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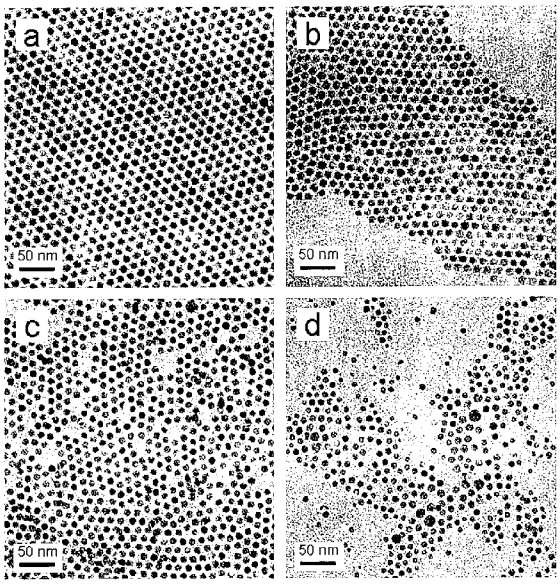
(54) **Title:** METAL OXIDE NANOCRYSTAL COMPOSITION AND METHODS

Figure 2



(57) **Abstract:** Improved methods of making magnetic nanocrystals are provided. According to certain embodiments, a method of making magnetic nanocrystals is provided, the method comprising: providing a metal component comprising at least one metal component selected from the group consisting of: a metal oxide; a metal hydroxide; a metal hydrate; and any combination thereof; providing an oil comprising a free acid; and reacting the metal component and the oil comprising a free acid at a temperature sufficient to form metal oxide nanocrystals.

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METAL OXIDE NANOCRYSTAL COMPOSITIONS AND METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application Serial No. 60/864,780 filed November 7, 2006, which is incorporated by reference herein.

STATEMENT OF GOVERNMENT INTEREST

This disclosure was made with support under grant numbers EEC-0118007 and EEC-0647452 awarded by the National Science Foundation. The U.S. government has certain rights in the invention.

BACKGROUND

The present disclosure relates generally to synthesis of nanocrystals. More specifically, the present disclosure relates to improved methods of making magnetic nanocrystals.

Magnetic nanocrystals, including magnetite (Fe_3O_4) and maghemite (γ Fe_2O_3), have been intensively studied because of their unique and tunable magnetic properties. Their magnetic features have found wide spread use in applications including, but not limited to, environmental remediation, magnetic recording and magnetic resonance imaging. For all applications, synthetic techniques which provide, among other things, precise control over nanocrystal grain size may be useful in that they permit engineering of the magnetic properties (e.g. superparamagnetic versus paramagnetic). Additionally, in many cases large quantities of highly monodisperse materials may ultimately be required in order to enable large scale testing and development. Production of nanocrystals with large and permanent magnetic dipole moments may be required for magnetic separations, and such particles may have diameters from about 10 to about 25 nm.

There has been much interest in the development of synthetic methods to produce high quality iron oxide systems. Many traditional approaches to iron oxide colloids have relied on the aqueous precipitation or hydrolysis of Fe^{2+} and/or Fe^{3+} salt(s); these materials, however, can be poorly crystalline and polydisperse in many cases. Recently, high quality iron oxide nanomaterials have been generated using high temperature solution phase methods similar to those used for semiconductor quantum dots.

SUMMARY

The present disclosure relates generally to synthesis of nanocrystals. More specifically, the present disclosure relates to improved methods of making magnetic nanocrystals.

In certain embodiments, the present disclosure relates to a method of making magnetic nanocrystals, the method comprising: providing a metal component comprising at least one metal component selected from the group consisting of: a metal oxide; a metal hydroxide; a metal hydrate; and any combination thereof; providing an oil comprising a free acid; and reacting the metal component and the oil having a free acid at a temperature sufficient to form metal oxide nanocrystals.

DRAWINGS

Some specific example embodiments of the disclosure may be understood by referring, in part, to the following description and the accompanying drawings.

Figure 1 shows a transmission electron microscopy (TEM) image of metal oxide nanocrystals.

Figure 2 shows magnetite nanocrystal synthesis from FeOOH and (a) oleic acid, 10.84 ± 0.55 nm, (b) conc. oleic acid, 9.41 ± 0.92 nm, (c) stearic acid, 8.90 ± 0.60 nm, (d) linoleic acid, 7.68 ± 1.47 nm, and 1-octadecene.

Figure 3 shows magnetite synthesis with FeOOH and oleic acid (a) in ODE, 12.04 ± 1.23 nm, (b) with no ODE, 66.80 ± 13.56 nm.

While the present disclosure is susceptible to various modifications and alternative forms, specific example embodiments have been shown in the figures and are herein described in more detail. It should be understood, however, that the description of specific example embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, this disclosure is to cover all modifications and equivalents as illustrated, in part, by the appended claims.

DESCRIPTION

The present disclosure relates generally to synthesis of nanocrystals. More specifically, the present disclosure relates to improved methods of making magnetic nanocrystals.

The present disclosure provides, according to certain embodiments, a method of making magnetic nanocrystals, the method comprising: providing a metal component comprising at least

one metal component selected from the group consisting of: a metal oxide; a metal hydroxide; a metal hydrate; and any combination thereof; providing an oil comprising a free acid; and reacting the metal component and the oil having a free acid at a temperature sufficient to form metal oxide nanocrystals.

The methods of the present disclosure may benefit from, among other things, the use of environmentally friendly and relatively inexpensive starting materials. The metal oxide nanocrystals formed, although relatively inexpensive to produce, may be of a high quality and monodisperse. Such metal oxide nanocrystals may be used in applications including, but not limited to, water treatment (e.g., arsenic removal), magnetic resonance imaging (MRI), ferrofluids, data storage, sensors, medicinal and diagnostic imaging, drug delivery, catalysis, magnetic and optical devices, and protein separations.

The metal component may comprise any metal component suitable for the production of metal oxide nanocrystals by reaction with an oil comprising a free acid. Examples of such metal components include, but are not limited to, a metal oxide, a metal hydroxide or a metal hydrate. Such metal oxides, metal hydroxides, and metal hydrates may comprise titanium (Ti), zinc (Zn), nickel (Ni), manganese (Mn), cadmium (Cd), and any combination thereof. In a specific example, the metal component comprises iron oxide-hydrates, commonly referred to as "rust." For metal components such as rust, the metal component may be ground into a fine powder before reaction with the oil. One of ordinary skill in the art, with the benefit of the present disclosure, may recognize additional metal components that may be suitable for use in the methods of the present disclosure. Such metal components are still considered within the spirit of the present disclosure.

The oil comprising a free acid may be any oil comprising a free acid and suitable for use in the production of metal oxide nanocrystals by reaction with a metal component. In certain embodiments, the oil comprising a free acid may be a naturally occurring oil. Examples of suitable oils include, but are not limited to, olive oil (glyceryl trioleate and/or oleic acid), coconut oil, corn oil, vegetable oil, oleic acid ((9Z)-octadec-9-enoic acid), linoleic acid ((9Z, 12Z)-octadeca-9, 12-dienoic acid), stearic acid (octadecanoic acid), palmitic acid (hexadecanoic acid), and any combination thereof. For example, in the case of rust, the metal component may be mixed with the oil having a free acid, such as olive oil, to form a 0.1M solution. One of ordinary

skill in the art, with the benefit of the present disclosure, may recognize additional oils that may be suitable for use in the methods of the present disclosure. Such oils are still considered within the spirit of the present disclosure.

In certain embodiments, a solvent may be used in the synthesis of metal oxide nanocrystals. A solvent may be used, among other things, to tailor the size of the metal oxide nanocrystals. For example, 1-octadecene (ODE) may be used to achieve smaller metal oxide nanocrystals.

In certain embodiments, once the metal oxide or metal hydroxide or metal hydrate and oil comprising a free acid are mixed, heat may be applied in an amount sufficient to produce a crystalline structure. For example, when rust and olive oil are reacted, a temperature sufficient to produce a crystalline structure may be about 350°C. In certain embodiments, the metal oxide nanocrystals formed by the methods of the present disclosure may be purified following their synthesis.

After the metal component and oil having a free acid are at least partially reacted, the resulting metal oxide nanocrystals may be separated from the solution using any technique suitable for such a separation. An example of such a suitable separation technique comprises the use of a polar solvent followed by centrifugation and extraction with a hydrocarbon based solvent, such as hexane. One of ordinary skill in the art, with the benefit of the present disclosure, will recognize additional separation techniques that may be suitable. Such additional separation techniques are still considered within the spirit of the present disclosure.

EXAMPLES

Example 1

Table 1 shows the reactants and reaction temperature for a number of test samples. Table 2 shows the reaction time, as well as any observations pertaining to magnetism and TEM images.

TABLE 1

Sample	Precursor 1	Amount	Precursor 2	Amount	Solvent	Amount	Temp.
CSI-1	FeO(OH) Aldrich (Ground)	0.4 g	Oleic Acid Aldrich 90%	5.71 mL	1-octadecene Aldrich 90%	45.0 mL	320 °C
CSI-9	FeO(OH) Aldrich (Ground)	0.3 g	Glycerol trioleate Aldrich 65%	13.09 mL	1-octadecene Aldrich 90%	33.7 mL	320 °C
CSI-15	FeO(OH) Aldrich (Ground)	0.3 g	Glycerol trioleate Aldrich 65%	33.7 mL	none		320 °C
CSI-23	Rust (from rusted nail)	.001 g	Oleic Acid Aldrich 90%	7 mL	1-octadecene Aldrich 90%	12 mL	320 °C
CSI-31	FeO(OH) Aldrich (Ground)	0.4 g	Olive oil	6.47 mL	1-octadecene Aldrich 90%	45 mL	320 °C
CSI-37	Rust	.001 g	Olive Oil	7.00 mL	1-octadecene	22 mL	320 °C
CSI- 51	Rust	.3 g	Olive Oil	33.7 mL	none		320 °C
CSI-45	FeOOH	.4 g	none		1-octadecene	45 mL	320 °C
CSI-57	Rust (filtered)	.3 g	Olive Oil	33.7 mL	none		320 °C
CSI-61	FeOOH	.3 g	Olive Oil	33.7 mL	none		320 °C

TABLE 2

Sample	Time	TEM results
CSI-1	50 min	Polydisperse, variation in color contrast
	60 min	Monodisperse, variation in color contrast
	70 min	Monodisperse, variation in color contrast
	80 min	Monodisperse with some aggregation, variation in color contrast
	90 min Magnetic behavior observed	Monodisperse with some aggregation, variation in color contrast
CSI-9	50 min	Polydisperse with aggregation, variation in color contrast, average particle size: 11.79 nm*
	60 min	Polydisperse with aggregation, variation in color contrast, average particle size:12.44 nm*
	80 min	Polydisperse with aggregation, variation in color contrast, average particle size: 14.06 nm*
	100 min	Polydisperse with aggregation, variation in color contrast, average particle size: 17.05 nm*
	120 min	Polydisperse with aggregation, variation in color contrast, average particle size: 18.02 m *
	150 min Magnetic behavior observed	Polydisperse with aggregation, variation in color contrast
CSI-15	40 min	Polydisperse, variation in color contrast, average particle size: 12.59 nm*
	50 min	Polydisperse with aggregation, variation in color contrast, average particle size: 19.62 nm*
	70 min	Few, large particles, little variation in color contrast, average particle size: 23.36 nm*
	90 min	One large particle, dark in color, average size: 38.39 nm*
	120 min	No sample visible
	150 min No magnetic behavior observed	Polydisperse with aggregation, variation in color contrast
CSI-23	80 min	Small, single particle
	90 min	Small, single particle
	110 min	Large particle, aggregation, variation in color
	120 min	Large particle, aggregation
	150 min	Large particle, aggregation
	160 min No magnetic behavior observed	Large particle, aggregation

CSI-31	40 min	No particles visible
	60 min	Tiny particles, monodisperse
	80 min	Polydisperse with aggregation, variation in color contrast
	100 min	Polydisperse with aggregation, color variation
	120 min	Polydisperse, large aggregate, variation in color contrast
	150 min Magnetic behavior observed	Polydisperse, large aggregation, variation in color contrast, average particle size: 14.110 nm -Other TEM images showed monodisperse particles with average size 5.011 nm
CSI-37	60 min	
	80 min	
	100 min	
	120 min	
	150 min Samples show magnetic behavior	
CSI-51	70 min	No particles visible
	90 min	No particles visible
	120 min	Small monodisperse particles visible, variation in color contrast
	150 min	
CSI-45	60 min	No particles visible
	80 min	Aggregation, little color contrast
	90 min Magnetic behavior observed	Few particle, small
CSI-57	50 min	
	60 min	
	5 hours	
	10 hours No magnetic behavior observed	
CSI-61	60 min	
	5 hours	
	10 hours No magnetic behavior observed	

* These averages are estimates from about 40 particles.

Example 2

In an example synthesis, oil, vinegar, a pan, CRYSTAL DRAIN OPENER (sodium hydroxide; ROEBIC Laboratories, Orange, Connecticut) and rust were used. First, the oil, CRYSTAL DRAIN OPENER and water were mixed to form a soap. After curing for about 24 hours the soap solidified. For efficient dissolution in subsequent steps, the soap was ground into a fine powder and mixed with vinegar while heating on a conventional stove. Once the soap was dissolved, the solution forms two layers: a yellow (fatty acid) top layer and a cloudy white/yellow bottom layer. The solution was then heated at 110 °C to remove excess water and vinegar by-products. The clear yellow fatty acid components was then collected and mixed with rust. The resulting mixture was heated for 2 hours at below and near boiling temperatures. A TEM micrograph of the nanocrystals formed was obtained after magnetic separation in chloroform and is shown in Figure 2.

Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as illustrated, in part, by the appended claims.

What is claimed is:

1. A method for making metal oxide nanocrystals comprising:

providing a metal component comprising at least one metal component selected from the group consisting of: a metal oxide; a metal hydroxide; a metal hydrate; and any combination thereof;

providing an oil comprising a free acid; and

reacting the metal component and the oil comprising a free acid at a temperature sufficient to form metal oxide nanocrystals.

2. The method of claim 1 wherein the metal component comprises an iron-oxide hydrate.

3. The method of claim 1 wherein the oil comprising a free acid is chosen from olive oil, coconut oil, corn oil, vegetable oil, oleic acid, linoleic acid, stearic acid, palmitic acid, and any combination thereof.

4. The method of claim 1 wherein the oil comprising a free acid comprises glycerol trioleate.

5. The method of claim 1 wherein the temperature sufficient to form metal oxide nanocrystals is about 350°C.

6. The method of claim 1 wherein reacting the metal component and the oil comprising a free acid at a temperature sufficient to form metal oxide nanocrystals further comprises reacting 1-octadecene with the metal component and the oil comprising a free acid.

7. The method of claim 1 further comprising purifying the metal oxide nanocrystals.

8. The method of claim 1, wherein the metal oxide or the metal hydroxide or the metal hydrate is rust, the oil having a free acid is olive oil, and the temperature sufficient to form metal oxide nanocrystals is about 350°C.

FIGURES

Figure 1

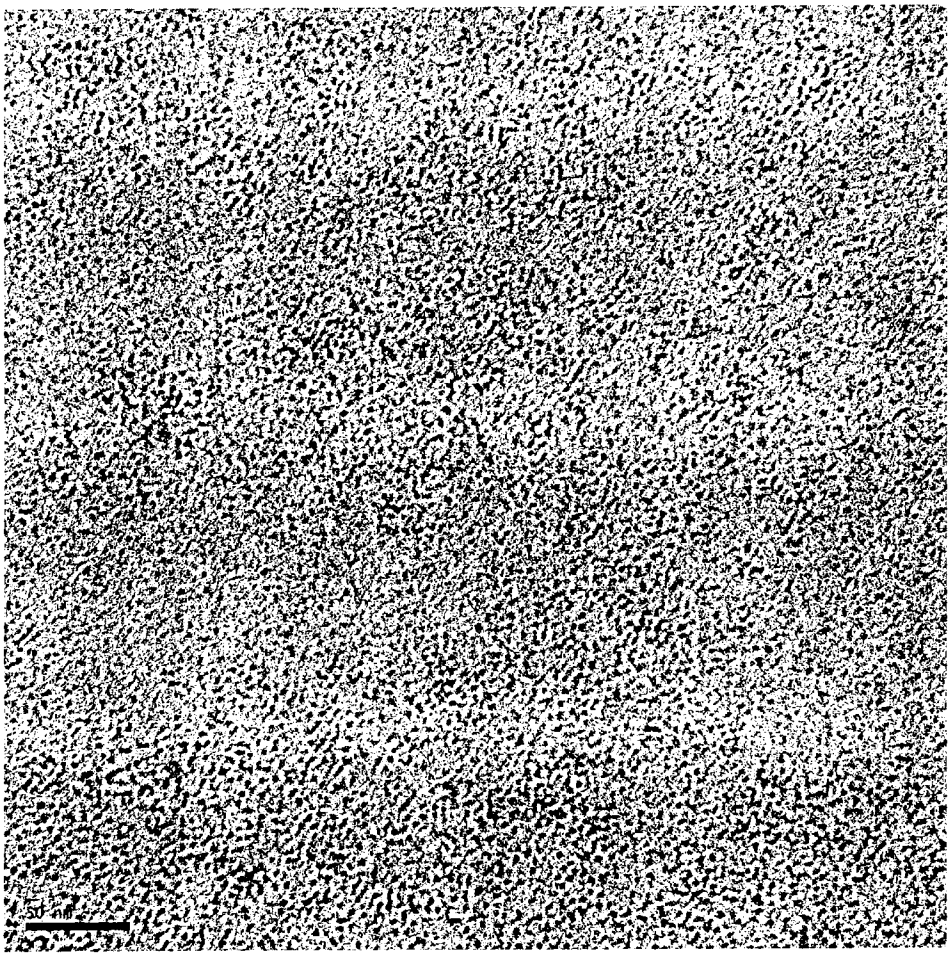

Figure 2

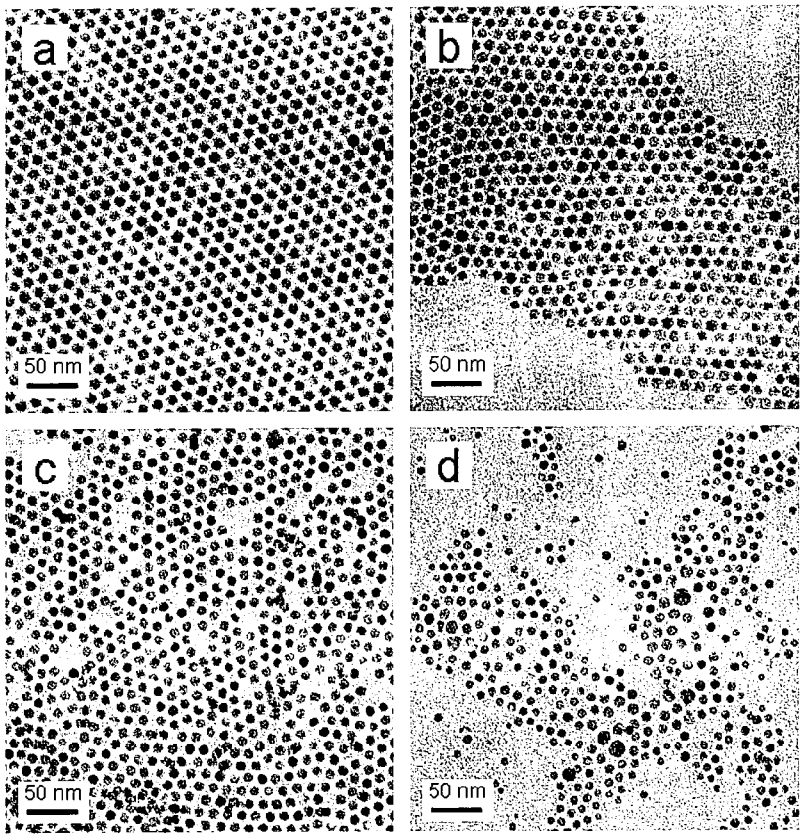

Figure 3