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Surfactant effects on the particle size of iron (III) oxides formed by sol–gel synthesis

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ABSTRACT

In this work, we probed the effects of a common surfactant, sodium dodecylbenzene sulfonate (NaDDBS), on the particle size of iron (III) oxides formed via a modified sol–gel synthesis. The goal was to create tunable nanosized particles via a method that combines the efficiency and advantages of the sol–gel process, but inhibits the formation of a gel. Two different metal salt precursors were used, ferric nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$, and ferric chlorate hexahydrate, $FeCl_3 \cdot 6H_2O$. The particle size of the dried gel was 4.5 nm for $Fe(NO_3)_3 \cdot 9H_2O$ and 3.6 nm for $FeCl_3 \cdot 6H_2O$. In the presence of the surfactant $FeCl_3 \cdot 6H_2O$ formed a gel and $Fe(NO_3)_3 \cdot 9H_2O$ was unable to gel, but the new particle sizes were 4.9 nm and 3.2 nm, respectively. The addition of the surfactant in the later stages of the process afforded the stabilization of independent nanoparticles of the same size as those obtained in the systems that gelled.

1. Introduction

The design, development, manufacturing and utilization of nanomaterials have become very broad and vigorously growing fields of research in recent years [1–17]. Nanomaterials represent a new class of materials that possess distinctive physical and chemical properties that differ substantially from their micron-size and bulk counterparts [3–5,7,8,10,12–19]. In order to harvest and translate the fascinating properties of materials at the nanoscale size domain into viable, affordable new technologies, it is imperative that new, facile synthesis and manufacturing methods could be developed in order to create the fundamental building blocks of the nanomaterials and their subsequent assembly into useful devices. These new methods should afford a high degree of reproducibility in terms of nanomaterial size, structure and morphology and also allow process scale-up without adverse effects on the quality of the products [17,20–22].

Of the multitude materials of interest, iron oxide nanoparticles offer a potential compatibility as material building blocks for a particularly broad range of applications, such as magnetic materials, catalysts, sensors (chemical, electronic and biological), data storage materials, MRI contrast agents and drug delivery facilitators [7,8,10,12–15,17,19,21]. Hence, the design, synthesis and large scale manufacturing of various types iron oxides with tight control on particle size, size distribution and particle geometry and morphology, has become one the most important research avenues in the area of nanomaterials synthesis.

There are currently several different methods for creating iron oxide nanoparticles such as sol–gel processing, synthesis using microemulsions, hydrothermal synthesis, and high temperature reactions in solution [7,8,10,12–15,17,21]. All the above-mentioned methods, with the exception of the sol–gel synthesis, constitute reliable and controllable methods for the formation of iron oxide nanoparticles, however, they require high temperature, high pressure and/or hazardous environments, which can be difficult and costly to produce in bulk [7,17,23,24]. Conversely, sol–gel synthesis does provide an extremely easy method of creating a large variety of metal oxides from metals salts, at low temperatures and ambient conditions. The reaction proceeds via the following pathway:

$$M^{III}(\text{Anion}^{-1})_3 \cdot xH_2O \xrightarrow[\text{Gelation agent}]{\text{EtOH}} M_2^{III}O_3 \qquad (1)$$

The process involves the scavenging of protons from the aqueous coordination sphere of the metal salt (sol formation), followed by condensation and formation of the metal oxide product characterized by a three-dimensional network [7,17]. The process is facilitated by the addition of a gelation agent, such as propylene oxide. This molecule acts as an effective proton scavenger from the water molecules in the immediate coordination sphere of the hydrated metal complex, resulting in a protonated epoxide. The protonated epoxide subsequently undergoes irreversible ring-opening by reacting with a nucleophile present in solution, either a nitrate ion, a chloride ion or water. Then, as a result of this ring-opening reaction in which a protonated diol is formed, deprotonation occurs and a diol is formed in conjunction with a net elimination of protons from

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solution. After further hydrolysis and condensation of the original hydrated metal complex and increased heating, stoichiometric Fe_2O_3 is formed [3,17,21,25]. The formation of a metal oxide 3D network may not be conducive to the development of materials where the presence of separated, individual, functionalized nanoparticles is essential, such as in magnetic or medical applications [23,24,26–28]. Hence, the ability to create independent nanosized particles, with tunable size and surface properties, via a method that combines the efficiency and advantages of the sol–gel process, but inhibits the formation of a gel, becomes a very important endeavor.

In this research, we have applied a modified sol–gel processing method to create iron (III) oxide nanoparticles in a manner that would utilize the advantages of the traditional sol-gel process, but circumvent the pitfalls of network formation. Our strategy was the addition of a common surfactant, sodium dodecyl benzene sulfonate (NaDDBS), to the reaction mixture, at different stages of the reaction, in order to provide an adequate stabilization mechanism for the growing iron oxide nanoparticles, and arrest their growth and the network formation at the optimal step, as shown in the process schematics in Fig. 1. Probing the effect of the NaDDBS molecules on the iron oxide nanonetwork formation when introduced into the reaction solution at different stages, will provide insight into the nucleation and aggregation of the fundamental particles and will offer opportunity for process optimization without gelation.

2. Experimental procedure

Ferric nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$ (crystalline form); ferric chlorate hexahydrate, $FeCl_3{\cdot}6H_2O$ (crystalline form); propylene oxide, C_3H_6O (1,2 epoxide); and stock absolute ethanol, were purchased from Fisher Scientific and used as received. Sodium dodecyl benzene sulfonate (NaDDBS, molecular weight of 348.48 g/mol, from TCI) was used in the same concentrations and methods as described in Matarredona et al. [29]. The syntheses were performed in 20 mL glass scintillation vials under ambient conditions. Six separate solutions were made in order to test the effects of the surfactant on the final iron oxide particle size.

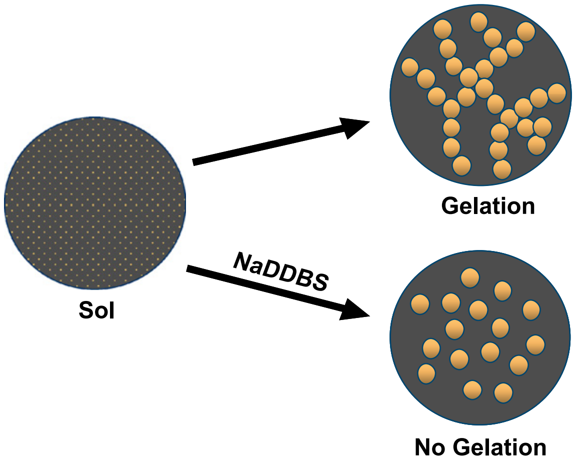

Fig. 1. Schematic representation of the modified sol–gel process involving the use of a surfactant, NaDDBS. In the absence of NaDDBS, the system undergoes gelation (top process), while in the presence of NaDDBS the system either does not gel or gelation is delayed (bottom process), but the particles formed are of similar size as the primary particles in the systems formed by the regular sol–gel method.

For the synthesis with $Fe(NO_3)_3 \cdot 9H_2O$ (solution 6), 0.65 g $Fe(NO_3)_3 \cdot 9H_2O$ was added to 3.5 mL of ethanol (100% purity) and stirred until the $Fe(NO_3)_3 \cdot 9H_2O$ dissolved completely. Then, 1.2 mL of propylene oxide was added as the gelation agent. Solutions 2 and 4 were prepared following the same procedure as that of solution 6, but with the addition of 3.5 mL of 1.2 mM NaDDBS before the addition of propylene oxide. For the synthesis with $FeCl_3 \cdot 6H_2O$, (solution 5), 0.42 g $FeCl_3 \cdot 6H_2O$ was added to 3.5 mL of ethanol and stirred until the $FeCl_3{\cdot}6H_2O$ dissolved completely. Then, 1.2 mL of propylene oxide was added. Solutions 1 and 3 were prepared following the same procedure as that of solution 5, but with the addition of 3.5 mL of 1.2 mM NaDDBS before the addition of propylene oxide. All solutions were then placed in a Fisher Scientific iso-temperature oven to dry for 72 h at 100 °C. After this time, water was added to solutions 3, 4, 5, and 6, and 1.2 mM NaDDBS was added to solutions 1 and 2, as summarized in Table 1.

The average particle size, as determined from the HRTEM micrographs and color of the various solutions are illustrated in Table 2. The error is determined by the standard deviation of the particle sizes of more than 100 particles as measured from the HRTEM micrographs. This is common practice in the use of electron microscopy imaging techniques for the determination of nanoscale particle sizes.

All the solutions were placed in a sonic dismembrator (Fisher Scientific, 20 kHz) at 35% amplification for 30 min. After sonication, transmission electron microscopy (TEM) samples of both solutions were measured to determine particle size. TEM samples were pre-

Table 1
Summary of the characteristics of the modified sol–gel process for the various reactions performed in this study

Sample number	Metal salt precursor	Gelation agent	NaDDBS addition	Water addition
1	$FeCl_3 \cdot 6H_2O$	C_3H_6O	Before gel process and after drying	None
2	$Fe(NO_3)_3 \cdot 9H_2O$	C_3H_6O	Before gel process and after drying	None
3	$FeCl_3 \cdot 6H_2O$	C_3H_6O	Before gel process	After drying
4	$Fe(NO_3)_3 \cdot 9H_2O$	C_3H_6O	Before gel process	After drying
5	$FeCl_3 \cdot 6H_2O$	C_3H_6O	None	After drying
6	$Fe(NO_3)_3 \cdot 9H_2O$	C_3H_6O	None	After drying

Specific molar quantities for each reactant are described in Section 2.

Table 2
Summary of the iron oxide product size and morphology resulting from the modified sol–gel process for the various reactions performed in this study

Sample number	Metal salt precursor	Gel formation	Average particle size (nm)	Sample color
1	$FeCl_3 \cdot 6H_2O$	Yes	4.9 ± 1.6	Brown
2	$Fe(NO_3)_3 \cdot 9H_2O$	No	3.2 ± 1.23	Light brown
3	$FeCl_3 \cdot 6H_2O$	Yes	84.6 ± 26.7	Orange
4	$Fe(NO_3)_3 \cdot 9H_2O$	No	5.1 ± 1.45	Light brown
5	$FeCl_3 \cdot 6H_2O$	Yes	3.6 ± 1.28	Brown
6	$Fe(NO_3)_3 \cdot 9H_2O$	Yes	4.5 ± 0.98	Light Brown