the synthesis and characterization of neodymium nanoparticles. The neodymium clusters are produced by the reverse micelle method, which consists of creating small spherical cages that are formed around the reactants when the surfactant is combined with a polar and non-polar solvent. A solution containing the reducing agent is then added to produce the desired neodymium nanoparticles. The small cages protectively confine the reduced reactant and prevent it from combining into larger size. Vacuum filtration is used to separate our products and excess surfactant. Three reverse micelle systems are under investigation for their ability to efficiently form small and stable reverse micelles: hexane/methanol/AOT, heptane/methanol/AOT, and heptane/methanol/DDAB. Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) and light microscope analysis showed that the most effective micelle system was heptane/methanol/AOT because its resulting neodymium particles had small diameters and were more uniform in shape. The size of the synthesized particles using this arrangement was in the range of 1-10 micrometers. The system hexane/methanol/AOT produced uniform neodymium particles of 10-45micrometers in diameter while the remaining system did not show any formation of uniform particles.

#### Keywords: Reverse Micelle, Neodymium, Nanoparticles.

# 1. Introduction

In the last decade, the demand of nanoparticles for research has increased enormously because they offer countless beneficial applications to areas such as optics, biomedicine, and electronics<sup>1</sup>. Nanoparticles, whose size vary between 1 to 100 nm, exhibit new and enhanced physical properties compared to their bulk materials. For instance, particles at the nanoscale exhibit larger surface-area-to-volume ratios, changes in color, melting temperature, magnetism, etc<sup>2</sup>. These unique properties make them very valuable and versatile in the scientific community. For these reasons, a great amount of research has been dedicated to their synthesis. Some applications of nanoparticles include catalysis, magnetic resonance imaging (MRI) contrast agents, biosensors, and ultra-high density magnetic data storage<sup>3</sup>.

There are many well-known methods for the creation of nanoscale materials, for example: solution phase reduction of a metal salt, decomposition of metal carbonyl, and reverse micelle reduction<sup>4</sup>. This research in particular focuses in the synthesis of neodymium nanoparticles using the reverse micelle technique. Reverse micelles are spherical structures that are formed by the combination of surfactant, polar solvent, and non-polar solvent<sup>5</sup>. The desired nanoparticles can be formed and controlled within these spherical cages which have diameters that range from nano- to micro-meters. Figure 1 shows the schematic of a reverse micelle and the structure of the surfactant's molecule. The hydrophilic heads of the surfactant molecule are oriented towards the small polar solvent



Figure 1. (a) A reverse micelle is illustrated. It has surfactant molecules forming a spherical cage around the reactants [RE] and polar solvent. The entire reverse micelle arrangement is suspended in a non-polar solvent. (b) A surfactant molecule structure is shown. It has a hydrophilic head that is attracted to the polar solvent and hydrophobic tails which are attracted to non-polar solvents.

pools and the hydrophobic tails point towards the non-polar organic phase creating a specific micro reactor system for the synthesis of nanoparticles. The shape and size of the spherical aggregates depend greatly on the molecular geometry of its surfactant and the molarity ratio of surfactant to polar solvent  $(W_o)^6$ .

There are three types of surfactants: anionic, cationic and non-ionic. The head groups of the surfactants are negative for anionic, positive for cationic, and uncharged for non-ionic<sup>7</sup>. When the surfactant, polar, and non-polar solvents are combined above a minimum ratio (i.e., critical micelle concentration), the reverse micelle spheres start to form. This means that any additional surfactant added after the system reaches the critical micelle concentration (CMC) goes directly to the formation of the micelles. The CMC value also varies among the different types of surfactant; in general it follows the inequality: non-ionic CMC < anionic CMC < cationic CMC<sup>8</sup>. These characteristic may improve or decrease the efficiency of the micelle system that is used to grow nanoparticles.

# 2. Methodology

All glassware was cleaned with soap, deionized water, and wiped with acetone right before the experiment in order to avoid any kind of contamination. The following chemicals were purchased from Fisher Scientific and used as received: dioctyl sodium sulfosuccinate (AOT), methanol, heptane, and hexane. Neodymium nitrate hexahydrate, didodecyldimethylammonium bromide (DDAB), and sodium borohydride were purchased from Sigma Aldrich. All chemicals were carefully weighed in an analytical balance using plastic trays, and were stored in beakers covered with parafilm for later use. Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was crushed into a fine powder and baked at 65°C for 36 hours to remove the hydrate and prevent any unwanted addition of water to the reactions.

Three reverse micelle systems with the following chemical combinations were studied: hexane/methanol/AOT, heptane/methanol/DDAB. Because our equipment for imaging and elemental analysis of our samples is limited, we decided to use a large  $W_o$  value in order to synthesize sub-micron size particles which are easier to detect by a simple light microscope. In this way, we can later modify the  $W_o$  value of the most efficient reverse micelle in order to obtain the desired Nd nano-size particles.

A 0.3 M reverse micelle solution was prepared by the addition of 20  $\mu$ l of methanol, 10 ml of non-polar solvent (heptane or hexane), and the appropriate amount of surfactant to maintain a W<sub>o</sub> value of 2.6 (1.337 g of AOT or 1.387 g of DDAB). Heat was added only to the heptane/DDAB solution since this surfactant is not very soluble in heptane. After the surfactant was dissolved, 45.79 mg of Nd(NO<sub>3</sub>)<sub>3</sub> was added to the reverse micelle solution. This solution was then sonicated until Nd(NO<sub>3</sub>)<sub>3</sub> was completely dissolved; it took 4 hours in the case of hexane/AOT, 3 hours for heptane/DDAB, and 25 minutes when using heptane/methanol/AOT.

A 1.5 M reduction solution was prepared with 170 mg of  $NaBH_4$  and 3 ml of methanol. Only 300 µl of this solution was added to the reverse micelle solution to keep the  $W_0$  value constant. The reaction solution was sonicated again for about 15 minutes for each system to ensure the reaction between the reducing agent and the reactant. A white precipitant was formed only in the hexane/AOT and heptane/AOT arrangement but it was

dissolved after the 15 minute sonication. The white precipitant, which is one of the byproducts in the reaction, was confirmed to be NaNO<sub>3</sub> through powder X-ray diffraction. To reproduce and collect this white powder, a bench test was performed by directly mixing  $Nd(NO_3)_3$  and  $NaBH_4$  in heptane.

The next step in our experiment was the filtration of the sample solution which allowed us to eliminate some byproducts and excess surfactant from the Nd particles. Figure 2 shows the teflon vacuum filtration system that we designed and built for our nanoparticle synthesis. A Nuclepore membrane with a pore size of 8  $\mu$ m was used for the filtration of each growth.



Figure 2. (a) The vacuum filtration system consists of four main parts: a teflon filter holder which was hand made in the laboratory, a rubber stopper that seals the vacuum, a vacuum flask, and a hose which is connected to a pump. (b) The top view of the filter holder is depicted on the right.

For each experiment we stored two samples in dram vials, one containing the unfiltered solution and the other with the filtrand solution. Glass slides were also prepared for each sample in order to examine them through a Leica DM4000 light microscope. This initial microscopic examination is used to determine if the samples have clusters or spherical formations before we perform any additional spectroscopy analyses.

# 3. Results and Discussion

Figure 3 shows the images from light microscope analysis of specimens for each growth. In Figure 3(a) the hexane/methanol/AOT system displays spherical particles of uniform shape. The problem with this growth is that the micelles regrouped after filtration, forming structures with diameters between 20 and 45  $\mu$ m. In addition, Nd(NO<sub>3</sub>)<sub>3</sub> was very difficult to dissolve in the hexane/methanol/AOT solution; it took 4 hours to dissolve the Nd salt. During these 4 hours the polar and non-polar solvents started to evaporate and it became difficult to determine the exact amount of solvents evaporated. Because of these complications, we decided to discard this system.



Figure 3. Three reverse micelle systems: (a) Hexane and AOT reverse micelles have regrouped after filtration producing micelles with large diameters, 20-45 μm. (b) The heptane and DDAB system did not yield spherical clusters. The observed flake structures are the DDAB surfactant that regrouped after filtration. (c) and (d) Heptane and AOT systems show smaller particle with diameters less than 5 μm in diameter.

Figure 3(b) shows that the heptane/methanol/DDAB system produced flaky formations that were evenly distributed across the sample. This chemical arrangement did not exhibit any spherical clusters; instead it produced string-like structures which correspond to the shape of the elongated surfactant DDAB. The large size of the structures is due to the regrouping of the surfactant after filtration. We also added heat to the arrangement in order to dissolve DDAB in heptane, which could have affected the reverse micelle formation since their structures are also sensitive to temperature. These complications made us also discard this arrangement. Lastly, Figure 3(c) and (d) reveal particles of uniform shape and diameters of 5 µm or less for the heptane/methanol/AOT system. We did not have any significant complications in the procedure of this synthesis. Since heptane/methanol/AOT was the most effective and least problematic system, we repeated the same procedure using this reverse micelle arrangement inside a PlasLabs 855AC glovebox with ultra-high purity nitrogen gas to prepare Nd clusters in an oxygen free environment. The change of environment setting did not add any difficulties to the experiment, so we decided to use these samples for further spectroscopy analyses.

A few drops of our heptane/methanol/AOT-Nd samples were deposited on carbon coated copper grids for scanning electron microscopy and energy dispersive x-ray spectroscopy. An Evex energy dispersive x-ray (EDX) spectrometer coupled to a Hitachi S-3500N scanning electron microscope (SEM) was used in order to characterize our samples. The SEM uses a high energy electron beam to scan the specimen in order to produce an image with higher resolution than a light microscope. When the electrons from the beam interact with the specimen, they produce secondary electrons, backscatter electrons and characteristic x-rays. Secondary electrons are generated when high energy electrons inelastically collide with the atom of a sample. This collision ionizes the atom by ejecting electrons from the inner shells of the atom. The emitted electrons are captured by a scintillator detector, which subsequently produces a high resolution surface image<sup>9</sup>. When high energy electrons interact with the inner shell orbitals, it creates vacancies in the inner shells. Outer-shell electrons fall to fill the inner shell vacancies, generating specific amounts of energies which are released as characteristic x-rays to construct and analyze the chemical composition of the sample.

EDX analysis of raw materials  $Nd(NO_3)_3$ · $GH_2O$  and AOT are shown in Figure 4 in order to be compared and examined with the results of the Neodymium-cluster specimens produced in various systems. For instance, we can observe that for  $Nd(NO_3)_3$ · $GH_2O$  the maximum peaks of oxygen to neodymium have an approximate ratio of 3:1, while the peaks of sulfur, sodium, and oxygen in the AOT analysis show a ratio of 2.1:1.26:1. With this information, we will be able to identify if the  $Nd(NO_3)_3$  in the nanoparticle growth was reduced to Nd.



Figure 4. (a) Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was examined using EDX spectroscopy to analyze the reaction. The largest peak-to-peak ratio of Nd and O is about 1:3 (b) EDX spectroscopy measurement of AOT is used as a reference to compare with the reaction solution. The peak-to-peak ratio of S to O is about 2:1.

Since the best reverse micelle clusters were synthesized using the heptane/methanol/AOT system, we focus on presenting the analysis of this system from now on. SEM analysis in Figure 5 shows that spherical structures of  $5 \,\mu$ m in diameter or less were produced. These formations were evenly distributed throughout the sample. However, by examining the SEM image we can tell that the sample still has too much byproducts and excess surfactants.



Figure 5: SEM image of a random point in the sample shows spherical formation of 5µm or less. This sample was formed by the heptane/AOT system.

The image in Figure 6(a) is a multipoint analysis of SEM/EDX taken at a higher magnification compared to Figure 5. In order to take a multipoint analysis, the SEM electron beam had to be directed to the same point for a longer period of time, which caused the charging of the sample and therefore the deterioration of the image. Some spherical formations seemed to have burst when the sample was charged. We tried to reduce this problem by cooling down our sample to -186°C and carbon coating the samples, but this did not make a significant difference.



Figure 6. (a) SEM analysis of heptane/methanol/AOT sample shows small clusters of 1 µm and less in diameter.(b) EDX analysis of point 4 shows that the maximum peaks of S, Na, O, and Nd are in the ratio of 9.6:2.4:1:4.(c) EDX analysis of point 5. The ratio of S, Na, O, and Nd is determined to be 3:1.28:1:0.86.

Point 4 in Figure 6(a) indicates the presence of neodymium in the sample because the EDX analysis, displayed in Figure 6(b), shows high intensity peaks of neodymium compared to the EDX analysis of the unreacted material Nd(NO<sub>3</sub>)<sub>3</sub> in Figure 4(a). The ratio of the maximum peaks of oxygen and neodymium is 1:4, which is different from the ratio of 3:1 shown in the raw material analysis. This confirms the reduction of the neodymium salt. The peaks of sulfur, sodium, and oxygen are expected since the raw AOT has these elements. However, the oxygen peak is quite small and the sulfur peak is much larger than expected. This might have resulted from the deformation or damage of the surfactant AOT due to the high-energy electron beam used for the multipoint analysis. The spherical structures in Figure 5 burst into numerous uneven formations shown in Figure 6(a); by comparing these two SEM images we see how much the sample deteriorated. The EDX at point 5, shown in Figure 6(c), exhibits the oxygen and neodymium maximum peak ratio 1:0.86, but the sulfur, sodium, and oxygen peak ratio is 3:1.28:1, which is close to the ratio of raw AOT. Therefore, it is still reasonable to consider that the neodymium reduction is complete.

## 3. Conclusion

In this research, the reverse micelle technique was used to synthesize neodymium submicron particles. Three reverse micelle systems were studied using different combinations of surfactants and non-polar solvents: heptane/methanol/AOT, hexane/methanol/AOT, and heptane/methanol/DDAB. The most stable system was heptane/methanol/AOT, which produced neodymium particles with less than 10 $\mu$ m in diameter. Scanning electron microscope and energy dispersive x-ray analysis showed the presence of spherical submicroscopic neodymium particles. EDX analysis showed that the levels of oxygen in our samples have been significantly reduced compared to our previous Gd reverse micelle synthesis results<sup>10</sup>. Now that we know which reverse micelle system synthesizes Nd submicron particles, future work is focused on reducing the W<sub>o</sub> value to yield neodymium particles with smaller diameters.

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#### 5. References

1. Shuming Nie, Yu Xing, Gloria J. Kim, and Jonathan W. Simons, "Nanotechnology Applications in Cancer," Annual Review of Biomedical Engineering, Vol. 9 (April 2007) 257-288

2. Bashar Issa, Ihab M. Obaidat, Borhan A. Albiss, and Yousef Haik, "Magnetic Nanoparticles: Surface Effects and Properties Related to Biomedical Applications," Int J Mol Sci. 14 (November 2013): 21266-21305

3. Joseph Govan and Yurii K. Gun'Ko, "Recent Advances in the Application of Magnetic Nanoparticles as a Support for Homogeneous Catalysts," Nanomaterial Journal (April 2014): 222-242.

4. Serge P. Gubin, "Magnetic Nanoparticles," (Germany: WILEY-VCH, 2009), 25-53.

5. S. Krishnakumar and P. Somasundaran, "Aggregation Behavior of Aerosol OT in Nonaqueous Solvents and Its Desorption – An ESR Study," Colloid and Interface Science Journal 162 (September 1993): 425-430.

7. Manisha Mishra, P. Muthuprasanna, K. Surya Prabha, P. Sobhita Rani, I. A. Sathish Babu, I. Sarath Chandiran, G. Arunachalam and S. Shalini, "Basics and Potential Applications of Surfactants – A Review," International Journal of PharmTech Research Vol1, No4, (December 2009): 1354-1365.

<sup>6.</sup> Ashok K. Ganguli, Sonalika Vaidya and Aparna Ganguly, "Design of anisotropic nanostructures using microemulsions," Indian Journal of Chemistry Vol. 51A (February 2012): 245-251.

8. Y. Vahidshad, H. Abdizadeh, M. Akbari Baseri and H. R. Baharvandi, "Size-controlled synthesis of CuO – ZrO2 nanoparticles prepared through reverse micelle method," Sol-Gel Science and Technology Journal 53 (February 2010): 263-271

9. Weiie Zhou, Robert Apkarian, Zhong Lin Wang and David Joy, "Scanning Microscopy for Nanotechnology," (New York: Springer New York, 2007) pp1-40

10. Carmin J. Liang, Dulce G. Romero, and Jossi J. Amaral. "Synthesis and Characterization of Rare-Earth Gadolinium Nanoparticles," Proceedings of National Conference on Undergraduate Resear (April 2011): 1-7.