

Proceedings

Influence of Aging on the Structure and Magnetic Properties of Surface Deposited Single-Molecule Magnets [†]

Oleksandr Pastukh * and Łukasz Laskowski

Institute of Nuclear Physics Polish Academy of Sciences, PL-31342 Krakow, Poland;

lukasz.laskowski@ifj.edu.pl

* Correspondence: oleksandr.pastukh@ifj.edu.pl

† Presented at the 2nd International Online-Conference on Nanomaterials, 15–30 November 2020; Available online: <https://iocn2020.sciforum.net/>.

Published: 15 November 2020

Abstract: In this paper the main issues concerning the possibility of organization of Mn₁₂-based single-molecule magnets (SMMs) on the surface of silica nanostructures with preservation of its structure and magnetic properties were summarized. Also, the aging effects on structural and magnetic properties in Mn₁₂-stearate SMMs deposited on the surface of spherical silica nanoparticles were discussed.

Keywords: surface functionalization; single-molecule magnets; silica; surface deposition; magnetic aging

1. Introduction

Single-molecule magnets are the new class of nanoscale materials with unique magnetic properties of purely molecular origin [1]. Such structures possess high spin of the ground state and large magnetic anisotropy, which opens up a great potential in terms of their applications in nanoelectronics [2]. The realization of highly-performance nanoelectronic devices based on the manipulation of SMMs requires surface deposition of such entities. The organization of individual bistable magnetic molecules on the surface, however, demands the precise chemical method and searching of proper supporting material, since any changes at structure may influence on the magnetic properties [3].

Since for practical application it is important to follow the changes of SMMs magnetic performance over long period of time, here we aimed to discuss the structure modifications and their influence on the magnetic properties of such surface deposited entities. Such discussion bases on the series of articles, dedicated to the synthesis, structural and magnetic properties investigation of Mn₁₂-based SMMs deposited on the surface of silica nanostructures [4–7].

2. Discussion

The synthesis procedure of investigated material was based on anchoring the individual SMMs onto the silica support using propyl carbonic acid groups [4]. As the substrate the spherical silica nanoparticles (of diameter about 300 nm) were chosen. It possesses large specific surface area and functional units that are placed at the external surface of this material, what is important for large molecules separation. The Mn₁₂-stearate SMMs were used for surface deposition, as they have total spin $S = 10$ of the ground state and also possess high structural stability due to the outside bulky ligands, are soluble in most organic solvents and stable against water catalyzed reduction [8].

At first, to confirm successful deposition of molecules on the surface the transmission electron microscopy (TEM) measurements were done. On the TEM images at high magnification an individual molecules of Mn₁₂-stearate SMMs were unambiguously observed in the form of islands [4,5]. Then, the performed Raman spectroscopy analysis was applied to confirm correct anchoring of molecules on the surface. The presence of all typical bands, corresponding for the vibrations of stearate groups were observed, which confirms the preservation of structure of SMMs after deposition [6]. What is the most important, the retaining of magnetic properties were confirmed with the use of SQUID magnetometry. Magnetic measurements show retaining of magnetic hysteresis in $M(H)$ dependence and presence of slow relaxation process in molecules after surface deposition [6].

In order to analyze how the characteristics of such material change over long time period the aging effect was investigated [7]. The aging studies (about seven month period) revealed significant decrease in basic magnetic parameters (exponential decrease of coercive field and remnant magnetization) and change in magnetic relaxation behavior. The Raman spectroscopy measurements revealed gradual degradation of the compound and formation of hydroxyl stearate system over time, which explain the observed magnetic changes. Also, the aged samples were compared with the as-synthesized material after thermal decomposition. For both samples similar bands at the MnO region of Raman spectra as well as partial covering of hysteresis loops were observed, which confirms that the structural modifications caused by the temperature, affect the similar way as aging process.

Author Contributions: Conceptualization, Ł.L. and O.P.; methodology, Ł.L. and O.P.; investigation, Ł.L. and O.P.; writing—original draft preparation, O.P.; writing—review and editing, Ł.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Science Centre, grant number: 2017/26/E/ST5/00162.

Acknowledgments: The authors are grateful to Piotr Konieczny, Magdalena Laskowska and Dominik Czernia for fruitful discussions and support during research.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. Magnetic bistability in a metal-ion cluster. *Nature* **1993**, *365*, 141–143.
2. Bartolomé, J.; Luis, F.; Fernández, J.F. *Molecular Magnets: Physics and Applications*; Springer: Berlin/Heidelberg, Germany, 2013; 395p.
3. Cornia, A.; Mannini, M.; Sainctavit, P.; Sessoli, R. Chemical strategies and characterization tools for the organization of single molecule magnets on surfaces. *Chem. Soc. Rev.* **2011**, *40*, 3076–3091.
4. Laskowski, L.; Kityk, I.; Konieczny, P.; Pastukh, O.; Schabikowski, M.; Laskowska, M. The Separation of the Mn₁₂ Single-Molecule Magnets onto Spherical Silica Nanoparticles. *Nanomaterials* **2019**, *9*, 764.
5. Laskowska, M.; Pastukh, O.; Kuźma, D.; Laskowski, Ł. How to Control the Distribution of Anchored, Mn₁₂-Stearate, Single-Molecule Magnets. *Nanomaterials* **2019**, *9*, 1730.
6. Laskowska, M.; Pastukh, O.; Konieczny, P.; Dulski, M.; Zalsiński, M.; Laskowski, L. Magnetic behaviour of Mn₁₂-stearate single-molecule magnets immobilized on the surface of 300 nm spherical silica nanoparticles. *Materials* **2020**, *13*, 2624.
7. Pastukh, O.; Konieczny, P.; Czernia, D.; Laskowska, M.; Dulski, M.; Laskowski, Ł. Aging effect on the magnetic properties of Mn₁₂-stearate single-molecule magnets anchored onto the surface of spherical silica nanoparticles. *Mater. Sci. Eng. B* **2020**, *261*, 114670.
8. Park, C.D.; Jeong, D.Y. Soluble Single-Molecule Magnet: Mn₁₂-stearate. *Bull. Korean Chem. Soc.* **2001**, *22*, 611–615.

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

