

EFFECT OF SYNTHESIS CONDITIONS ON THE PROPERTIES OF MAGNETIC NANOFLOWERS

Viktória Hornok¹, Erzsébet Illés²

¹*Department of Physical Chemistry and Materials Science, University of Szeged, H-6720 Szeged, Aradi vt. tere 1, Hungary*

²*Department of Food Engineering, University of Szeged, H-6724 Szeged, Mars tér. 7, Hungary*
e-mail: vhornok@chem.u-szeged.hu

Abstract

Magnetic nanoflowers (MNF) can be applied in complementary cancer therapy treatment, however, some of the preparation conditions and stability experiments have not been examined in great detail. In this study, magnetite nanoparticles (NPs) with flower-like architecture were synthesized, characterized and tested by magnetic hyperthermia. The preparation and characterization of flower-shaped magnetic objects were optimized in two types of reaction vessels. The two different synthesis methods resulted in magnetic nanoparticles (MNP) of slightly different morphology, resulting in different behavior for hyperthermia. The stability of the NPs was achieved by the application polymer functionalization both by in situ and post-coating methods.

Introduction

The colloid aqueous dispersion of superparamagnetic iron oxide nanoparticles (SPIONs) is very popular partly due to their potential theranostic application, indicating the combined possibility of therapy and diagnosis. Moreover, SPIONs can be used as a complementary therapy in cancer treatment. Their favorable magnetic properties can be further improved by preparing flower-like structures [1]. There have been some studies in recent years, aiming to prepare magnetite nanoflowers (MNF), however, the preparation conditions are quite different and lack detailed stability experiments.

Experimental

In this study, the MNFs were prepared from Fe(II) and Fe(III) chloride salts and NaOH dissolved in diethylene glycol (DEG) and N-methyl-diethanolamine (NMDA) mixture. The reaction was carried out both in an autoclave and in a round-bottom flask (either with or without continuous mixing) at 220 °C [2]. The magnetite structure was verified by X-ray diffraction measurements. As a stabilizing agent, based on earlier results [3], polyacrylic acid (PAA) and a copolymer, poly(acrylic acid-co-maleic acid) (PAM) was applied both during and after synthesis. The optimal pH and amount of stabilizing polymer were confirmed by both zeta-potential and dynamic light scattering (DLS) measurements. To provide information about their potential medical application, magnetic hyperthermia measurements were carried out [4].

Results and discussion

The results verified the crucial importance of some preparation conditions, such as the composition of the reaction solvent mixture, reaction time and rate of heating and cooling. Transmission electron microscopic images (TEM) of the nanoparticles revealed that as an effect of mixing, more fluffy structures with were obtained (Figure 1B).

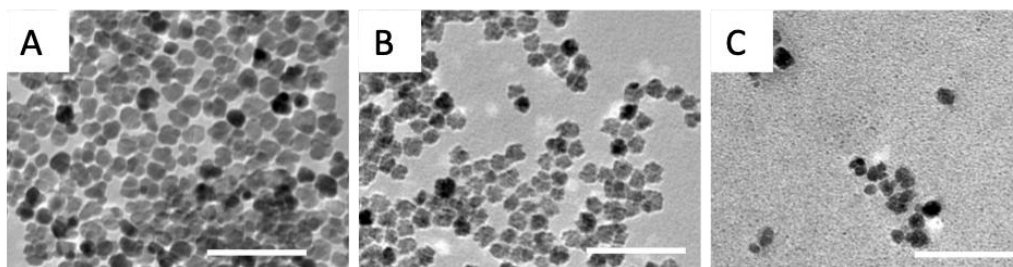


Figure 1. TEM images of MNF prepared without (A), with continuous mixing (B) and in-situ stabilized by PAA (C). The scale-bar above represent 100 nm.

To ensure NP stability for potential medical applications, the addition of polymers was carried out and zeta-potential measurements indicated the pH-dependent characteristics. If PAM polymer was added to the system during synthesis, the NP average diameter, determined by TEM, was significantly smaller, 14.0 ± 2.8 nm compared to the value of 19.5 ± 4.8 nm obtained for the NPs prepared in autoclave. During the post-coating method, a minimum of 0.7 mmol/g of polymer proved to be necessary for the stabilization of MNF.

Conclusion

Magnetic flower-like structures were prepared by the polyol method by two methods with difference in mixing or not. As a result, MNFs were obtained with similar average diameter but different primary particle size, resulting in different fine structures. With the variation of synthesis parameters, it has been revealed that the cooling rate plays a crucial part in the resulting NPs with an average particle diameter ranging from about 72 nm to ~20 nm. To obtain stable NPs, both in situ and post-coated method was applied with the help of two polymers. As for the hyperthermia result, our MNFs unquestionably possess a high effect, underlying the morphology suggestion for increased effect of the cooperation of small magnetic individuals. As a result, our NPs define the requirement of stable flower structures with increased hyperthermia effect.

Acknowledgements

This research was supported by the Hungarian National Research Development and Innovation Office (NRDIH) through the FK131739 project and by the ÚNKP-23-5-SZTE-700 New National Excellence Program of the Ministry for Culture and Innovation from the source of the National Research, Development and Innovation Fund.

References

- [1] V. Socoliuc *et al.*, Magnetic nanoparticle systems for nanomedicine-a materials science perspective”, *Magnetochemistry* 6 (2020) 1.
- [2] D. Caruntu *et al.*, Synthesis of Variable-Sized Nanocrystals of Fe_3O_4 with High Surface Reactivity, *Chem. Mater.* 16 (2004) 5527.
- [3] I. Y. Tóth, E. Illés, R.A. Bauer, D. Nesztor, M. Szekeres, I. Zupkó, E. Tombácz, *Langmuir*, 2012, 28: 16638 – 16646.
- [4] L. Lartigue *et. al.*, Cooperative Organization in Iron Oxide Multi-Core Nanoparticles Potentiates Their Efficiency as Heating Mediators and MRI Contrast Agents, *ACS Nano* 6, 12 (2012) 10935-10949.