Iron oxide nanoparticles for magnetically assisted patterned coatings

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ABSTRACT

Iron oxide nanoparticles able to magnetically assemble during the curing stage of a polymeric support to create micro-scale surface protuberances in a controlled manner were prepared and characterized. The bare Fe_3O_4 particles were obtained by two methods: co-precipitation from an aqueous solution containing Fe^{3+}/Fe^{2+} ions with a molar ratio of 2:1 and partial oxidation of ferrous ions in alkaline conditions. The products were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and magnetization measurement. They were subsequently functionalized using oleic acid, sodium oleate, or non-ionic surfactant mixtures with various hydrophilic to lipophilic balance (HLB) values. Composite nanoparticle-polymer films prepared by spraying were deposited and cured by drying on glass slides under a static magnetic field in the range of 1.5–5.5 mT. Magnetic field generated surface roughness was evidenced by optical and scanning electron microscopy. The optimum hierarchical patterning was obtained with the nanoparticles produced by partial oxidation and functionalized with hydrophobic surfactants. Possible applications may include ice-phobic composite coatings.

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1. Introduction

The interest for research directed toward achieving a better control over the mechanisms governing the interaction between solid surfaces and water drops is steadily growing. Synthetic surfaces with wetting behavior that is tailored according to the desired application are relevant to a wide array of modern technological fields, such as self-cleaning coatings for satellite dishes and automobile windshields, non-fouling surfaces in biomedical devices, drag-force reducing materials for micro-fluidic or aquatic sport applications, anti-corrosion or ice-accretion reducing treatments in power-lines, aviation or building industry. The strategies for engineering synthetic coatings with water/ice repellent properties have been inspired by the features of naturally occurring superhydrophobic materials, namely their resistance to water penetration and their low adhesion to droplets [1,2]. Examples of such natural surfaces that display a contact angle higher than 150° with the water drops, include the lotus and other plant leaves, bird and butterfly wings or the water strider's leg. Recent studies conclude that an optimum combination of low surface tension and hierarchical roughness is able to produce the superhydrophobic effect [3]. In natural surfaces, the morphology of the surface is the determining factor for its wetting properties: for example, the

lotus leaf is superhydrophobic, while the rose petal presents high adhesion to droplets although both surfaces have low surface tension. The difference is in the size of the protuberances (nano versus micro features). The presence of solid/liquid interface roughness in the nano-size range favors air pocket entrapment underneath the water drop, thus minimizing the contact area with it (Cassie–Baxter wetting regime) [4]. Various synthetic methods to produce patterned surface morphologies have been proposed, such as templating, lithography, etching, vapor-deposition, plasma treatment, sol–gel processes, layer-by-layer deposition [5,6]. While precise surface patterning and the high cost associated with multi-step processing may be justified for special applications (transparent coatings for electronics, surface treatments for biomedical devices or aircraft parts), accessible, less expensive technologies are also needed for high volume applications such as anti-icing coatings for automotive and construction parts, power lines or pipes. Current development in nanotechnology brought a possible solution. Among the various approaches for creating surfaces with hierarchical roughness, nanoparticle assembly is known to be facile and cost effective [7], but relatively difficult to control due to the nature of the particle interactions (mainly van der Waals forces) [8]. In order to improve the process control level, we propose the use of magnetic field assisted nanoparticle aggregation.

Magnetic nanoparticles, especially iron oxides, are currently intensely studied due to their unique properties and wide array of applications in biomedicine, separation and purification processes,

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catalysis and electronic data storage [9,10]. A variety of synthetic procedures for their preparation has been reported, such as co-precipitation, the reverse micelle method, micro/nano emulsion technology, laser pyrolysis, sol–gel techniques, pulsed wire eva-poration, thermal decomposition, hydrothermal methods, freeze drying, ultrasound irradiation, microwave plasma synthesis and flame spray synthesis [11,12], oxidation [13] or by using bio-in-spired routes [14]. The properties may be tuned according to specific applications by adding surface functional layers (surfac-tants, polymers, metals or metal oxide, silica, carbon) [12,15].

Despite the fact that magnetic iron oxide nanoparticles present multiple advantages such as easy manipulation in magnetic field, non-toxicity, cost effective preparation and functionalization, their use in water/ice repellent composite coatings has not been in-vestigated yet. This study aims to develop a method to prepare functional iron oxide nanoparticles that are capable to interact magnetically and assemble during the curing stage of a polymeric support to create micro/nano-scale surface protuberances in a controlled manner.

2. Materials and methods

2.1. Materials

Iron (III) chloride hexahydrate p.a. ($FeCl_3 \cdot 6H_2O$), iron (II) chloride tetrahydrate p.a. ($FeCl_2 \cdot 4H_2O$), oleic acid, Tween 80, Span 80 for synthesis and potassium nitrate (KNO_3) were purchased from Merck, Germany. Sodium oleate powder purum grade, so-dium hydroxide p.a. grade, low molecular weight chitosan (CS_LMW) ($M_w = 50–190$ kDa; degree of deacetylation 84.5%), acetic acid (99.8–100.5% by weight) and dodecane p.a. grade were obtained from Sigma-Aldrich, Germany; aqueous ammonia solu-tion (25% by weight), ethanol, acetone and isopropanol (IPA) were procured from the Chemical Company (Iasi, Romania).

Analytical grade chemicals were used as received, without further purification. All solutions were prepared with ultrapure water.

2.2. Magnetite nanoparticles preparation

2.2.1. Co-precipitation method

Magnetite nanoparticles (the lot obtained by this method de-signated as batch Mag 20) were prepared by co-precipitation from an aqueous solution containing Fe^{3+}/Fe^{2+} ions with a molar ratio of 2:1, upon addition of aqueous sodium hydroxide solution. In a typical synthesis, iron (III) chloride hexahydrate (0.0551 mol) dis-solved in 120 mL water and iron (II) chloride tetrahydrate (0.0275 mol) dissolved in 120 mL water were mixed (500 rpm) under mild nitrogen blanket in a 500 mL three-necked flask equipped with mechanical overhead stirring placed in a tem-perature controlled water bath. Aqueous sodium hydroxide solu-tion (12.8 g in 120 mL water) was then added using a peristaltic

pump with flow rate of 10 mL/min while stirring at 65 °C. The reaction was continued for 1 h under the same conditions.

2.2.2. Oxidation method

The Fe_3O_4 nanoparticles (the lot obtained by this method identified as batch Mag 24) were obtained by partial oxidation of ferrous ions, using nitrate ion as a mild oxidizing agent, in alkaline solution. Briefly, iron (II) chloride tetrahydrate (3.78 mmole) dis-solved in 150 mL water was mixed with 22.5 mL 1 M acetic acid solution and homogenized by ultrasonication under reduced pressure for 15 min. The mixture was transferred to a 500 mL three-necked round bottom flask previously filled with nitrogen, equipped with mechanical overhead stirrer and placed in a tem-perature controlled water bath. The reaction pH was gradually increased by the addition of 0.5 M aqueous ammonia solution with a peristaltic pump (10 mL/min flow rate), under stirring and gentle nitrogen blanket. The temperature of the bath was increased to 70 °C after adding 60 mL ammonia solution. A second portion of ammonia solution (67.5 mL) was subsequently added at the same flow rate and the resulting dark-green complex was maintained for 2 h at 70 °C, with stirring and nitrogen blanket. The mixture was then oxidized using 30 mL aqueous 10% KNO_3 solution and aged under stirring for another hour at the same temperature.

The black particles produced by either co-precipitation or oxi-dation were collected by magnetic sedimentation and washed repeatedly with water until neutral pH. Each batch was then dis-persed in 200 mL water and stored at 4 °C for further study. The solid content (w/w) was determined by drying an aliquot at 105 °C in a Mettler-Toledo HG63 moisture analyzer.

2.3. Particle functionalization

The magnetic materials obtained as previously described were subsequently functionalized in aqueous suspension using sodium oleate, oleic acid or mixtures of non-ionic surfactants (Span 80 and Tween 80) using the following procedure: a 10 mL aliquot of the respective 1% aqueous magnetite suspension (batch Mag 20 or Mag 24) was mixed with a certain amount of surfactant solution, as shown in Table 1, and placed in a thermostatic laboratory shaker at 70 °C, for 1 h, then left to cool and mature overnight at room temperature. The resulting product was washed several times with ethanol using magnetic field separation. The functio-nalized particles were re-dispersed in isopropyl alcohol (approxi-mately 1% solid content by weight) and stored at 4 °C for further use.

2.4. Two-phase partition

In order to check the functionalization uniformity, the nano-particles were tested by addition to a two-phase water-dodecane system. A sample of the 1% functionalized magnetite suspension in IPA, weighing 0.6 g, was added to a vial containing 10 mL water and 5 mL dodecane; the mixture was gently shaken, then allowed

Table 1
Functionalization study.

Batch	Magnetite suspension, mL	Surfactant	Surfactant solution amount, mL	Surfactant HLB value
Mag 20/Mag 24_AcOl	10	Oleic acid 1% in ethanol	2.0	–
Mag 20/Mag 24_NaOl	10	Sodium oleate 1% in water	2.0	–
Mag 20/Mag 24_Span	10	Span 80 1% in ethanol	0.4	4.3
Mag 20/Mag 24_S/T 75/25	10	Span 80 1% (75%)+Tween 80 1% (25%) in water/ethanol	0.4	7.0
Mag 20/Mag 24_S/T 50/50	10	Span80 1% (50%)+Tween 80 1% (50%) in water/ethanol	0.4	9.6
Mag 20/Mag 24_Tween	10	Tween 80 1% in water	0.4	15.0