GREEN SYNTHESIS OF IRON OXIDE NANOPARTICLES

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Abstract

The present article deals with the problematic of so called green synthesis of iron oxide nanoparticles. The iron oxide nanoparticles can be used e.g. for catalysators and gas sensors or in MRI. The green synthesis is an innovative environmental friendly method which uses exclusively natural raw materials to obtain desired compounds. $Fe(NO_3)_3.9H_2O$ was used as iron oxide precursor and red onion peel extract, green tea leaves extract and starch solution were chosen as precipitating agents in the present work. The shape, size and phase of resulting particles were investigated using scanning electron microscope and Raman spectroscopy. Through the green synthesis two different allotropic modifications of iron oxide nanoparticles were obtained. The use of starch and red onion peel extract led to formation of hematite while green tea leaves caused formation of mixture of hematite + maghemite. The average size of obtained hematite nanoparticles prepared using starch solution was (30 ± 10) nm. The size of bean-shaped hematite nanoparticles prepared by using red onion peel extras was (130 ± 40) nm length and (70 ± 20) nm width. The mixture size of hematite + maghemite was measured on (100 ± 20) nm length and (60 ± 10) nm width.

Keywords: Iron oxide, Nanoparticle, structure, natural extracts, tea leaves, onion peel, starch

1. INTRODUCTION

Iron oxides nanoparticles (NPs) were intensively studied in various research areas. It is mainly because these nanoparticles can be used in many different branches, such as removal of cadmium from aqueous solution [1]. Iron oxides are also important as gas sensors and catalysators [2]. Another area with promising potential for application is medicine. Iron oxide particles may be used as drug delivery system, biosensors [3] or for contrast enhancement in magnetic resonance imaging (MRI) [4].

There is a plenty of different methods enabling preparation of iron oxide nanoparticles. Very common method is simple hydrazine reduction [4]. Experiments showed, that ethylene glycol is also suitable reactant for preparation of iron oxide nanoparticles [6]. However, natural extracts, such as tangerine extract [1], or polysaccharides, such as starch [7], are used for synthesis. The most important benefit of green synthesis method lays in the low cost of extracts or other natural products and because of satisfying results. In our experiments were used green tea and onion peel extracts. Along with these extracts, starch was also tested.

2. PARTICLE PREPARATION

In the beginning, NPs were prepared according to following methods:

Onion peel extract

Firstly, 60 g of red onion peel was cut into small pieces. These pieces were boiled in 600 ml of distilled water for 2.5 hours. After cooling to room temperature, the final amount of extract was filtered.

1 g of ferric nitrate hexahydrate was dissolved in 10 ml of distilled water. 20 ml of onion peel extract were added to the solution. After vigorous stirring for 2 hours, the colour of solution was brighter.

Green tea leaves extract

The tea leaves extract was prepared by 20 min of boiling of 10 g pure green tea leaves in 250 ml water. Resulting dark green extract was subsequently filtered to remove any impurities.

1 g of ferric nitrate nonahydrate was dissolved in 10 ml of distilled water and mixed with 10 g of tea leaves extract. The resulting solution was warmed up to 60 °C and stirred until water evaporation.

Starch

1 g of starch and 20 ml of distilled water were stirred at 60 °C until the solution wasn't transparent. Subsequently, solution of 1 g of ferric nitrate nonahydrate was added to the starch solution. After vigorous stirring, concentrated ammonia was added.

Heat treatment

The resulting products from all reactions were put into aluminium oxide crucibles and heat treated according to **Figure 1**. The temperatures were elected with respect to reactions observed through TGA (**Figure 2**). At approx. 185 °C occurred a stormy chemical reaction, thus slower heating ratio was elected around this temperature. The observed mass decrease between 250 to 400 °C corresponds to evaporation of residual organic compound. At higher temperature took place stabilization of the obtained product.

The morphology and chemical composition of final products were analysed using UHR-SEM Zeiss Ultra Plus equipped with an energy-dispersive X-ray spectrometer Oxford X-Max for local chemical analysis. The particle size was evaluated using image analysis in NIS Elements SW.

The Raman spectra were recorded by DXR Raman Microscope (Thermo Scientific, USA) with 532 nm laser, Hi-Res grating 1800 lines/mm in spectral range 1850-50 cm-1 and objective Olympus LMPlanFL 50x. It was used 50 µm slit spectrograph aperture, level of laser power was 0.2 mW with 5 sec exposure time and 20 exposures.

TGA Q500 (TA Instruments, USA) was used for thermogravimetric (TG) analysis. The TG curve was recorded in reactive atmosphere of synthetic air with platinum pan and thermal ramp 10 °C per min from room temperature to 800 °C.

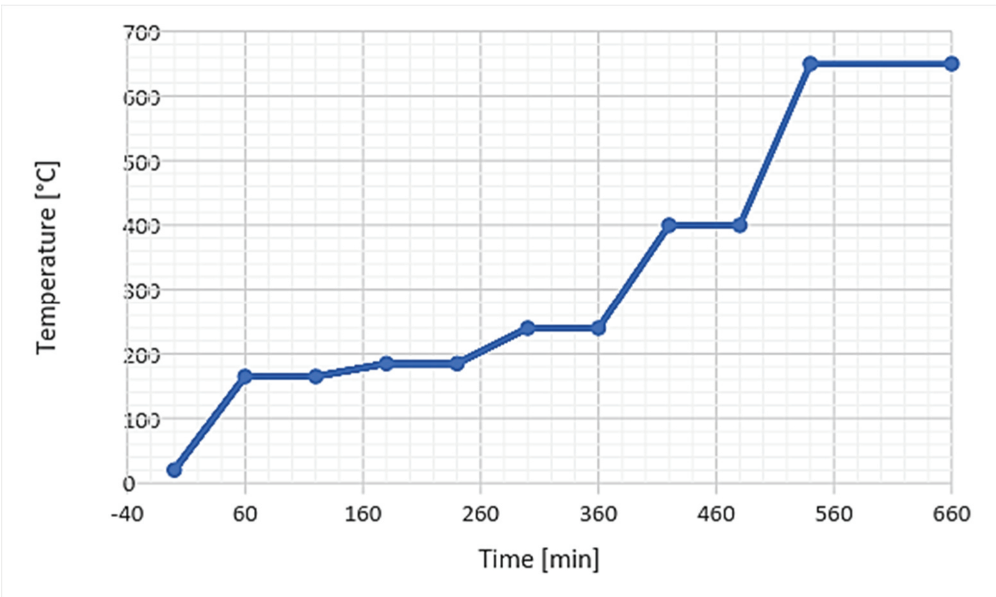

Figure 1 A graph showing the course of dried powder heat treatment.

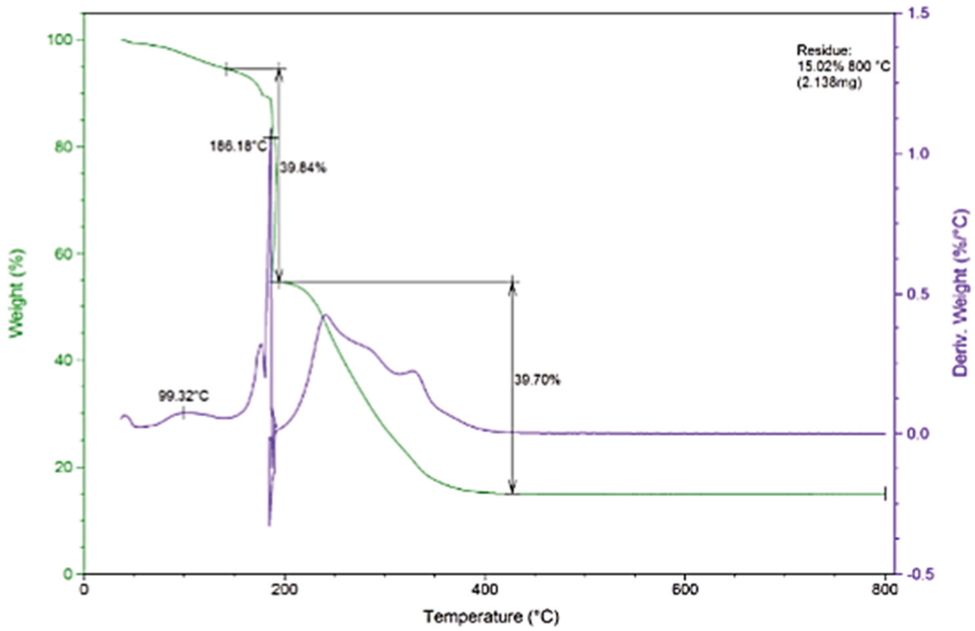

Figure 2 A graph taken from TGA analysis showing the dependence of sample mass on the temperature

3. RESULTS AND DISSCUSSION

3.1. Iron oxide nanoparticles made using onion peel extract

The onion peel extract was selected due to a high concentration on dyes presented in the peel. These dyes form complexes with iron ions and thus keep this ion more stable to higher temperature causing formation of huge amount of fine-sized precipitates and limits their tendency to coarse. The structure of resulting nanopowder is shown in **Figure 3**. The powder is composed of bean-shaped particles with average size (130 ± 40, 70 ± 20) nm. It is obvious, that the structure of sample is grooved, so it would be possible to disintegrate bigger structures to smaller ones, e.g. by the use of ultrasonic treatment. It can be suggested that the size of obtained particles is dependent of dyes concentration and thus further study for the dependence of concentration is necessary.

3.2. Iron oxide nanoparticles made using starch

The starch solution contains shorter chains of glucose, because of the hydrolysis of bonds between glucose units. It can be supposed that the iron ions are bonded through hydroxyl groups forming complexes which act similarly as was described previously. The resulting fine nanoparticles, with average size 30 ± 10 are in clusters with a crust on the top, as we can see in **Figure 4**.

3.3. Iron oxide nanoparticles made using tea leaves extract

Tea leaves contain high amount of polyphenolic dyes, especially quercetin. The final dry nanopowder is composed of bean shaped particles, with average length of 100 ± 20 nm and average width 60 ± 10 nm. The size and shape distribution is very homogenous as visible from **Figure 5**.

3.4. Phase identification

The phases present in the nanopowders were identified using Raman spectroscopy. An example of obtained spectra is shown in **Figure 6**. There are compared spectra of particles synthetized using tea leaves extract (red) and onion extract (cyan blue) and hematite (purple) as reference spectrum. It is clearly visible that the red line (green tea leaves extract) reports some peak difference compared to hematite. Peaks at 719, 456 and 368 cm^{-1} refers to maghemite phase. It is obvious, that the powder is not pure maghemite, but it is the mixture of maghemite and hematite. The formation of maghemite phase could be explained through the presence of quercetin in the green tea leaves. The quercetin is able to reduce Fe^{3+} to Fe^{2+} (green tea is well known as an antioxidant).

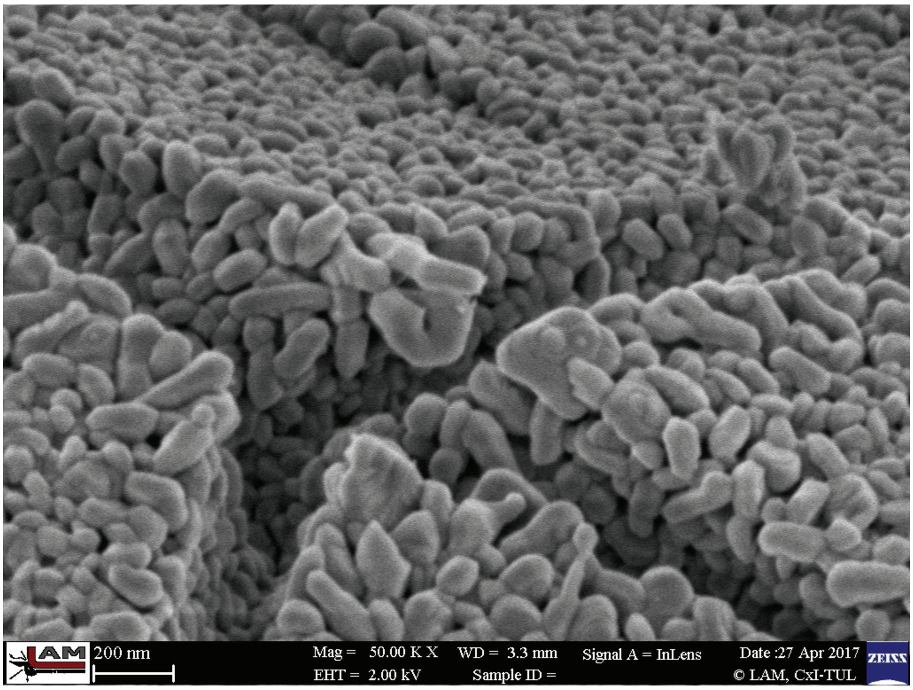

Figure 3 Iron oxide nanoparticles prepared with onion peel extract. Also, these particles are in cluster, which are strongly grooved

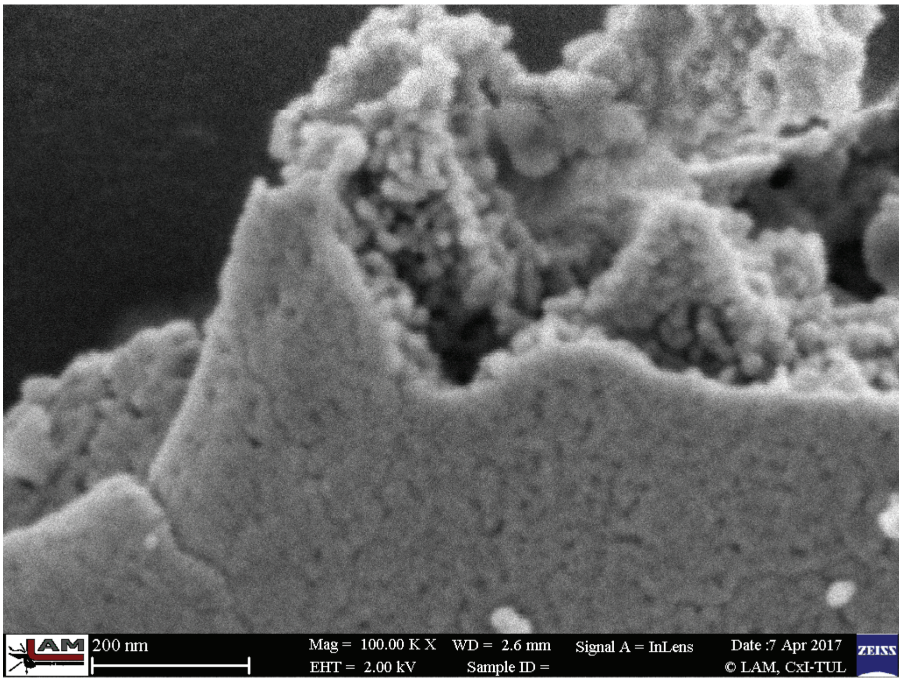

Figure 4 Iron oxide nanoparticles synthetized using starch

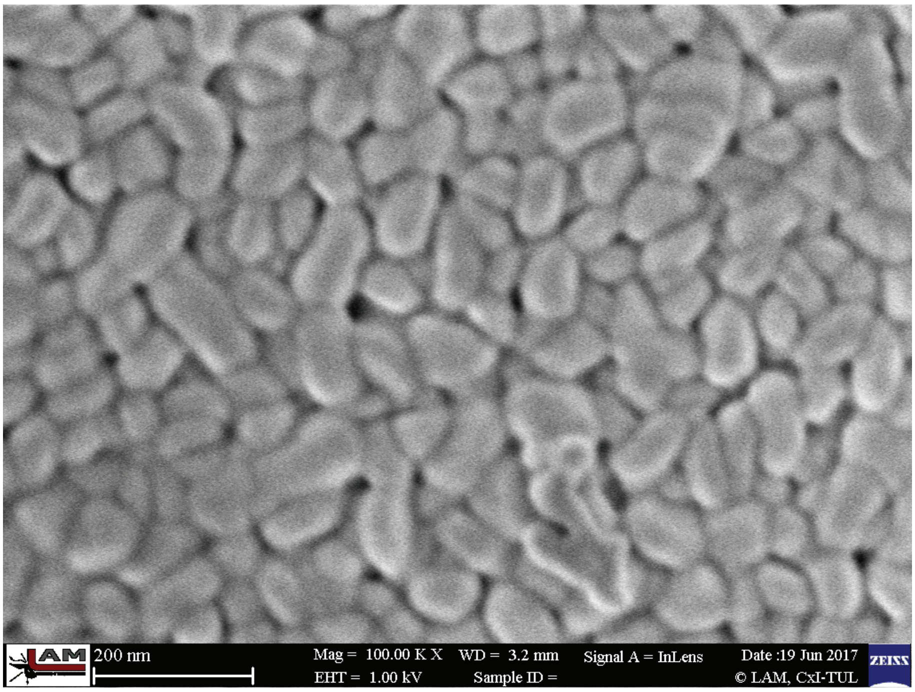

Figure 5 Bean shaped iron oxide nanoparticles, prepared using green tea leaves extract

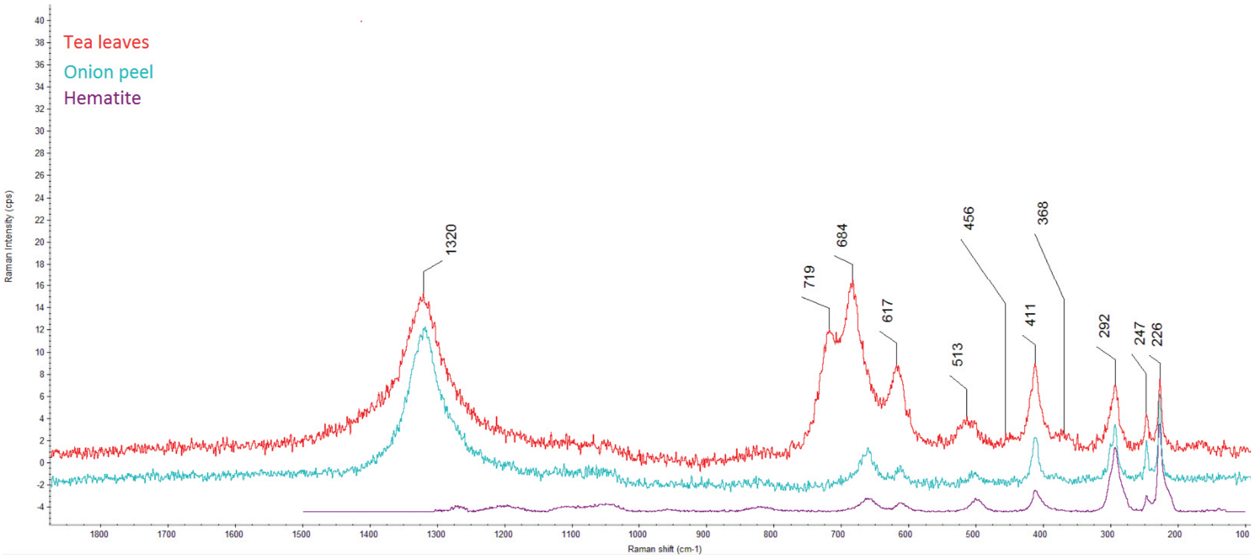

Figure 6 The spectrum obtained from Raman spectroscopy

Table 1 Measured particle size and phase of iron oxide for different green extracts

	Average particle size	**Phase**
Onion peel	130 ± 40, 70 ± 20	Hematite
Tea leaves	100 ± 20, 60 ± 10	Maghemite + Hematite
Starch	30 ± 10	Hematite

The macro image of resulting products using different “green” extracts is shown in **Figure 7**. We can observe, that the products differ slightly in their colour.

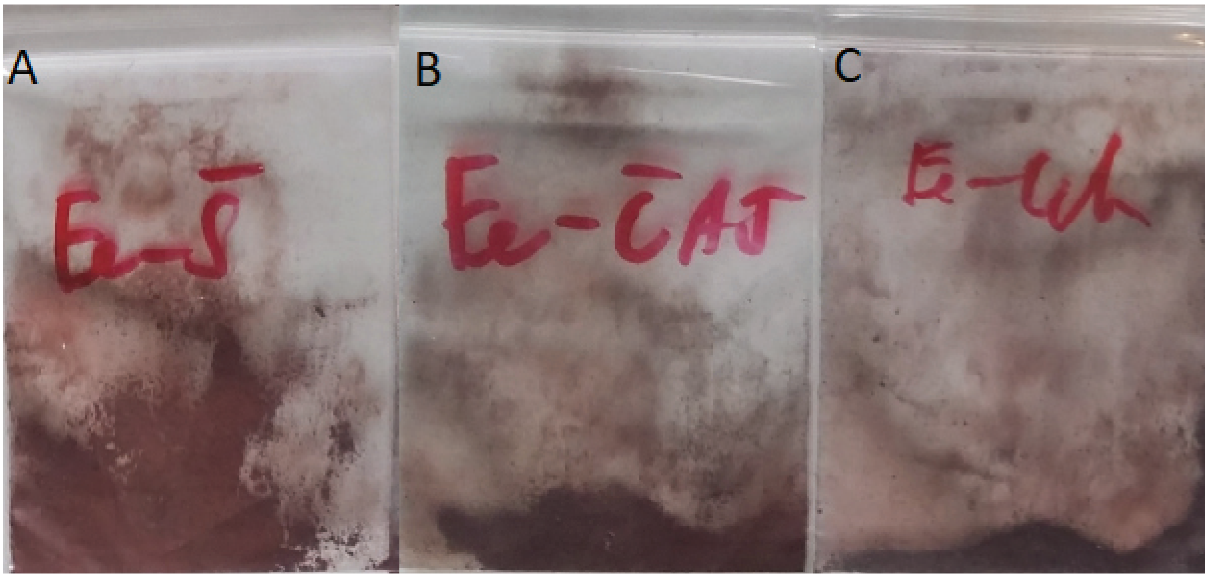

Figure 7 Macroimage of resulting products obtained by the reaction of green substance + $Fe(NO_3)_3.9H_2O$. Used green substances were: A) Starch; B) Green tea leaves extract; C) Onion peel extract

4. CONCLUSION

Green synthesis was successfully used for preparation of well-defined iron oxide nanoparticles. The smallest particles were obtained using starch solution. The synthesis with the use of onion peel extract and green tea leaves extract resulted with bean shaped iron oxide nanoparticles.

It is possible to synthetize maghemite (paramagnetic phase) using only green tea leaves extract. Despite the initial success, further research is necessary to study the reaction and the influence of type of tea, tea extract concentration etc. to the final product.

Hematite was synthetized using both, starch and red onion peel extract. Despite, onion peel is waste material, which is usually used only for composting, the result was truly satisfying. Iron oxide nanoparticles were well homogenous, composed from clusters, which are strongly grooved. This opens a possibility to try to use some disintegration methods to destroy massive structures to small pieces. Particles, prepared using starch reports structures with a crust on the top of the clusters. That is a difference, compared to the extracts.

To end up with, following research is necessary. It is obvious, that green synthesis is a promising way how to synthetize nanoparticles in the future. It is way, how to prepare well defined low cost nanoparticles with a minimum amount of pollution and zero toxic waste.

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