High temperature oxidation of iron-iron oxide core-shell nanowires composed of iron nanoparticles

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This work describes an oxidation process of iron-iron oxide core-shell nanowires at temperatures between 100 °C and 800 °C. Studied nanomaterial was synthesized through a simple chemical reduction of iron trichloride in an external magnetic field under a constant flow of argon. The electron microscopy investigations allowed determining that as-prepared nanowires were composed of self-assembled iron nanoparticles which were covered by 3 nm thick oxide shell and separated from each other by a thin interface layer. Both these layers exhibited the amorphous or highly-disordered characters which were traced by means of transmission electron microscopy and Mössbauer spectroscopy. The thermal oxidation was carried out under a constant flow of argon which contained the traces of oxygen. The first stage of process was related to slow transformations of amorphous Fe and amorphous iron oxides into crystalline phases and a disappearance of interfaces between iron nanoparticles forming studied nanomaterial (regime: 25 °C – 300 °C). After that, the crystalline iron core and iron oxide shell became oxidized and signals for different compositions of iron oxide sheath were observed (regime: 300 °C – 800 °C) by X-ray diffraction, Raman spectroscopy and Mössbauer spectroscopy. According to the thermal gravimetric analysis, the nanowires heated up to 800 °C under argon atmosphere gained 37% of mass in respect to their initial weight. The structure of studied nanomaterial oxidized at 800 °C was mainly composed of α -Fe₂O₃ (~ 93%). Moreover, iron nanowires treated above 500 °C lost their wire-like shapes due to their shrinkage and collapse caused by the voids coalescence.

S1 Details regarding the formation of iron nanowires

The applied preparation route is extremely important with regard to the studies related to thermal oxidation, so the detailed description of synthesis setup and the subsequent steps of iron nanowires (Fe NWs) formation are presented in the Scheme 1 and explained as following.



Scheme 1 Preparation of iron nanowires.

Studied iron nanowires were prepared through a simple chemical reduction of 0.2 mL 0.5 M hexahydrated iron (III) chloride (FeCl₃ × $6H_2O$; 98%, Sigma-Aldrich) aqueous solution by 2 mL 1 M sodium borohydride (NaBH₄; 98%, Sigma-Aldrich) aqueous solution.

The synthesis was performed in a test tube covered by a cap with two glass tubes. Both tubes were inserted into the initial solution of iron (III) salt. A constant argon flow (> 99%, Linde LienHwa Industrial Gases Co., Ltd. (Taiwan)) was set through one of the tube to purge out the dissolved oxygen from the aqueous iron (III) precursor for 10 min (Scheme 1a). The second advantage

of bubbling argon was related to the stirring of reaction precursor without application of magnetic stirrer which is inadequate for the magnetic nanomaterials fabrication. This stirring allowed dispersing dissociated Fe^{3+} ions homogeneously in the solution. Then, the test tube was placed in an external magnetic field of about 0.2 T (2000 Gs). This led to agglomerate the iron ions along the lines of applied magnetic field in such way as illustrated in Scheme 1b. The experimental setup was left under argon atmosphere for 30 min. After that time, a reducing agent (NaBH₄) was added into the iron salt solution with a use of syringe (Scheme 1c). This caused that the reaction, which is described by the chemical Eq. 1, occurred.¹

$$FeCl_{3} \times 6H_{2}O_{(I)} + 3NaBH_{4(I)} + 3H_{2}O_{(I)} \rightarrow Fe_{(s)} \downarrow + 3B(OH)_{3(I)} + 3NaCl_{(I)} + 10.5H_{2(g)} \uparrow$$
(1)

Agglomerated iron ions reacted with NaBH₄ forming the black precipitation which was floating in the post-reaction solution along the lines of applied magnetic field and perpendicularly to the walls of test tube. Additionally, during the reaction a large amount of hydrogen was produced which origin can be explained by analysing the electrochemical half-reaction accompanying the overall reaction (2, 3 and 4) and their standard potentials (E^0) (5, 6 and 7).²

$3BH_4^{-} + 9H_2O \rightarrow 3B(OH)_3 + 21H^{+} + 24e^{-}$ Fe ³⁺ + 3e ⁻ → Fe 21H ⁺ + 21e ⁻ → 10.5H ₂		(2) (3) (4)
BH ₄ ⁻ + 3H ₂ O ↔ B(OH) ₃ + 7H ⁺ + 8e ⁻	$E^0 = -0.481 \text{ V}$	(5)
Fe ³⁺ + 3e ⁻ ↔ Fe	$E^0 = -0.036 \text{ V}$	(6)
2H ⁺ + 2o ⁻ ↔ H	$E^0 = 0.000 \text{ V}$	(7)

It is well known that NaBH₄ is a versatile reducing agent.³⁻⁶ Therefore, the first stage of overall reaction was related to oxidation reaction of BH_4^- ions. This led to formation of $B(OH)_3$ (one of the final products of the total reaction) and it was also a source of H^+ ions and electrons. A part of electrons was consumed for the reduction of Fe³⁺ ions (Eq. 3) and rest of them was used for the creation of gaseous H_2 (Eq. 4). The values of standard potentials of Eq. 6 and Eq. 7 are less negative than that of Eq. 5. Hence, it is evident that the reactions of Fe³⁺/Fe and H^+/H_2 can be treated as the reduction reactions in relation to Eq. 5. Moreover, it is worth noting that the formation of gaseous hydrogen provided the continuous stirring of solution and it could protect against the initial oxidation of obtained iron nanostructure which may occur in a reaction with water.⁷

The synthesis of studied iron nanowires was performed in aqueous environment where the reduction of iron chlorides leads mainly to formation of non-crystalline and nanoscale iron. Moreover, the choice of hydrated $FeCl_3$ instead of hydrated $FeCl_2$ was caused by faster reduction of Fe^{3+} ions than Fe^{2+} .¹

Besides the efficient production of hydrogen, the reaction (1) is highly exothermic. This issue cannot be neglected because it could influence the fast oxidation of iron nanowires especially in the presence of oxygen coming from air.⁸ Therefore, the reaction system remained under argon inert gas during the reaction period and even for 10 min after addition of last drops of NaBH₄.

Finally, the obtained products of reaction were transferred from the test tube (reactor) to the beaker. Then, the liquid products were replaced by 99.5% ethanol (Shimakyu's Pure Chemicals Company) which was used for washing of as-prepared iron nanostructure in an ultrasonic bath. This process was repeated several times to ensure that obtained iron nanowires were not contaminated by other products of overall reaction. After that, the fabricated nanomaterial was being dried in a vacuum oven at 80 °C until evaporation of ethanol. Then, iron nanowires were exposed to air and were transferred and stored in the sealed vials at air-containing atmosphere. Such prepared and cleaned nanostructure constituted an initial material for further studies related to their thermal treatment.

S2 EDX measurements



Fig. S1 FE-SEM image of as-prepared iron nanowires with EDX spectra.

The EDX spectra were recorded on the aluminum holder covered by graphite which enhances the conduction of electrons. Therefore, both presented diagrams contain the signals coming from aluminum as well as carbon. Moreover, the peak corresponding to oxygen is visible due to its easy adsorption on the surfaces of graphite cover. The peaks originating from iron can be seen only when the spot signal has been collected on the iron nanowires. At the same time, the intensity of oxygen signal has been increased. This confirms that as-prepared material has been already oxidized initially even at ambient atmosphere.



Fig. S2 SEM images of a) as-prepared Fe NWs, b) Fe NWs 300 °C, c) Fe NWs 600 °C, d) Fe NWs 800 °C and corresponding elemental mapping spectra of iron and oxygen.

S3 XRD patterns



Fig. S3 XRD patterns collected between 42 ° and 48 ° for iron nanowires (Fe NWs) annealed at 500 °C (f) and 600 °C (g), 700 °C (h) and 800 °C (i). The dashed line seen in this figure represents the position of the most intense peak for a crystalline α -Fe.



S4 Mössbauer spectra

Fig. S4 Transmission Mössbauer spectra of a) as-prepared Fe NWs and iron nanowires annealed at (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C, (g) 600 °C, (h) 700 °C and (i) 800 °C.

References

- 1 G. N. Glavee, K. J. Klabunde, C. M. Sorensen and G. C. Hadjipanayis, Inorg. Chem., 1995, 34, 28.
- 2 L. R. Lu, Z. H. Ai, J. P. Li, Z. Zheng, Q. Li and L. Z. Zhang, Cryst. Growth Des., 2007, 7, 459.
- 3 A. Giannis and K. Sandhoff, Angew. Chem.-Int. Edit., 1989, 28, 218.
- 4 Y. Shimazaki, Y. Kobayashi, S. Yamada, T. Miwa and M. Konno, J. Colloid Interface Sci., 2005, 292, 122.
- 5 H. J. Shin, K. K. Kim, A. Benayad, S. M. Yoon, H. K. Park, I. S. Jung, M. H. Jin, H. K. Jeong, J. M. Kim, J. Y. Choi and Y. H. Lee, Adv. Funct. Mater., 2009, 19, 1987.
- 6 I. A. Wani, S. Khatoon, A. Ganguly, J. Ahmed, A. K. Ganguli and T. Ahmad, Mater. Res. Bull., 2010, 45, 1033.
- 7 N. Kumar, M. Auffan, J. Gattacceca, J. Rose, L. Olivi, D. Borschneck, P. Kvapil, M. Jublot, D. Kaifas, L. Malleret, P. Doumen q and J. Y. Bottero, *Environ. Sci. Technol.*, 2014, **48**, 13888.
- 8 D. L. Huber, Small, 2005, 1, 482.