

Bioengineered



ISSN: 2165-5979 (Print) 2165-5987 (Online) Journal homepage: https://www.tandfonline.com/loi/kbie20

Controlled synthesis of iron oxyhydroxide (FeOOH) nanoparticles using secretory compounds from *Chlorella vulgaris* microalgae

Ali Ghanbariasad, Seyedeh-Masoumeh Taghizadeh, Pau Loke Show, Saifuddin Nomanbhay, Aydin Berenjian, Younes Ghasemi & Alireza Ebrahiminezhad

To cite this article: Ali Ghanbariasad, Seyedeh-Masoumeh Taghizadeh, Pau Loke Show, Saifuddin Nomanbhay, Aydin Berenjian, Younes Ghasemi & Alireza Ebrahiminezhad (2019) Controlled synthesis of iron oxyhydroxide (FeOOH) nanoparticles using secretory compounds from *Chlorella vulgaris* microalgae, Bioengineered, 10:1, 390-396, DOI: <u>10.1080/21655979.2019.1661692</u>

To link to this article: https://doi.org/10.1080/21655979.2019.1661692

9	© 2019 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.	Published online: 09 Sep 2019.
	Submit your article to this journal $arsigma$	Article views: 1100
à	View related articles 🗷	Uiew Crossmark data 🗹
ආ	Citing articles: 3 View citing articles 🗷	

RESEARCH PAPER

Taylor & Francis Taylor & Francis Group

OPEN ACCESS Check for updates

Controlled synthesis of iron oxyhydroxide (FeOOH) nanoparticles using secretory compounds from *Chlorella vulgaris* microalgae

Ali Ghanbariasad^a*, Seyedeh-Masoumeh Taghizadeh^b*, Pau Loke Show ^b^c, Saifuddin Nomanbhay^d, Aydin Berenjian^e, Younes Ghasemi^b, and Alireza Ebrahiminezhad^f

^aDepartment of Medical Biotechnology, School of Medicine, and Noncommunicable Diseases Research Centre, Fasa University of Medical Sciences, Fasa, Iran; ^bDepartment of Pharmaceutical Biotechnology, School of Pharmacy, and Pharmaceutical Sciences Research Center, Shiraz University of Medical Sciences, Shiraz, Iran; ^cDepartment of Chemical and Environment Engineering, Faculty of Science and Engineering, University of Nottingham, Semenyih, Malaysia; ^dInstitute of Sustainable Energy (ISE), Universiti Tenaga Nasional (The Energy University), Kajang, Malaysia; ^eFaculty of Science and Engineering, The University of Waikato, Hamilton, New Zealand; ^fDepartment of Medical Nanotechnology, School of Advanced Medical Sciences and Technologies, Shiraz University of Medical Sciences, Shiraz, Iran

ABSTRACT

FeOOH nanoparticles are commonly synthesized at very high temperature and pressure that makes the process energy consuming and non-economic. Recently, novel approaches were developed for the fabrication of these particles at room temperature. But, the main problem with these methods is that the prepared structures are aggregates of ultra-small nanoparticles where no intact separate nanoparticles are formed. In this study, for the first time, secretory compounds from *Chlorella vulgaris* cells were employed for the controlled synthesis of FeOOH nanoparticles at room atmosphere. Obtained particles were found to be goethite (α -FeO(OH)) crystals. Controlled synthesis of FeOOH nanoparticles resulted in uniform spherical nanoparticles ranging from 8 to 17 nm in diameter with 12.8 nm mean particle size. Fourier-transform infrared and elemental analyses were indicated that controlled synthesized nanoparticles have not functionalized with secretory compounds of *C. vulgaris*, and these compounds just played a controlling role over the synthesis reaction.

ARTICLE HISTORY

Received 10 July 2019 Revised 19 August 2019 Accepted 20 August 2019

KEYWORDS

Carbohydrate; iron nanoparticles; iron oxide hydroxide nanoparticles; iron oxide nanoparticles; secretory compounds



CONTACT Saifuddin Nomanbhay Saifuddin@uniten.edu.my Distitute of Sustainable Energy (ISE), Universiti Tenaga Nasional (The Energy University), Jalan IKRAM-UNITEN, Kajang 43000, Malaysia; Alireza Ebrahiminezhad a_ebrahimi@sums.ac.ir School of Advanced Medical Sciences and Technologies, Unit 23, Floor 2, Almas Building, Mulla Sadra Intersection, Shiraz 71336-54361, Iran

*These authors coordinated equally in this work.

This article has been republished with minor changes. These changes do not impact the academic content of the article.

© 2019 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. Introduction

Iron-based nanoparticles are one of the most applied nanostructures in science, technology, and medicine. These particles represent unique physicochemical and biological properties that make them interesting compounds in various fields of nanotechnology and nanosciences. Ironbased nanoparticles are now being used in diverse applications such as environmental remediation [1], microbial sciences, imaging systems [2], pharmaceutical sciences [3,4], biological products [5,6], civil engineering [7], immobilization techniques [8-10], and chemical industries [11]. Among these particles, iron oxide hydroxide (FeOOH) nanoparticles have gained unique technical applications such as pigment industries, environmental remediation, and medical supplements [12-16]. FeOOH nanoparticles have a promising capacity for toxic ion uptake and hence are widely employed in environmental remediation activities. These particles are able to remove metallic cation pollutants such as arsenic and chromium [17-19]. FeOOH nanoparticles are also able to remove fluoride from contaminated aqueous environments [20]. Besides adsorbent capacities, these particles are emerged as effective nanocatalyst in chemical reduction reactions [21].

Increasing applications of FeOOH nanoparticles in various fields resulted in increasing demand for production of these nanostructures in a sustainable manner. FeOOH nanoparticles are commonly synthesized at a high temperature which makes the process energy consuming and non-economic [22,23]. Recently, some efforts have been made to develop a procedure for fabrication of FeOOH nanoparticles at room temperature [16,24]. However, the major problem with these techniques is that the produced nanoparticles are not uniform in shape and size. For instance, Luna et al. have reported the fabrication of FeOOH nanoparticles at room temperature. The prepared particles were reported to be agglomerates of ultrafine nanoparticles with about 3.3 nm in diameter. The authors also reported the presence of some large rod-like structures with 23 ± 5 nm in length and 5 ± 1 nm in width [24]. Similar problems were found in the biosynthesized nanoparticles using Klebsiella oxytoca and Ralstonia sp. [25,26].

Previous investigations revealed that both intracellular and extracellular bioactive compounds from Chlorella vulgaris microalgae can play a shape-directing role in the fabrication of metallic nanoparticles [27-29]. Algal proteins and carbohydrates were identified as the main intracellular and secretory shape-controlling factors, respectively [27-29]. The carboxyl groups in Asp and/or Glu residues of algal proteins were driving the anisotropic growth of Ag nanocrystals into nanoplates [28,29]. Nevertheless, secretory carbohydrates made the particles fairly uniform in both shape and size. Also, secretory carbohydrates controlled the nanoparticle growth pattern and induced isotropic growth of nanocrystals [27]. The present investigation, therefore, aims at evaluating secretory carbohydrates from C. vulgaris for shape-controlling fabrication of uniform FeOOH nanoparticles at room atmosphere.

2. Materials and methods

2.1. Materials

All chemicals were purchased from Merck in analytical grade and used as received without any further purification. Millipore water (resistance >18 M Ω cm⁻¹) was used throughout the experiment.

2.2. Culture of microalgal cells

C. vulgaris cells were cultured $(10^7 \text{ cell ml}^{-1})$ in 250 ml Erlenmeyer flask containing 100 ml of BG-11 broth medium and incubated at 27°C in 16 h light/8 h dark cycle with light intensity of 60 μ Em⁻¹ s⁻¹ cool white fluorescent lamp. After 20 days, at the end of growth logarithmic phase, cells were harvested by centrifugation, and the supernatant was employed for nanoparticle synthesis [27].

2.3. Uncontrolled synthesis of FeOOH nanoparticles

Uncontrolled synthesis of FeOOH nanoparticles was performed as described previously by Luna et al. with some modification [24]. Briefly, 1.1 g FeCl₃.6H₂O was dissolved in 25 ml deionized

water and then 30 ml sodium hydroxide solution (5 M) was rapidly added to start the reaction. The mixture was maintained 15 min under vigorous steering at room atmosphere. The resulting suspension was centrifuged at 4000 rpm for 20 min. The precipitate was washed three times by deionized water and dried in an oven at 50°C for 48 h.

2.4. Controlled synthesis of FeOOH nanoparticles

Controlled synthesis of FeOOH nanoparticles was performed in the presence of *C. vulgaris* secretory carbohydrates. Briefly, 1.1 g FeCl₃.6H₂O was dissolved in 25 ml culture supernatant and then 30 ml sodium hydroxide solution (5 M) was rapidly added under vigorous steering. The reaction was followed for 15 min at room temperature. The dark brown precipitate was harvested by centrifugation at 4000 rpm for 20 min. The resulting precipitate was washed three times by deionized water and dried in an oven at 50°C for 48 h.

2.5 Characterization of the synthesized nanoparticles

A drop of the prepared nanoparticle suspension was dripped on a carbon-coated grid Cu Mesh 300 Formvar and dried at room temperature. Transmission electron microscopy (TEM) analysis was done by using Zeiss EM10C, TEM, operated at HT 80 kV. Diameters of 100 particles were measured randomly using ImageJ (version 1.47v), an image analyzing software developed by the National Institutes Health (http://imagejnihgov/ij/). of Fourier-transform infrared (FTIR) spectroscopy analysis was done on a PerkinElmer FTIR spectrometer using KBr pellets. The crystallinity of the particles was evaluated by x-ray diffraction patterns (XRD, Siemens D5000) using fine powder of nanoparticles. Chemical composition of the sample was analyzed by using a CHNS elemental analyzer (Costech, ECS 4010).

3. Results and discussion

By the addition of sodium hydroxide solution to the reaction mixture, a sudden change in the color was occurred from light orange to yellowish-brown, suggesting the formation of iron oxyhydroxide (FeOOH) colloidal suspension. In this reaction, FeOOH nanoparticles precipitate upon hydrolysis of ferric ions. Sodium hydroxide acts as a precipitating agent and FeOOH nanoparticles are formed as represented in Equation (1) [12,30].

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$$

 $\rightarrow FeOOH + H_2O$ (1)

After centrifugation and harvesting FeOOH nanoparticles, a completely clear supernatant was obtained. TEM micrographs revealed that uncontrolled synthesis of FeOOH nanoparticles resulted in large aggregates of ultrafine nanoparticles (Figure 1(a)). However, controlled synthesis in the presence of secretory carbohydrates from *C. vulgaris* resulted in the discrete spherical nanoparticles ranging from 8 to 17 nm in diameter with an average size of 12.8 nm (Figures 1(b) and 2). It has been reported that uncontrolled synthesis of FeOOH nanoparticles at room temperature resulted in the aggregates of ultrafine nanoparticles. At this reaction condition also, a second community of large

a Too ma

Figure 1. TEM micrographs of the uncontrolled (a) and controlled (b) synthesized FeOOH nanoparticles.



Figure 2. Particle size distribution of the controlled synthesized FeOOH nanoparticles.



Figure 3. FTIR spectra of the uncontrolled (a) and controlled (b) synthesized FeOOH nanoparticles.

nanorods can be observed [24]. In this experiment, the presence of secretory carbohydrates in the controlled synthesis reaction inhibited the formation of second community of large nanostructures. These results are in close agreement with previous findings of the shape-controlling effect of the secretory carbohydrates from C. vulgaris [27]. In addition, a similar controlling effect reported was for monosaccharides such as dextrose [31]. It is believed that carbohydrates can control the reaction in both nucleation and growth phases. In the nucleation phase, carbohydrates prevent monotonic nucleation by chelation of iron ions and limit the size of nuclei. In the growth phase, carbohydrates control the growth of formed nuclei and inhibit the formation of large particles [31]. Besides biochemical species, chemical polymers can also control the fabrication of FeOOH nanoparticles and are employed for the shape- and size-controlled synthesis reactions [32]. It is obvious that reaction protocol and reaction conditions are other parameters that can control the resulted particle size and morphology [33,34].

FTIR spectra of uncontrolled and controlled synthesized particles were recorded and depicted in Figure 3. Characteristic peak of iron oxides which is from Fe–O bond was appeared at 617 cm⁻¹ [5,35,36]. The peak at 1339 cm⁻¹ is usually considered as C–O groups which may be from impurities. The O–H groups deforming and stretching vibration recorded at about 1502 and 3360 cm⁻¹, respectively. It has been reported that polysaccharides like guar gum and xanthan gum could be adsorbed to the surface of iron-based

nanoparticles [1]. Also, it has been shown that secretory carbohydrates from *C. vulgaris* can engulf silver nanoparticles in about 1 nm thickness. However, in the case of controlled synthesized FeOOH nanoparticles, secretory carbohydrates from *C. vulgaris* have not played any capping role.

XRD patterns of the uncontrolled and controlled synthesized nanostructures are shown in Figure 4. Recorded spectra revealed that the prepared structures are nanocrystals of goethite (a-FeOOH) [37]. The similarity in the crystalline structure of the uncontrolled and controlled synthesized nanoparticles revealed that secretory carbohydrates from C. vulgaris have not disturbed or modified the formation of nanocrystals. The recorded patterns seem to be nearly amorphous. However, similar broad hump-like peaks with very low intensity are usual for FeOOH nanoparticles [38]. Based on the pattern, both uncontrolled and controlled synthesized nanoparticles can be assigned to goethite (a-FeOOH) (JCPDS No. 22-0713) [32,39,40].

Results for elemental analysis of the prepared nanostructure are tabulated in Table 1. The corresponding CHNS chromatogram is also shown in Figure 5. Nitrogen, carbon, and hydrogen are made 0.02, 1.56, and 0.91 weight percent of the uncontrolled synthesized nanomaterial, respectively. These data are not significantly different from the uncontrolled synthesized nanoparticles. Elemental content of the controlled synthesized nanostructures was measured as N/A, 0.59, and



Figure 4. XRD pattern of the uncontrolled (a) and controlled (b) synthesized FeOOH nanoparticles. (c) XRD pattern of goethite crystals based on JCPDS card No. 22-0713.

1.03 for nitrogen, carbon, and hydrogen, respectively. These data are supporting the FTIR findings and confirm that secretory carbohydrates from *C. vulgaris* have a capping role in the formation of controlled synthesized FeOOH nanostructures. In addition to the previous report which has been shown that secretory carbohydrates from *C. vulgaris* can play a capping role in biologically synthesized silver nanoparticles [27], similar results were also reported for biosynthesized FeOOH nanoparticles. Carbohydrate contents of the biosynthesized nanoparticles were reported to be 17 and 25 weight percent in the case of *K. oxytoca* and *Ralstonia* sp. synthesized nanoparticles, respectively [25,26]. Preparation of pure FeOOH nanoparticles without the addition of any biological compound or surface modification can be a significant advantage as these particles are suitable for any required functionalization.

4. Conclusions

Culture supernatant of C. vulgaris is abundant with bioactive compounds where carbohydrates are the major part of these biomolecules. Current investigation revealed that culture supernatant of the C. vulgaris can be employed as a sustainable source of bioactive compounds for the controlled synthesis of FeOOH nanoparticles at ambient atmosphere. The prepared particles were pure (free of any biologic compound), spherical, uniform, and in the size range that is ideal for nanos-Characteristic advantages tructures. of the controlled synthesized nanoparticles over



Figure 5. CHNS chromatogram of the uncontrolled (a) and controlled (b) synthesized nanoparticles.

Table 1. Elemental composition (nitrogen, carbon, and hydrogen content) of the prepared nanostructures recorded by a CHNS elemental analyzer.

	Retention time		Weight		Weight	
Element	(min)		(mg)		(%)	
Sample	Uncontrolled synthesized	Controlled synthesized	Uncontrolled synthesized	Controlled synthesized	Uncontrolled synthesized	Controlled synthesized
Ν	1.257	1.287	0.001	N/A	0.02	N/A
С	2.517	2.520	0.062	0.018	1.56	0.59
Н	8.207	8.073	0.036	0.032	0.91	1.03
Total	-	-	3.993	3.071	2.49	1.62

uncontrolled synthesized FeOOH can make them a promising substitute for previously employed particles.

Highlights

- FeOOH nanoparticles were fabricated in a controlled synthesis reaction.
- Secretory compounds from *C. vulgaris* were used as a controlling agent.
- Secretory compounds have not disturbed or modified the formation of nanocrystals.
- Small nanospheres with a narrow particle size distribution were resulted.
- The resulted structures were uniform in shape and size.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This study was financially supported by a grant (Grant No. 97034) from the Research Deputy of Fasa University of Medical Sciences and a note of appreciation to iRMC UNITEN for the financial support through publication fund BOLD 2025 (RJO10436494).

ORCID

Pau Loke Show D http://orcid.org/0000-0002-0913-5409

References

- Xue D, Sethi R. Viscoelastic gels of guar and xanthan gum mixtures provide long-term stabilization of iron micro-and nanoparticles. J Nanopart Res. 2012;14(11). DOI:10.1007/s11051-012-1239-0
- [2] Ebrahiminezhad A, Ghasemi Y, Rasoul-Amini S, et al. Preparation of novel magnetic fluorescent nanoparticles using amino acids. Colloid Surf B. 2013;102:534–539.
- [3] Akbarzadeh A, Mikaeili H, Zarghami N, et al. Preparation and in vitro evaluation of doxorubicinloaded Fe_3O_4 magnetic nanoparticles modified with biocompatible copolymers. Int J Nanomedicine. 2012;2012(7):511–526.
- [4] Chertok B, Moffat BA, David AE, et al. Iron oxide nanoparticles as a drug delivery vehicle for MRI monitored magnetic targeting of brain tumors. Biomaterials. 2008;29(4):487–496.

- [5] Ranmadugala D, Ebrahiminezhad A, Manley-Harris M, et al. Impact of 3-aminopropyltriethoxysilane-coated iron oxide nanoparticles on menaquinone-7 production using *B. subtilis*. Nanomaterials. 2017;7(11). DOI:10.3390/nano7110350
- [6] Ranmadugala D, Ebrahiminezhad A, Manley-Harris M, et al. Reduced biofilm formation in menaquinone-7 production process by optimizing the composition of the cultivation medium. Trend Pharm Sci. 2017;3 (4):245–254.
- [7] Seifan M, Ebrahiminezhad A, Ghasemi Y, et al. Aminemodified magnetic iron oxide nanoparticle as a promising carrier for application in bio self-healing concrete. Appl Microbiol Biotechnol. 2017;102(1):175–184.
- [8] Ranmadugala D, Ebrahiminezhad A, Manley-Harris M, et al. Magnetic immobilization of bacteria using iron oxide nanoparticles. Biotechnol Lett. 2017;40(2):237–248.
- [9] Ebrahiminezhad A, Varma V, Yang S, et al. Magnetic immobilization of *Bacillus subtilis* natto cells for menaquinone-7 fermentation. Appl Microbiol Biotechnol. 2016;100(1):173–180.
- [10] Ebrahiminezhad A, Varma V, Yang S, et al. Synthesis and application of amine functionalized iron oxide nanoparticles on menaquinone-7 fermentation: a step towards process intensification. Nanomaterials. 2015;6 (1):1–9.
- [11] Green A, Isseroff R, Lin S, et al. Synthesis and characterization of iron nanoparticles on partially reduced graphene oxide as a cost-effective catalyst for polymer electrolyte membrane fuel cells. MRS Commun. 2017;7 (2):166–172.
- [12] An B, Liang Q, Zhao D. Removal of arsenic (V) from spent ion exchange brine using a new class of starchbridged magnetite nanoparticles. Water Res. 2011;45 (5):1961–1972.
- [13] Obregón S, Mendoza-Reséndez R, Luna C. Facile synthesis of ultrafine akaganeite nanoparticles for the removal of hexavalent chromium: adsorption properties, isotherm and kinetics. J Nanosci Nanotechnol. 2017;17(7):4471-4479.
- [14] Singh P, Tiwary D, Sinha I. Improved removal of Cr (VI) by starch functionalized iron oxide nanoparticles. J Environ Chem Eng. 2014;2(4):2252–2258.
- [15] Wu S, Fu F, Cheng Z, et al. Removal of Cr (VI) from wastewater by FeOOH supported on Amberlite IR120 resin. Desalin Water Treat. 2016;57(38):17767–17773.
- [16] Yusan SD, Akyil S. Sorption of uranium (VI) from aqueous solutions by akaganeite. J Hazard Mater. 2008;160(2-3):388-395.
- [17] Ghosh MK, Poinern GEJ, Issa TB, et al. Arsenic adsorption on goethite nanoparticles produced through hydrazine sulfate assisted synthesis method. Korean J Chem Eng. 2012;29(1):95–102.
- [18] Nguyen V, Kynicky J, Ambrozova P, et al. Microwaveassisted synthesis of goethite nanoparticles used for removal of Cr(VI) from aqueous solution. Materials. 2017;10(7):783.

- [19] Adegoke H, Adekola F, Ashola M. Adsorptive removal of hexavalent chromium using synthetic goethite nanoparticles. Niger J Chem Res. 2018;23(2):20–38.
- [20] Ahmmad B, Leonard K, Islam MS, et al. Green synthesis of mesoporous hematite (α-Fe2O3) nanoparticles and their photocatalytic activity. Adv Powder Technol. 2013;24(1):160–167.
- [21] Mohapatra M, Anand S. Synthesis and applications of nano-structured iron oxides/hydroxides – a review. Int J Eng Sci Technol. 2010;2(8):127–146.
- [22] Fan H, Song B, Yang Z, et al. Fast inducing synthesis of spherical superparamagnetic β-FeOOH nanoparticles without aggregation. Chem Lett. 2004;33(5):576–577.
- [23] Chai L, Han N, Wei L, et al. Hydrothermal synthesis of β-FeOOH with different morphologies using NaH 2 PO 4 as structural modifier. J Wuhan Univ Technol Mater Sci Ed. 2012;27(4):662–664.
- [24] Luna C, Ilyn M, Vega V, et al. Size distribution and frustrated antiferromagnetic coupling effects on the magnetic behavior of ultrafine akaganéite (β-FeOOH) nanoparticles. J Phys Chem C. 2014;118(36):21128–21139.
- [25] Kianpour S, Ebrahiminezhad A, Mohkam M, et al. Physicochemical and biological characteristics of the nanostructured polysaccharide-iron hydrogel produced by microorganism *Klebsiella oxytoca*. J Basic Microbiol. 2016;2016(56):132–140.
- [26] Kianpour S, Ebrahiminezhad A, Negahdaripour M, et al. Characterization of biogenic Fe (III)-binding exopolysaccharide nanoparticles produced by *Ralstonia* sp. SK03. Biotechnol Prog. 2018;34(5):1167–1176.
- [27] Ebrahiminezhad A, Bagheri M, Taghizadeh S-M, et al. Biomimetic synthesis of silver nanoparticles using microalgal secretory carbohydrates as a novel anticancer and antimicrobial. Adv Nat Sci Nanosci Nanotechnol. 2016;7. DOI:10.1088/2043-6262/7/1/ 015018.
- [28] Xie J, Lee JY, Wang DI, et al. Silver nanoplates: from biological to biomimetic synthesis. ACS Nano. 2007;1 (5):429-439.
- [29] Xie J, Lee JY, Wang DI, et al. Identification of active biomolecules in the high-yield synthesis of single-crystalline gold nanoplates in algal solutions. Small. 2007;3 (4):672–682.

- [30] Cai J, Liu J, Gao Z, et al. Synthesis and anion exchange of tunnel structure akaganeite. Chem Mater. 2001;13 (12):4595-4602.
- [31] Parameshwari R, Priyadarshini P, Chandrasekaran G. Optimization, structural, spectroscopic and magnetic studies on stable akaganeite nanoparticles via co-precipitation method. Am J Mater Sci. 2011;1(1):18–25.
- [32] Kasparis G, Erdocio AS, Tuffnell JM, et al. Synthesis of size-tuneable β-FeOOH nanoellipsoids and a study of their morphological and compositional changes by reduction. CrystEngComm. 2019;21(8):1293–1301.
- [33] Liu Z, Puumala E, Chen A. Sensitive electrochemical detection of Hg (II) via a FeOOH modified nanoporous gold microelectrode. Sens Actuators B Chem. 2019;287:517–525.
- [34] Lee CW, Wu PC, Hsu IL, et al. New templated Ostwald ripening process of mesostructured FeOOH for thirdharmonic generation bioimaging. Small. 2019;15(20). DOI:10.1002/smll.201805086
- [35] Raee MJ, Ebrahiminezhad A, Gholami A, et al. Magnetic immobilization of recombinant *E. coli* producing extracellular asparaginase: an effective way to intensify downstream process. Sep Sci Technol. 2018;53 (9):1–8.
- [36] Ranmadugala D, Ebrahiminezhad A, Manley-Harris M, et al. The effect of iron oxide nanoparticles on *Bacillus subtilis* biofilm, growth and viability. Process Biochem. 2017;62(2017):231–240.
- [37] Kim J, Ilott AJ, Middlemiss DS, et al. 2H and 27Al solid-state NMR study of the local environments in Aldoped 2-line ferrihydrite, goethite, and lepidocrocite. Chem Mater. 2015;27(11):3966–3978.
- [38] Bakoyannakis D, Deliyanni E, Zouboulis A, et al. Akaganeite and goethite-type nanocrystals: synthesis and characterization. Microporous Mesoporous Mater. 2003;59(1):35–42.
- [39] Xiao M, Zhao Y, Li S. Facile synthesis of chrysanthemum-like mesoporous α-FeOOH and its adsorptive behavior of antimony from aqueous solution. J Dispers Sci Technol. 2019;1–9.
- [40] Xu Z, Xie M, Ben Y, et al. Efficiency and mechanism of atenolol decomposition in Co-FeOOH catalytic ozonation. J Hazard Mater. 2019;365:146–154.