Particle Size Determination from Magnetization Curves in Reduced Graphene Oxide Decorated with Monodispersed Superparamagnetic Iron Oxide Nanoparticles

Arnau Bertran† 1, 2, Stefania Sandoval 1, Judith Oró-Solé 1, Àlvar Sánchez* 2 and Gerard Tobias* 1

1 Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), 08193 Bellaterra, Barcelona, Spain.
2 Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain.

KEYWORDS: Reduced graphene oxide, iron oxide nanoparticles, microwave-assisted synthesis, superparamagnetism, size determination.

ABSTRACT: Reduced graphene oxide (RGO) decorated with superparamagnetic iron oxide nanoparticles (SPION) is a novel composite nanomaterial with a myriad of promising applications. However, processes such as the fast and simple synthesis of non-agglomerated monodispersed SPION on RGO and the accurate characterization of particle size distributions remain challenging. Here we present how to solve these two problems. Firstly, we introduce a new microwave-assisted synthesis of stabilized SPION on RGO which is fast, simple and up-scalable but at the same time renders well dispersed SPION with narrow size distributions. The coverage of the RGO flakes with SPION is extensively tuned and the results are compared with a non-stabilized microwave-assisted method. Secondly, we implement an accurate method for the determination of particle size distributions from magnetization curves in RGO-SPION composite nanomaterials. This method is applied to the prepared composites with different particle size distributions, degrees of particle agglomeration and coverage of the RGO flakes. The influence of sample characteristics in the size determination method is discussed and the results are compared with the values obtained from transmission electron microscopy (TEM) and X-ray diffraction (XRD), showing that the method is well suited for these and potentially other types of superparamagnetic composite nanomaterials.

INTRODUCTION
Magnetic nanoparticles, and iron oxide nanoparticles in particular,1 have gathered remarkable interest in the last decades due to the phenomenon of superparamagnetism. Superparamagnetic iron oxide nanoparticles (SPION) have been used in a large number of applications, such as in the magnetic separation of heterogeneous catalysts8 or water pollutants,9 as material for composite electrodes in Li-ion batteries10 and supercapacitors, as and as magnetic resonance imaging (MRI) contrast agent,9 magnetically-guided drug delivery vehicle7,8 and magnetic hyperthermia mediator in cancer therapy.9,10

In recent years, the decoration of SPION on graphene to form composite nanomaterials has been shown to offer several advantages for the aforementioned applications. Graphene is a two-dimensional carbon material with remarkable physical properties, such as ballistic charge transport, high thermal conductivity, large mechanical strength and high optical transmittance.11 Its large ratio of surface area per unit mass makes it an ideal substrate for the dispersion of nanoparticles.12,13 The increased surface area of the resulting graphene-SPION composites is advantageous for applications in wastewater treatment14–17 and drug delivery.18–20 Nano-sized graphene can be easily prepared via its oxidized form, graphene oxide (GO).9 The presence of oxygen-containing functional groups in GO makes the material hydrophilic,21 allowing for its use in aqueous media. These functional groups also expand the chemistry of the graphene-SPION composites, providing electron microscopy; TG, thermogravimetry; DSC, differential scanning calorimetry; FWHM, full width at half maximum; XPS, X-ray photoelectron spectroscopy; SQUID, superconducting quantum interference device; %ION, percent weight of iron oxide nanoparticles.
different paths for their biofunctionalization. In addition, GO flakes, having typical sizes much larger than free SPION, show longer circulation lifetimes in blood. In the particular case of magnetic hyperthermia applications, the high thermal conductivity of graphene also improves heat transfer, which is typically not efficient in SPION ferrofluids. Complementary, the high absorbance of graphene in the near infra-red (NIR) range allows for photothermal therapy. For applications requiring good electrical conductivity, such as electrochemical energy storage, GO can be reduced to reduced graphene oxide (RGO), partially restoring the original properties of pristine graphene.

There are two chemical approaches for the decoration of graphene with SPION: the functionalization of graphene followed by the attachment of SPION already synthesized, or the synthesis of SPION in situ on GO. The later approach is desirable as it renders GO- or RGO-SPION composites in a simple one-step process. The iron oxide content of the composites can be easily tuned by changing the ratio between the GO and the iron precursor. However, the in situ approach is based on the heterogeneous nucleation of SPION on GO, which is a very non-uniform substrate. It is therefore challenging to obtain non-agglomerated nanoparticles of controlled sizes.

Avoiding nanoparticle agglomeration is especially important for applications in catalysis, as it maximizes the surface area of iron oxide per unit mass of catalyst and consequently its reactivity. In addition, when a post-synthesis annealing is required (i.e. to remove organic stabilizers capping the surface of the SPION, to improve the crystallinity of the iron oxide or to reduce the GO to RGO), the fact of having well-dispersed SPION strongly anchored to the GO helps prevent nanoparticle sintering.

The control of particle size is of great interest because it affects the catalytic and magnetic properties of the material. The reactivity of nanoparticles is strongly influenced by the values of lattice constant, surface stress and surface energy, which change with particle size. For MRI and magnetic hyperthermia applications, both proton transverse spin relaxation rate and magnetic-to-thermal energy conversion per unit mass of iron oxide depend on the diameter of the nanoparticles. A narrow size distribution therefore allows for a fine tuning of the catalytic activity and better optimization of the magnetic response of the materials.

The most successful methods at obtaining well-dispersed SPION with narrow size distributions are thermal decomposition, solvothermal, and polylol methods, which incorporate stabilizers and involve high temperatures and long reaction times. To the best of our knowledge, the best results reported so far were obtained by Baaziz et al., using the thermal decomposition of an iron(II) stearate complex in octyl ether in the presence of oleic acid for 2 h at 278 °C. The SPION obtained were very well dispersed on the RGO, with a narrow distribution and an average diameter of 8±2 nm. However, the high temperatures and long reaction times required for these methods increase the total duration and cost of the synthesis process. The development of new methods using shorter reaction times and lower temperatures is a subject of remarkable interest.

In the last few years, microwave-assisted synthesis has become an interesting alternative to traditional methods for inorganic nanoparticle synthesis, due to its energetic efficiency, short reaction times and simplicity. Microwave-assisted synthesis is especially effective for the decoration of GO with inorganic nanoparticles. GO has a high absorption capacity for microwave radiation, much higher than commonly employed solvents or iron oxide precursors, causing a selective heating of the GO and favoring the formation of nanoparticles on its surface. This effect shortens reaction times even further and ensures that nucleation takes place at the GO interface and not in the solution, rendering more efficiently-covered RGO sheets.

Zou et al. reported a microwave-assisted hydrothermal method using FeCl₃, GO and NH₄H₂PO₄ at 200 °C, with a reduced reaction time of 20 min. They tuned the morphology of the nanoparticles by changing the concentration of NH₄H₂PO₄, but the size distributions were broad and the average sizes were too large for superparamagnetism. Karthikeyan et al. heated an aqueous mixture of Fe(NO₃)₃ and RGO in the presence of urea (Fe:urea = 1:10 molar) for only 10 min using microwaves, obtaining polydisperse nanoparticles with average diameters between 20 and 40 nm, again too large for superparamagnetism. Following a similar procedure but using Fe(NO₃)₃ and reducing the ratio Fe:urea to 1:2.5, Liu et al. obtained RGO decorated with SPION with average diameters between 4 and 8 nm but significant agglomeration. Alternatively, Baek et al. found benzyl alcohol to be a particularly effective dielectric solvent in combination with microwave irradiation. They used the microwave-assisted heating of iron(III) acetylacetonate and GO in benzyl alcohol at 200 °C for only 10 min, obtaining RGO sheets homogeneously covered with SPION with an average diameter of 6 nm and a reasonably narrow size distribution.

However, the microwave-assisted methods reported so far have always obtained agglomerated SPION and have not shown accurate control of the particle size distribution. Another current challenge in the development of composite nanomaterials with supported nanoparticles is the accurate characterization of the particle size distribution. This is important for the control and assessment of synthesis methods, and it also allows to draw relationships between the particle size and the physical and chemical properties of the material. Particle size determination methods typically used for this purpose suffer from high time consumption and/or high error. Transmission electron microscopy (TEM) requires a long time for acquiring micrographs and measuring a large number of nanoparticles, and yet the size distribution is obtained from a very small fraction of the sample, which might not be representative.
of the whole. Representativity is especially critical in the case of composite carbon nanomaterials, where the heterogeneity of the starting material (i.e. the different concentrations of functional groups and other defects between different GO flakes) adds a source of variability of particle sizes. On the other hand, size determination from powder X-ray diffraction (XRD) peak broadening is fast and involves a large amount of sample, but the presence of the nanosized graphene flakes substantially rises the noise of the patterns, increasing the uncertainty of the results. This method renders average crystallite sizes, which can be considered as particle sizes only if all particles are single crystals.

The theory of superparamagnetism makes it possible to estimate particle sizes by fitting the Langevin function to the measured magnetization curves.\(^48\)-\(^50\) This method is representative of the entire sample, making it advantageous with respect to TEM. It has already been extensively used for superparamagnetic nanoparticles of diverse compositions and with different coatings. Assuming non-interacting spherical particles, Bean et al. determined the average particle sizes of iron amalgame by weighting the expressions for the low-field part of the curve and for the approach to saturation, separately.\(^51\) Becker estimated the extreme particle sizes of a Cu-Co alloy by weighting the expression for the low-field magnetization by a uniform size distribution.\(^52\) By assuming a log-normal particle volume distribution, Chantrell et al. determined the median volume and the corresponding standard deviation.\(^53\) This method was improved by Chen et al., introducing a core-shell particle model with a ferrimagnetic core and a paramagnetic shell, which gave very accurate fits to the full magnetization curves.\(^54\) Particle size determination from magnetization curves in composite nanomaterials has been mostly restricted to silica-embedded nanoparticles,\(^55\)-\(^56\) with scarce examples involving carbon-based nanomaterials,\(^57\) despite its potential.

In this work we present a novel microwave-assisted synthesis of RGO-SPION composites which is fast, simple and up-scalable but at the same time renders well-dispersed SPION with narrow size distributions on the RGO. Our method combines the advantages of microwave chemistry (with reaction times of a few minutes and temperatures below 200 °C) with the superior control provided by the thermal decomposition of iron complexes in the presence of organic stabilizers. The coverage of the RGO flakes with SPION was extensively tuned by changing the GO:Fe ratio and the results were compared with an analogous set of samples prepared following a non-stabilized microwave-assisted method. As to the problem of a precise particle size determination, we demonstrate here also a method for the accurate determination of particle size distributions from magnetization curves in RGO-SPION composite nanomaterials. Samples with different particle size distributions, degrees of particle agglomeration and coverage of the RGO flakes are studied with this method, assuming a log-normal distribution of particle volumes and comparing uniform and core-shell particle models. The good dispersity of the nanoparticles, the assumption of a core-shell particle model and the correction of demagnetizing effects are found to be necessary for the accurate fit to the measured magnetization curves. The excellent agreement between measured and simulated data proves the suitability and potential of the method. This method could be applied to superparamagnetic nanoparticles of other compositions supported or embedded in other materials, as long as the support is non-magnetic or its contribution to the magnetization of the composite can be adequately subtracted.

**METHODS**

**Preparation of GO**

GO was prepared following a reported modified Hummers’ method.\(^58\)-\(^59\) In brief, graphite powder (2.5 g, < 20 µm, Sigma-Aldrich, Lot # CBM3462V) and concentrated sulfuric acid (57.5 mL, 95-97 %, Scharlab) were added to a round-bottom flask and the mixture was cooled in an ice/water bath. Sodium nitrate (1.25 g, > 99.0 %, Sigma-Aldrich) was slowly added to the flask and the black mixture was allowed to cool down for 30 min. Potassium permanganate (7.5 g, > 99.0 %, Sigma-Aldrich) was slowly added while the temperature was kept below 20 °C. The mixture was then warmed to 35 °C under continuous stirring for 30 min. Deionized water (105 mL) was added very slowly to the resulting greenish mixture and it was then heated to reflux at 98 °C for 2 h. Finally, more deionized water (500 mL) and hydrogen peroxide (2.5 mL, 30%, Panreac química, SLU) were added and the mixture was allowed to precipitate for 2 days. The concentrated suspension was centrifuged at 20000 rpm for 15 min (Allegra 64R centrifuge, Beckman Coulter) and the obtained precipitate was washed with deionized water. This process was repeated until neutral pH was reached. The resulting solid was dried for 3 days at 60 °C, then crushed into a fine powder and dried overnight at 80 °C.

**Decoration of RGO with non-stabilized SPION**

RGO-SPION composites were synthesized following a one-step microwave-assisted method in benzyl alcohol, based on a recent report.\(^60\) In brief, GO (15 mg) and benzyl alcohol (5 mL, 99.8 %, Sigma-Aldrich) were placed into a 10 mL microwave glass tube with sealing cap and they were ultrasonicated for 30 min (Branson 3800 ultrasonic cleaner). Afterwards, the corresponding amount of iron(II) acetate (> 99 %, Sigma-Aldrich) was added (3,7, 7.4, 14.8 and 29.5 mg, for samples GOAc1, GOAc2, GOAc3 and GOAc4, respectively) and the mixture was thoroughly stirred for 1 min using a vortex stirrer (LBX V05). The tube was subsequently transferred to the synthetic microwave oven (Discover Explorer Hybrid, CEM) and a two-stage program (5 min at 56 °C followed by 10 min at 176 °C) was performed, at a frequency of 2.45 GHz and a power of 300 W. Once cool, the resulting black suspension was filtrated under vacuum using a polycarbonate membrane filter (0.2
um, Whatman) and it was copiously washed with deionized water. The residue was finally dried overnight at 60 °C. A control sample was prepared following the same procedure but omitting the iron precursor (GO-MW).

Decoration of RGO with stabilized SPION

Oleate-coated SPION were synthesized in situ on GO by microwave-assisted thermal decomposition of an iron(III) oleate complex. The complex was synthesized as reported. In brief, iron(III) chloride hexahydrate (5.4 g, 20 mmol, > 99.9 %, Sigma-Aldrich) and sodium oleate (18.25 g, 60 mmol, > 97 %, Tokio Chemical Industry) were placed in a 250 mL round-bottom flask. Ethanol (40 mL, 99.98 %, Panreac química, SLU), deionized water (30 mL) and hexane (70 mL, 95 %, Sigma-Aldrich) were added to the flask, and the mixture was refluxed at 70 °C for 4 h under magnetic stirring. After cooling to room temperature, the reaction mixture was transferred to a separatory funnel and the upper organic layer was washed 3 times with 15 mL of deionized water. The hexane was evaporated at 50 °C under vacuum using a rotatory evaporator, and the product was dried at 60 °C for 2 days.

The novel microwave-assisted method for the decoration of RGO with stabilized SPION was based in reported non-microwave-assisted syntheses. A solution of the prepared iron(III) oleate complex (19.6, 39.1, 78.3 and 156.5 mg, for samples GOOle1, GOOle2, GOOle3 and GOOle4, respectively) in 2.5 mL of benzyl alcohol (99.8 %, Sigma-Aldrich) was prepared, and oleic acid (> 70 %, Fisher Chemicals) (4, 8, 16 and 32 µL, respectively) was added. Separately, GO (15 mg) was dispersed in 2.5 mL of benzyl alcohol by ultrasonicating for 30 min. The two solutions were mixed together in a 10 mL microwave glass tube with sealing cap for 1 min using a vortex stirrer, to give mixtures with the same Fe:GO weight ratios as for GOAc samples. The same two-stage microwave program used for GOAc samples was run, and the mixture was magnetically precipitated using a Nd magnet. The solvent was decanted and the precipitate was washed with 15 mL of hexane and magnetically precipitated 3 times. The product was finally dried overnight at 60 °C.

Characterization

Fourier transform infrared (FTIR) spectra of the purchased oleic acid and the synthesized iron(III) oleate were collected (Spectrum One, Perkin Elmer) from 1000 to 4500 cm⁻¹. Concentrated chloroform (> 99 %, Sigma-Aldrich) solutions were drop-casted on KBr (99.95 %, Sigma-Aldrich) pellets and evaporated on a hot plate.

TEM micrographs and selected area electron diffraction (SAED) patterns were acquired in a TEM JEM-1210 (JEOL) operating at 120 kV. Size distributions were determined by measuring approximately 400 nanoparticles per sample using image processing software ImageJ. The specimens were prepared by evaporating a droplet of dilute dispersion of material in anhydrous ethanol (> 99.98 %, Panreac química, SLU) on Cu grids (Lacey, Carbon Film 200 Mesh Copper). Suspensions were previously ultrasonicated for 1 min.

Scanning electron microscopy (SEM) micrographs were acquired in a SEM Quanta 200 ESEM FEG (FEI) operating at 20 kV. Flake area distributions were obtained by measuring 100 flakes per sample using pixel counting on ImageJ. The specimens previously prepared for TEM were used.

Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves were measured from room temperature to 800 °C at a rate of 10 °C·min⁻¹, using a simultaneous TG/DSC instrument (NETZSCH-STA 449 F1 Jupiter) in oxidizing atmosphere (air flow). The temperature onsets and mass losses were computed using Netzsch Proteus Thermal Analysis software.

XRD patterns were obtained in a powder diffractometer (D-500, Siemens) using a Cu anode (Kα=1.5406 Å). Scans from 2θ=5 ° to 2θ=90 ° were performed in steps of 0.02 °, and the patterns were analyzed with DRXWin software. Average crystallite sizes were estimated from peak broadening using Scherrer’s equation

\[ D = \frac{\lambda}{\beta \cos \theta} \]  

where K=0.9, λ=0.15406 nm, β is the full width at half maximum (FWHM) and θ is the Bragg angle.

X-ray photoelectron spectroscopy (XPS) spectra, with high resolution at the C, O and Fe signals, were obtained using a hemispherical energy analyzer (PHOIBOS 150, SPECS) installed in an ultra-high vacuum chamber. Concentrated ethanol (> 99.98 %, Panreac química, SLU) suspensions were drop-casted on 5x5 mm Si wafers and evaporated at room temperature.

A superconducting quantum interference device (SQUID) magnetometer (MPMS-XL, Quantum Design) was used to measure the magnetization curves of the materials form –50 to 50 kOe, at 10 and 300 K. The measurements were done on powder samples compacted inside gelatin capsules.

Particle size determination from magnetization curves

Particle size distributions were determined by fitting a distribution-weighted Langevin function \( p(v) = \frac{1}{\sqrt{2\pi \sigma \sigma^3}} \exp\left[-\frac{(lnv-v_0)^2}{2\sigma^2}\right] \) to the magnetization curves measured at 300 K, where

\[ L(x) = \cosh(x) - \frac{x}{x} \]  

\[ p(v; u, \sigma) = \frac{1}{\sqrt{2\pi \sigma \sigma^3}} \exp\left[-\frac{(lnv-v_0)^2}{2\sigma^2}\right] \]  

where \( u \) is the mean and standard deviation of \( lnv \), and \( v_0 \) is the median particle volume. Two nanoparticle models were studied: uniform (model 1) and core-shell with ferrimagnetic core and paramagnetic shell (model 2). In both cases, nanoparticles were assumed to be single-domain and spherical. Therefore the particle diameter \( D_0 \) corresponding to a particle with median volume was given by

\[ v_0 = \frac{\pi}{6} D_0^3 \]
Magnetization curves were computed through numerical integration of the log-normal-weighted Langevin function for values of $\mu M$ between 0 and 5 T ($H = 50$ kOe). Values as the Boltzmann constant ($k_B = 1.38 \cdot 10^{-23}$ J/K), the magnetic permeability of vacuum ($\mu_0 = 4\pi \cdot 10^{-7}$ H/m) and the temperature of the experiment ($T = 300$ K) were fixed. The fitting to the measured magnetization curves, having subtracted both mass and magnetic contribution of the RGO, was done by variation of the morphological and magnetic parameters of the models. The SQUID curves were converted to the international system of units for the fits, that is, $\mu M(T)$ vs $\mu H(T)$, using the density of bulk maghemite ($4870$ kg/m$^3$ $\text{GO}$).

In model 1 the magnetization is given by

$$M(H) = \int_0^\infty p(v; u, \sigma)\{M_L(x) + \chi_{pm} H\}dv,$$

where $x = \mu M_v H/(k_B T)$, $v$ is the total volume of the particle, $M_v$ is the spontaneous magnetization of the particle, and $\chi_{pm}$ is the susceptibility of a paramagnetic contribution. All nanoparticles are assumed to have the same $M_v$. The fitting was carried out by changing $v_o, \sigma, \chi_{pm}$ and $M_v$.

In model 2, a ferrimagnetic single-domain core of volume $v_c$ and spontaneous magnetization $M_b$ is surrounded by a paramagnetic shell of thickness $\delta$, volume $v_s$ and susceptibility $\chi_{pm}$. The magnetization is given by

$$M(H) = \int_0^\infty q(D)\{M_v(D)L(x) + v_s(D)\chi_{pm} H\}dD,$$

where $q(D)$ is the log-normal volume distribution expressed in the variable $D$ and all volumes are also expressed as a function of $D$, as $\nu(D) = \pi D^3/6$, $\nu_s(D) = \pi (D - 2\delta)^3/6$ and $\nu_c(D) = \pi (D^3 - (D - 2\delta)^3)/6$. The spontaneous magnetization of the core was fixed to $\mu M_b = 0.55$ T, the average value between the bulk saturation magnetizations of maghemite ($0.50$ T) and magnetite ($0.60$ T) at 300 K.

Different average diameters can be calculated from the log-normal distributions obtained from the fits. The particle-volume-weighted average diameter,

$$D_{vd} = \int_0^\infty \rho(v; u, \sigma)D(v)dv,$$

is the quantity comparable to the diameter obtained from XRD patterns of samples consisting of single-crystal particles (using Scherrer’s equation), since the peak width is directly related to the particle size and the peak intensity is proportional to the total volume of particles of that specific diameter. The particle-number-weighted average diameter,

$$D_{nd} = \int_0^\infty \frac{\rho(v; u, \sigma)v^{-1}D(v)dv}{\int_0^\infty \rho(v; u, \sigma)v^{-1}dv},$$

is the quantity comparable to the diameter obtained from TEM micrographs by particle counting.

RESULTS AND DISCUSSION

GO and RGO

The successful preparation of single and few layer GO is confirmed by bright-field TEM and the SAED pattern of the sample (Fig. S5). Powder XRD shows an interplanar (002) distance of 6.51 Å, much larger than in graphite, which decreased to 3.36 Å after microwave treatment in benzyl alcohol (Fig. S2). The TG curve of GO has a small initial weight loss up to ca. 100 °C, associated to the loss of adsorbed water, and two large exothermic events starting at ca. 210 °C and 495 °C. The thermal event at 210 °C corresponds to the loss of a ca. 30 % in weight of oxygen-containing functional groups. The final weight loss is attributed to the complete combustion of the conjugated network of the material along with the most stable functionalities (Fig. S3). This is in agreement with the DSC curve, which also reveals the presence of thermal events at slightly different temperatures. These events might be caused by heterogeneities in the degree of oxidation and exfoliation of the GO flakes, with more oxidized and exfoliated flakes burning at lower temperatures. The smaller weight loss due to the elimination of aliphatic functional groups (18.3 %) and the increase of the combustion temperature (ca. 560 °C) in GO-MW demonstrate the reductive effect of the microwave treatment, which has been previously attributed to the reductive character of benzyl alcohol. The effect is further confirmed by high resolution C1s and O1s XPS spectra (Fig. S4), showing relative O/C atomic ratios of 0.33 and 0.12 for GO and GO-MW, respectively. The most labile groups are C=O, which are also the most abundant groups in the prepared GO, while hydroxyl and epoxy groups are the most stable (Table 1). These functional group stabilities have also been reported upon annealing of GO in inert atmosphere.

The magnetization curves of GO and GO-MW (Fig. S5) show a distorted paramagnetic behavior at low temperature, resulting from the superposition of paramagnetic and diamagnetic components. The paramagnetic component becomes very small at room temperature, and diamagnetism prevails. The paramagnetism of GO has been attributed to the formation of sp$^2$ defect-induced magnetic moments, mainly at oxygen-containing functional groups on the basal plane, such as hydroxyl or epoxy. The slight decrease in magnetization upon reduction has been associated with the removal of some of these defects.

RGO-SPION composites

Two sets of four samples were prepared, using commercial iron(II) acetate and a synthesized iron(III) oleate complex, respectively. The comparison of the FTIR spectra of oleic acid and the iron(III) oleate complex (Fig. S6) shows the appearance of symmetric ($1440$ cm$^{-1}$) and antisymmetric ($1522$ and $1599$ cm$^{-1}$) stretching bands characteristic of coordinating carboxylates in a bidentate mode, confirming the successful formation of the complex.

Initial characterization of the prepared samples by TEM imaging shows the presence of nanoparticles on the RGO flakes (Fig. 1). Larger images can be found in the Supporting Information (Figs. S7 to S14). Comparing pairs of samples with the same Fe:GO synthetic ratio, nanoparticles are significantly more agglomerated in GOAc samples than in
GOOle samples. The presence of well-dispersed nanoparticles in GOOle samples confirms the successful steric stabilization by oleate. Flake coverage decreases when reducing the Fe:GO ratio (from top to bottom in Fig. 1), as expected. However, even at very low coverages, non-stabilized nanoparticles agglomerate (GOAc1 and GOAc2), forming nanoflower-like clusters. Nanoparticles in GOOle1 and GOOle2 still show a clear tendency to group in certain regions of the RGO flake, despite being stabilized. This might be a consequence of the heterogeneous distribution of surface defects on GO, mainly oxygen-containing functional groups, which are expected to act as nucleation points for the nanoparticles.

Figure 1. TEM micrographs of the composites.

Nanoparticle size distributions of GOOle samples are markedly narrower than those of GOAc samples (Fig. 2). This is a consequence of the oleate coating acting as a diffusion barrier during nanoparticle growth. They also have smaller median particle diameters (D\text{med}) than GOAc samples (6.80, 6.17, 7.12 and 7.89 nm, from GOAc1 to GOAc4), which can again be explained by the diffusion-controlled growth in the presence of oleate.

Figure 2. Particle size histograms of the composites measured on TEM micrographs. Median particle diameters (D\text{med}) obtained from the histograms are indicated. Average diameters (D\text{avg}) are also included for the most symmetric histograms, which could be fitted by a log-normal distribution (fits are shown in red).

Particle size distributions become more asymmetric upon reduction of the Fe:GO synthetic ratio, extending to diameters much larger than the median value. As it is statistically incorrect to use mean values in asymmetric distributions, medians have been used for comparison (Fig. 2). Samples with higher coverages have nearly symmetric histograms with mean diameters of 7.27±0.09 and 8.00±0.09 nm (GOAc3, GOAc4), and of 4.95±0.04 and 4.98±0.05 nm (GOOle3 and GOOle4). The statistical analysis of the particle size distributions can be found in Fig. S15 (box plot) and Table S1 (descriptive).

SEM imaging shows irregularly-shaped flakes with a very broad area distribution. The results for sample GOAc3 are shown in Fig. S16 and Table S2 as example, with a median flake area of 2.7 μm².

SAED patterns of samples GOAc3 and GOOle3 (Fig. S17) show the characteristic reflections of graphene (1 0 0) and

\[
\begin{align*}
\text{GOAc4} & : D_{\text{med}} = 7.89 \text{ nm} \\
\text{GOAc3} & : D_{\text{med}} = 7.12 \text{ nm} \\
\text{GOAc2} & : D_{\text{med}} = 6.17 \text{ nm} \\
\text{GOAc1} & : D_{\text{med}} = 5.80 \text{ nm} \\
\text{GOOle4} & : D_{\text{med}} = 4.98 \text{ nm} \\
\text{GOOle3} & : D_{\text{med}} = 4.95 \text{ nm} \\
\text{GOOle2} & : D_{\text{med}} = 3.38 \text{ nm} \\
\text{GOOle1} & : D_{\text{med}} = 2.63 \text{ nm}
\end{align*}
\]
(1 1 0)) and a set of four rings in agreement with both maghemite (PDF 39-1346)\(^{(67)}\) ((2 0 6), (1 1 9), (2 2 12) and (1 1 15)) and magnetite (PDF 19-0629)\(^{(67)}\) ((2 2 0),(3 1 1),(4 2 2) and (5 1 1)). No hematite signals are observed.

Powder XRD patterns of samples GOAc3 and GOOle3 show essentially the same peaks (Fig. 3). The lower signal-to-noise ratio for GOOle3 with respect to GOAc3 is attributed to the smaller coverage of the RGO flakes with nanoparticles in the former. Peaks labelled with “*” correspond to the RGO, while the remaining peaks are in agreement with both magnetite (PDF 19-0629)\(^{(67)}\) and maghemite (PDF 39-1346)\(^{(67)}\) patterns. For both samples, the most intense peak appears at \(-35.0^\circ\) (corresponding to interplanar distances of 2.5 and 2.6 Å), which matches with the most intense diffraction signal of both magnetite and maghemite ((1 1 9) and (3 1 1), respectively). No signals from hematite are observed. Thus, it can be concluded from both SAED and XRD that the composition of the nanoparticles is iron oxide (either magnetite, maghemite or a mixture of both). The presence of the hematite phase can be discarded.

Scherrer’s equation applied to the most intense peak of iron oxide gives an estimated mean crystallite size of 5.3 ± 1.8 and 4.6 ± 1.8 nm for GOAc3 and GOOle3, respectively. It must be noted that the uncertainty in the result is of more than 30 %, compared to the \(-1\%\) uncertainty of the particle size values for these samples obtained from TEM. Even assuming the presence of single-crystal particles, these large uncertainties show why particle size determination from XRD peak broadening would be an unsuitable method for this type of hybrid materials. Comparison of mean crystallite and particle sizes shows a clear discrepancy for sample GOAc3, inferring the presence of polycrystalline particles. In the case of sample GOOle3, both crystallite and particle sizes are compatible within the experimental error, suggesting that particles in this sample are single crystals.

TG curves of all GOAc samples show a very similar thermal behavior (Fig. 4 (a)). The small weight loss between 200 and 300 °C indicates that the amount of remaining functional groups after nanoparticle synthesis is approximately 3 % in weight. This value is much smaller than that of GO-MW (Fig. S3), indicating that the addition of iron(II) acetate to the reaction medium has caused a further reduction of the GO, which might be due to the formation of the metal oxide. The large weight loss at 360 °C corresponds to the combustion of the conjugated network of the material. The significantly lower onset temperature of this loss in comparison with that of GO and GO-MW (Fig. S3) indicates that the presence of nanoparticles catalyzes the complete oxidation of the material. The amount of residue remaining at 800 °C increases from sample GOAc1 to GOAc4 (9.9, 15.5, 27.3 and 43.6 %, respectively), consistently with the increase in flake coverage observed by TEM (Fig. 1). For the microwave-assisted synthesis of SPION in benzyl alcohol, without GO, the oxygen necessary for the formation of iron oxide is known to be supplied by traces of water present in the reaction medium or by the acetate ions themselves, which can undergo an esterification reaction with benzyl alcohol to form benzyl acetate and OH\(^{-}\).\(^{(68)}\) When GO is present, its oxygen-containing functional groups are likely to act as an additional source of oxygen.

The thermal behavior of GOOle samples is substantially different from that of GOAc samples (Fig. 4 (b)). Two marked weight losses are observed. The first weight loss, which occurs between 230 °C and 240 °C, can be associated to the desorption of physisorbed oleic acid\(^{(69)}\) and the loss of the remaining oxygen-containing functional groups on the RGO. The major weight loss corresponds to the combustion of the conjugated network of the material, although the shape and width of the DSC peaks (Fig. S18) suggest it is overlapping with some other thermal event. This other event could be the removal of oleate ligands chemisorbed on the surface of the nanoparticles, which has been reported to happen above 300 °C.\(^{(69)}\) As expected, the solid residue at 800 °C increases from sample GOOle1 to GOOle 4 (8.7, 10.3, 16.8 and 22.1 %).

Figure 3. Powder XRD patterns of samples GOAc3 (a) and GOOle3 (b), measured with Cu K\(_{\alpha}\). The interplanar distance corresponding to each peak is indicated in Å. Peaks labelled with “*” correspond to RGO.
Figure 4. TG curves for GOAc samples (a) and GOOle samples (b), measured at 10 °C min⁻¹. The curve for the starting GO (continuous line) is included for comparison.

The inorganic content in carbon nanocomposites can be quantitatively determined from TG analysis. The percent weight of iron oxide nanoparticles (%ION) present in the hybrid materials was calculated from their residues at 800 °C. This was performed by subtracting the inorganic impurity in GO-MW, rescaled to the amount of RGO in the composite (obtained from the major mass loss), using equation

\[
%I_{ON} = \frac{R_2 - \left( \frac{R_1}{R_2} \right) R_1}{1 - \frac{R_1}{R_2}},
\]

where \( R_1 \) is the percent weight residue at 800 °C in GO-MW and \( R_2 \) is the percent weight residue at 800 °C in the composite. Iron oxide was assumed to be already in its fully oxidized state (Fe₂O₃) before the heat treatment. The iron oxide weight contents obtained are 8.2, 13.9, 25.9 and 42.5 % for samples GOAc1, 2, 3 and 4, and 6.9, 8.6, 15.2 and 20.6 % for samples GOOle1, 2, 3 and 4, respectively.

High resolution C1s (a, b), O1s (c, d) and Fe2p (e, f) XPS spectra of samples GOAc3 and GOOle3 (Fig. 5) reveal O/C atomic ratios of 0.31 and 0.26, respectively, indicating that almost no loss of O has occurred during nanoparticle synthesis with respect to the starting GO (O/C = 0.33). Taking into account both the reducing effect of the microwave treatment in benzyl alcohol and the fact that only a ~3 % mass loss associated to O-containing functional groups is observed in the TG of these samples (Fig. 4), this suggests that most of the original O from the GO has been used to form iron oxide. The deconvolution of the Cis and O1s spectra reveals the same types of C and O already observed in samples GO and GO-MW (Fig. S4), as well as an additional Fe-O peak. From lower to higher binding energy, the deconvoluted peaks are assigned as C=C, C-OH / C-O-C (epoxide), C=O and O-C=O in the Cis spectra (a, d), and Fe-O, O=C-O, C=O and C-OH / C-O-C in the O1s spectra (b, e). The corresponding elemental compositions (at. %) are presented in Table 1. Functional group stabilities under microwave treatment in the presence of the iron precursor are similar to those observed in GO-MW, with C=O being the most labile group and C-OH and C-O-C being the most stable groups.

The doublet corresponding to Fe₂p₃/2 and Fe₂p₅/2 can be seen in both samples (Fig. 5 (e) and (f)). The position (711.2 and 724.8 eV) and separation (13.6 eV) of the two peaks is in good agreement with the reported values for Fe(III) in maghemite and hematite nanoparticles. In addition, both samples clearly show the characteristic Fe(III) satellite at 719 eV. There are no clear signs of the presence of Fe(II). However, the deconvolution reveals a peak at 715 eV, which could be attributed to a small amount of Fe(II) (and thus magnetite) in the sample. Therefore, these results suggest that the nanoparticles are mostly composed by maghemite, but they might also contain a fraction of iron oxide that has not been fully oxidized during the aerobic synthesis, potentially located in the center of the nanoparticle as a small magnetite core.

Figure 5. High-resolution C1s (a, b), O1s (c, d) and Fe2p (e, f) XPS spectra of samples GOAc3 (a, c, e) and GOOle3 (b, d, f). The measured spectra (black lines) have been fitted (red lines) by the convolution of Gaussian/Lorentzian mixed functions (colored lines).

The adiabatic magnetization curves measured at 10 K (a and c) and 300 K (b and d) are presented in Fig. 6. Most magnetization loops enclose no appreciable area (see insets), with coercive field values smaller than 20 Oe. Only samples GOAc1 and GOAc2 show some hysteresis at 10 K,
with coercive fields of 95 and 50 Oe, respectively. This suggests that a small fraction of the SPION in these samples has blocking temperatures above 10 K. Assuming spherical particles, and taking an ensemble magnetization relaxation time of 100 s as the limit for superparamagnetic behavior, the critical particle volume $v_c$ for superparamagnetism can be determined from

$$\frac{K_{cc}}{8\pi T} = 25.$$  \hspace{1cm} (10)

The corresponding critical diameters for maghemite particles are 11.3 and 35.0 nm at 10 and 300 K, respectively, and the values for magnetite are 7.9 and 24.5 nm (uniaxial crystal anisotropies $K$ of $4.60 \times 10^3$ J cm$^{-3}$ for maghemite and $1.35 \times 10^4$ J cm$^{-3}$ for magnetite have been used). It must be noted that particle size distributions for all GOAc samples clearly extend beyond the critical diameter for magnetite at 10 K (Fig. 2). However, these samples do not show significant magnetic hysteresis, which suggests that the nanoparticles are not pure magnetite. The fact that GOAc1, being the only sample with a fraction of particles with diameters larger than the critical value for maghemite, also has a clearly larger coercive field is consistent with the nanoparticles being maghemite.

Figure 6. Magnetization curves of the composites measured 10 K (a, c) and 300 K (b, d). Insets show the low-field part of the curves.

The magnetization of the composites is not fully saturated at 50 kOe, which might be due to the fraction of very small nanoparticles. The higher magnetization values at low temperature were expected from the temperature dependence of the saturation magnetization of bulk maghemite and magnetite.

Magnetization at 50 kOe scales linearly with the iron oxide content of the composites for both precursors, with no significant differences in magnetization for samples with similar iron oxide contents (Fig. 7 (a)). However, if the mass and the corresponding magnetic contribution of the RGO (rescaled from Fig. S5) are subtracted, the magnetization at 50 kOe for GOAc samples seems to show a plateau at high iron oxide contents (Fig. 7 (b)). There is even a decrease in magnetization from sample GOAc3 to GOAc4, unexpected from the typical tendency of saturation magnetization of iron oxide nanoparticles to be smaller for
smaller particles due to spin canting effects. In addition to particle diameter, the other features changing the iron oxide content are flake coverage and degree of particle agglomeration. These results suggest that higher flake coverage and particle agglomeration have a negative effect on magnetization, in accordance with previous reports. It must be noted that even after subtracting the magnetic contribution of RGO, magnetization curves do not reach saturation at 50 kOe. The non-saturating behavior of very small SPION (< 3 nm) at high fields has been previously attributed to surface anisotropy. This could be the case of samples GOOle1 and GOOle2, where a significant fraction of the particles has a diameter below 3 nm. For samples with larger nanoparticles, however, the non-saturating behavior must be due to some remaining paramagnetic contribution. A possible explanation is the formation of paramagnetic defects at the anchorage points of the nanoparticles on the RGO.

Figure 7. Magnetizations at 50 kOe for GOAc (squares) and GOOle (triangles) samples at 10 K (open) and 300 K (filled) as a function of the iron oxide weight content, before (a) and after (b) subtracting the contribution of the RGO. The magnetization values have been obtained from the average of the three SQUID data points at $|H| = 50$ kOe in Fig. 6, taking absolute values of magnetization.

Particle size determination from magnetization curves

Samples GOAc3, GOAc4, GOOle3 and GOOle4 were chosen for the particle size determination study because of their relatively high iron oxide content and log-normal particle size distribution, shown by TEM (Fig. 2). The Langevin fits to the measured magnetization curves of these samples at 300 K are presented in Fig. 8. Both models give a good description of the magnetization at high fields (Fig. 8 (a)). However, logarithmic plots of the low field region of the magnetization curves reveal slight deviations from the experimental data in all cases (Fig. 8 (b)). Only sample GOAc3 is perfectly fitted throughout the magnetic field range of the measurement. The parameters used for these fits are reported in Tables S3 and S4.

![Figure 8. Magnetization curves of samples GOAc3 (circles), GOAc4 (squares), GOOle3 (upright triangles) and GOOle4 (upside-down triangles) measured at 300 K, and Langevin fits with models 1 (red solid lines) and 2 (black dashed lines). Linear and logarithmic axes are used in plots (a) and (b), respectively. The four segments of curve corresponding to the full magnetization loop have been transported to the positive quadrant and plotted together for each sample.]
data was not improved for samples GOAc3 and GOAc4 after applying the demagnetizing correction. For that reason, only the fits for GOOle3 and GOOle4 samples are presented in Fig. 9. The parameters used for these fits are reported in Table S5. The agreement between model and experiment in this case is very good both at high (a) and low (b) fields.

Figure 9. Magnetization curves of samples GOOle3 (upright triangles) and GOOle4 (upside-down triangles) measured at 300 K, including a demagnetizing correction, and Langevin fits with models 1 (red solid lines) and 2 (black dashed lines). Linear and logarithmic axes are used in plots (a) and (b), respectively. The four segments of curve corresponding to the full magnetization loop have been transported to the positive quadrant and plotted together for each sample.

The average diameters obtained from all Langevin fits are summarized in Table 2, together with the average diameters determined by TEM (\(D_{\text{avg}}\)) and the average crystallite sizes determined by XRD (\(D_{XRD}\)). Comparison of the particle-number-weighted average diameter (\(D_{\text{nad}}\)) with \(D_{\text{avg}}\) for samples GOAc3 and GOAc4 shows a clear underestimation of the experimental values by both models. In the case of samples GOOle3 and GOOle4, the agreement between \(D_{\text{nad}}\) and \(D_{\text{avg}}\) is much better. Model 1 gives a better estimation of \(D_{\text{avg}}\) than model 2 when no demagnetizing correction is applied, with maximum relative errors in the set of two samples of 3 and 10 %, respectively. The application of a demagnetizing correction with model 2 reduces the relative error between \(D_{\text{nad}}\) and \(D_{\text{avg}}\) to 3 %, without significantly changing the values obtained from model 1.

Both the slight deviations between modelled and experimental magnetization curves at low fields and the discrepancies between \(D_{\text{avg}}\) and \(D_{XRD}\) for samples GOAc3 and GOAc4 could be related to particle size and aggregation. A requirement for the superparamagnetic behavior of an ensemble of nanoparticles is that the interaction energy between adjacent particles is smaller than \(k_B T\). In the case of densely packed iron oxide nanoparticles, this requirement corresponds to a particle diameter smaller than 8 nm.\(^{31}\) The particle size histograms of samples GOAc3 and GOAc4 (Fig. 2) show an important fraction of nanoparticles with diameters above this threshold value. Therefore, the superparamagnetic nanoparticle models used in this study do not provide a good description of this fraction of particles, and discrepancies between model and experiment are to be expected for these samples.

The standard deviation of the natural logarithm of the particle volumes (\(\sigma\)) is clearly larger than the corresponding value obtained from particle size histograms (\(\sigma_{\text{TEM}}\)) for all samples and models (Tables S1, S2 and S3). This could be indicative of the limited representativity of the size determination method by TEM, as only an extremely small fraction of the total number of nanoparticles in each sample could be measured. Taking into account the heterogeneity of the starting GO, the processes of nanoparticle nucleation and growth, and thus final size, are likely to be affected by the characteristics of each GO flake (e.g., degree of oxidation, stacking and defects). Therefore, the particle size distribution in each RGO flake is expected to be shifted above or below the overall sample average particle size for some flakes, which will broaden the overall distribution. Given the quality of the Langevin fits and the good agreement with \(D_{\text{avg}}\) especially with samples GOOle3 and GOOle4 after applying a demagnetizing correction, the log-normal particle size distributions obtained from these fits must be closer to the real size distributions of the samples than those obtained from TEM.

Considering the XRD results, \(D_{XRD}\) values are compatible with the calculated \(D_{\text{nad}}\) for GOOle3, as expected from single-crystal particles, but not for GOAc3, despite the large uncertainty. This further supports the hypothesis that particles in sample GOOle3 are single crystals while sample GOAc3 contains polycrystalline particles.

Regarding the other physical parameters of the models, paramagnetic shell thickness values extracted from model 2 are around 4 – 5 Å in all cases, in agreement with other published values for iron oxide nanoparticles of similar sizes.\(^{33,79}\) and \(X_{\text{bulk}}\) values are small (< 0.01). It must be noted that the spontaneous magnetizations obtained from model 1 are significantly smaller than the values for bulk maghemite and magnetite. These changes in spontaneous magnetization are inconsistent with the nanoparticles having the same composition and structure as the bulk, making model 1 less reliable for obtaining information.
about their magnetic structure and properties. Model 2 is more physically meaningful as it attributes the decrease in the spontaneous magnetization of the particles to surface effects, by considering a shell that behaves paramagnetically. Effects such as surface spin canting due to the incomplete coordination of surface ions are captured by including this paramagnetic shell.\(^{79-81}\) In addition, the fact of \(\chi_{\text{mag}}\) being morphologically associated to the shell is more reasonable, as the entire particle cannot be both ferrimagnetic and significantly paramagnetic at the same time. For these reasons, the core-shell model is preferable over the uniform one.

The particle size determination method shown here for RGO-SPION composites could potentially be applied to superparamagnetic nanoparticles of other compositions supported or embedded in other materials, as long as the support is non-magnetic or its contribution to the magnetization of the composite can be subtracted. The assumption of an adequate particle model and type of particle size distribution is key for the accurate size determination, together with the potential correction of demagnetizing effects, and must be individually considered for each particular material under study. However, these considerations can provide additional valuable information on the magnetic structure of the sample, making the presented method a good complement for the thorough characterization of the sample even in less complex cases where TEM or XRD can already provide accurate particle size information.

CONCLUSIONS

This work has presented the synthesis of non-agglomerated monodispersed superparamagnetic iron oxide nanoparticles (SPION) on reduced graphene oxide (RGO) and the accurate characterization of their particle size distribution, by introducing a fast and simple microwave-assisted synthesis using stabilizers and an accurate size determination method from magnetization curves. The novel synthesis method rendered RGO-SPION composites with well dispersed particles and narrow size distributions, thanks to the modification of the surface chemistry of the SPION and RGO by means of a steric stabilizer during microwave irradiation. This addressed the poor particle size control and agglomeration from previously reported microwave-assisted methods. In addition, this simple and cheap one-step process lasted for only 15 min and used temperatures below 200 °C, making it preferable to typical non-microwave-assisted stabilized methods. The fits of the Langevin function to the measured magnetization curves assuming log-normal particle volume distributions were excellent for samples with well-dispersed nanoparticles. The calculated nanoparticle diameters were within a 3 % of the values determined from transmission electron microscopy (TEM) for the best fits after accounting for demagnetizing effects, and the fact that the calculated size distributions were broader was attributed to the limited representativity of TEM studies. Crystallite size values obtained with Scherrer’s equation had a large uncertainty due to the high level of noise of the X-ray diffraction (XRD) patterns, and were only comparable to those obtained from TEM or magnetic fits in samples consisting of single-crystal particles. This exposed the limitations of size determination from powder XRD in such complex materials. Finally, the core-shell nanoparticle model was found to render more physically meaningful parameters in comparison to the uniform model, giving more insight into the magnetic structure of the nanoparticles.

In view of these results, the superparamagnetic nanoparticle size determination from magnetization curves has been shown to be a well-suited method for RGO-SPION composite nanomaterials when the characteristics of the sample and the model are adequate. This method, being accurate and sample-representative, can be advantageous over the typical size determination from TEM micrograph analysis in such complex samples, where the heterogeneity of the starting carbon matrix adds a source of variability of particle sizes. In addition, the comparison of different particle models can be used to gain insight into the magnetic structure of the nanoparticles. Future work should be directed towards testing this method in superparamagnetic nanoparticles of other compositions supported or embedded in other materials, in order to identify suitable assumptions for its application in those cases. This would help making the method more accessible to the whole magnetic nanoparticle research community.

ASSOCIATED CONTENT

Supporting Information. Data from the characterization of the prepared GO and control GO-MW, additional TEM and SEM images and TG/DSC data of the RGO-SPION samples, and parameter values used for the particle size determination from magnetization curves are available in the online version of this article.

AUTHOR INFORMATION

Corresponding Author
*alvar.sanchez@uab.cat
*gerard.tobias@icmab.es

Present Addresses
1 Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

ACKNOWLEDGMENTS

We thank financial support from projects 2017-SGR-105 and 2017-SGR-581 (Generalitat de Catalunya), and projects MAT2017-86066-R and MAT2016-79426-P from Agencia Estatal de Investigación (Spain) // Fondo Europeo de Desarrollo Regional (UE). A.S acknowledges a grant from ICREA Academia, funded by the Generalitat de Catalunya.

REFERENCES


(57) Bronstein, L.; Huang, X.; Retrum, J.; Schmucker, A.; Pink, M.;


Table 1. Elemental composition calculated from the C1s and O1s high resolution XPS spectra (in atomic %)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C content (at. %)</th>
<th>O content (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C=C</td>
<td>C-OH / C-O-C</td>
</tr>
<tr>
<td>GO</td>
<td>20.7</td>
<td>22.1</td>
</tr>
<tr>
<td>GO-MW</td>
<td>60.0</td>
<td>17.1</td>
</tr>
<tr>
<td>GOAc3</td>
<td>33.3</td>
<td>22.6</td>
</tr>
<tr>
<td>GOOle3</td>
<td>45.0</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Table 2. Particle size determination results for samples GOOle3 and GOOle4

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_{\text{avg}}$ (nm)</th>
<th>$D_{\text{XRD}}$ (nm)</th>
<th>$D_{\text{nd}}$ (nm)</th>
<th>$D_{\text{vd}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GOAc3</td>
<td>7.27±0.09</td>
<td>5.3±1.8</td>
<td>6.70</td>
<td>5.36</td>
</tr>
<tr>
<td>GOAc4</td>
<td>8.00±0.09</td>
<td>-</td>
<td>6.71</td>
<td>6.33</td>
</tr>
<tr>
<td>GOOle3</td>
<td>4.95±0.04</td>
<td>4.6±1.8</td>
<td>5.07</td>
<td>4.44</td>
</tr>
<tr>
<td>GOOle4</td>
<td>4.98±0.05</td>
<td>-</td>
<td>5.11</td>
<td>4.87</td>
</tr>
</tbody>
</table>

$D_{\text{avg}}$ is the experimental average diameter extracted from TEM (particle counting) and $D_{\text{XRD}}$ is the average crystallite size extracted from XRD (Scherrer equation). $D_{\text{nd}}$ is the particle-number-weighted average diameter, calculated using equation (8), and $D_{\text{vd}}$ is the particle-volume-weighted average diameter, calculated using equation (7).

* Fits after applying the demagnetizing correction.