Preparation and Properties Magnetite/Polyimide Composites

Xue FANG, Xianghong CUI *, Guiming SU, Mingyue CHEN, Meihui SONG, Xiaochen ZHANG, Yang WANG, Bo HUANG

Institute of Advanced Technology, Heilongjiang Academy of Sciences, Harbin, Heilongjiang, China, 150020

http://doi.org/10.5755/j02.ms.32188

Received 1 September 2022; accepted 11 November 2022

To make the polyimide (PI) composite material having both heat resistance and magnetic permeability, Fe_3O_4/PI magnetic polyimide composite powder was synthesized by one-step solvothermal method. 4,4′-diaminodiphenyl ether (ODA) as monomers, ether anhydride polyamic acid (PAA) was designed and prepared by Fe^{3+} and polyimide precursor-polyamic acid triethylamine salt (PAAS) was reacted in a reactor, and the PI/Fe_3O_4 composite powders were synthesized under the condition of high temperature and high pressure. The obtained PI/Fe_3O_4 composite powders were analyzed by infrared spectroscopy, microscopic morphology and thermal properties. The morphology and structure of the samples were both characterized by scanning electron microscopy (SEM) and infrared spectroscopy (IR). The thermal properties of the composite microspheres were studied via thermogravimetric analysis (TGA) and the magnetic properties were determined by a vibrating sample magnetometer (VSM). The saturation magnetization decreases gradually, increasing the polyimide content, with a saturation magnetization of PI/Fe_3O_4 determined to be 20.29 emu/g.
Keywords: polyimide, magnetism, composite powder, one-step solvothermal method.

1. INTRODUCTION

Polymer-based magnetic composites have received extensive attention in the industrial field in recent years. Due to their concentration of excellent properties of both inorganic and polymers, the design and preparation of different types of composite nanostructures have become the focus of research and development [1 – 3]. Magnetite (Fe_3O_4) is one of best-known magnetic materials and has been extensively studied in terms of properties involving high saturation magnetization, biocompatibility and low toxicity [4, 5]. Due to its superior performance characteristics, the material has been widely used in applications such as catalysis [6, 7], wave absorption [8, 9], environmental remediation, biotechnology/biomedicine [10, 11] and magnetic resonance imaging [12, 13]. However, bare magnetite microspheres proved to be highly reactive, and prone to oxidation and agglomeration in air. This usually results in a loss of magnetism and dispersibility.

Polyimide has excellent mechanical properties, thermal properties, electrical insulation properties, etc. As a high-performance polymer material, it has been widely used in aerospace, electronic packaging, rail transit and other fields. The composites prepared by combining Fe_3O_4 have both magnetic permeability and material properties. Specific applications such as matrix resins for composite materials, high-strength films and coatings, etc. Due to the potential applications of high-performance polyimide, various functional nanomaterials based on PI materials have also been developed and fabricated. Such as low-dielectric materials, high-temperature nanovessels, and nano-reaction vessels with heat resistance [14 – 16].

However, due to the rigid structure of polyimide, the composite powder is limited. It may also be that the low solid content in the experimental stage, the huge solvent consumption, and the difficulty in controlling the morphology have affected the successful preparation of the composite material. To solve this problem, in this study, PI@Fe_3O_4 magnetic polyimide composite powder was prepared by one-step solvothermal method, using the composite microsphere salt of poly(amic acid) triethylamine (PAAS) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) as the precursor of the reaction. The preparation of Fe_3O_4 does not need to be completed separately, which avoids the complicated production process caused by first preparing Fe_3O_4 and then compounding PI. In addition, no additional precipitant other than triethylamine is required to be added to the reaction system, which greatly simplifies the experimental process.

Polyimide (PI) is a kind of polymer material containing an imide ring in a molecular main chain, which is generally obtained by stepwise polymerization of a dibasic anhydride and a diamine. Since the aromatic ring on the main chain of the molecule is a rigid and very stable structure, the polyimide has outstanding heat resistance, mechanical properties and electrical properties [17 – 19]. In this report, we describe the development of a facile one-step solvothermal method for the preparation of PI@Fe_3O_4 composite microspheres using poly(amic acid) triethylamine salts (PAAS) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) as starting materials [20 – 22]. Subsequently, the thermal and magnetic properties of the prepared samples were tested.

2. EXPERIMENTAL

Diphenyl ether tetraacid dianhydride (Sinopharm Chemical Reagent Co., Ltd.); 4,4′-diaminodiphenyl ether

*Corresponding author. Tel.: 13624510365.
E-mail: *xiaoxue@iathas.ac.cn* (X. Cui)

Polystyrene nanoparticles (Jenus New Materials Co., Ltd.); (Sinopharm Chemical Reagent Co., Ltd.); N,N-dimethylacetamide (AR Tianjin Komi Chemical Reagent Co., Ltd.); Ethylene glycol(AR Tianjin Komi Chemical Reagent Co., Ltd.); Triethylamine (AR Tianjin Komi Chemical Reagent Co., Ltd.); $FeCl_3 \cdot 6H_2O$(analytical grade and purchased from Zhongguo Group Chemical Reagent Co., Ltd.); Absolute ethanol (Tianjin Yongda Chemical Reagent Co., Ltd.); the water used in the experiment is distilled water.

The structures of nanoparticles and nanocomposites were investigated by Lambda 7600 -FT-IR. A JEOL JSM-6700F scanning electron microscope (SEM) with primary electron energy of 3 keV was employed to examine the surface morphologies of products. X-ray diffraction (XRD) data were collected on an X'Pert PRO X-ray diffractometer. TG data was collected on a TG209F3 thermogravimetric tester by NETZSCH, Germany.

0.1 mol ODA was placed in a 500 mL three-neck flask, added 250 mL of DMAc with a mechanical stirrer. After ODA was completely dissolved in DMAc, 0.1 mol of ODPA was added in batches. After the ODPA was dissolved, the reaction was continued. After stirring for 6 h, 0.2 mol of triethylamine was gradually added dropwise with a dropper, so that the carboxylic acid in the generated polyamic acid was completely reacted with triethylamine. After the triethylamine was added dropwise, the mechanical stirring was continued for 2 h, and the stirring was stopped after the reaction was complete, and the finally obtained triethylamine salt solution of polyamic acid was allowed to stand for later use. Then $FeCl_3 \cdot 6H_2O$ was dissolved in ethylene glycol to prepare a 0.5 mol/L Fe^{3+} solution. A certain amount of polyamic acid triethylamine salt solution was mixed, Then Fe^{3+} solution, ethylene glycol and DMAc, were stirred evenly and transferred to the reaction kettle, the products were placed in the reaction kettle in a blast drying oven. After the reaction, the products were separated with a magnet, washed three times with distilled water and anhydrous ethanol, and dried in an oven at 60 ºC for 6 h to obtain the final products.

3. RESULTS AND DISCUSSION

In previous studies, scholars have found that polyamic acid was prone to flocculation in the presence of ethylene glycol, and cannot exist stably in a solvent containing ethylene glycol. A necessary condition for the sphere, it acts as a reaction medium and a reducing agent in the reaction, so this study excludes the use of polyamic acid as the precursor of polyimide; polyamic acid ester can exist in alcohols such as ethylene glycol [7]. In the solvent, however, to precipitate Fe^{3+}, the additional precipitating agent needs to be added to the reaction. After adding an alkaline precipitating agent, it will cause the rapid precipitation of polyamic acid ester, and it cannot exist stably; in the test of polyamic acid triethylamine salt It is found that it can exist stably in a solvent containing ethylene glycol, and when synthesizing PI/Fe_3O_4 composite microspheres, polyamic acid triethylamine salt is used as the precursor of polyimide without adding a precipitant to make Fe^{3+} Precipitation yields a magnetic substance. Therefore, in this study, different from other researchers in the past, polyamic acid triethylamine salt was used as the precursor of polyimide to synthesize PI/Fe_3O_4 composite microspheres.

The whole procedure to prepare Fe_3O_4/PI magnetic polyimide composites is illustrated in Fig. 1.

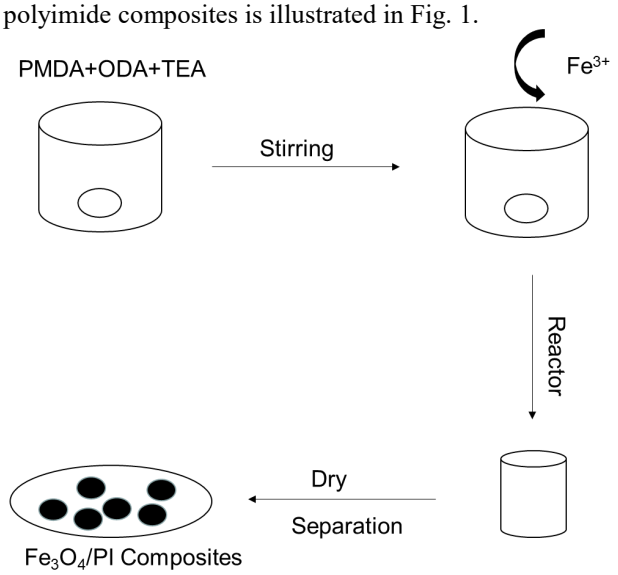


Fig. 1. Synthesis route to Fe_3O_4/PI magnetic composites

A possible mechanism for the synthesis of PI@Fe_3O_4 composites is illustrated in Fig. 1. At first, a polyimide precursor (PAAS) was synthesized. PAAS was dissolved in a mixed solvent consisting of DMAC and EG and $FeCl_3 \cdot 6H_2O$ in ethylene glycol was added dropwise.

In the teflon-lined autoclave and with rising temperature, triethylamine gets removed from the PAAS main chain and dissipates in solution. Then combine it with Fe^{3+} solution mixing, high in the reactor PI/Fe_3O_4 composites were synthesized under the condition of high temperature and high pressure.

The entire process for preparing the Fe_3O_4/PI magnetic polyimide composites is shown in Fig. 1. First, the PAAS were dispersed in ethylene glycol, amount of Fe^{3+} solution was added into the above solution with mechanical stirring. After stirring evenly, it was transferred to the reaction kettle, and the reaction kettle was heated to 200 °C in a blast drying oven to make the reaction. Then the Fe_3O_4/PI magnetic polyimide composites were obtained.

Fig. 2 shows the IR spectra of pure Fe_3O_4 and Fe_3O_4/PI composites. Curve a in Fig. 2 is the infrared spectrum of pure Fe_3O_4. In the spectrum of pure Fe_3O_4, an intense absorption band at 586 cm^{-1} can be observed, which is the stretching vibration peak of Fe–O. This signal can be assigned to a characteristic band of the Fe–O group, characteristic for the presence of Fe_3O_4. Curve b is the infrared spectrum of PI/Fe_3O_4 composite powder. On curve b, the band at 1776 cm^{-1} is the stretching vibration peak of carbonyl in polyimide, and the band at 1367 cm^{-1} is the stretching vibration of polyimide C-N bond. The peak at 1262 cm^{-1} is the stretching vibration peak of =C–O–C=, and these absorption peaks can be regarded as the characteristic absorption peaks of polyimide.

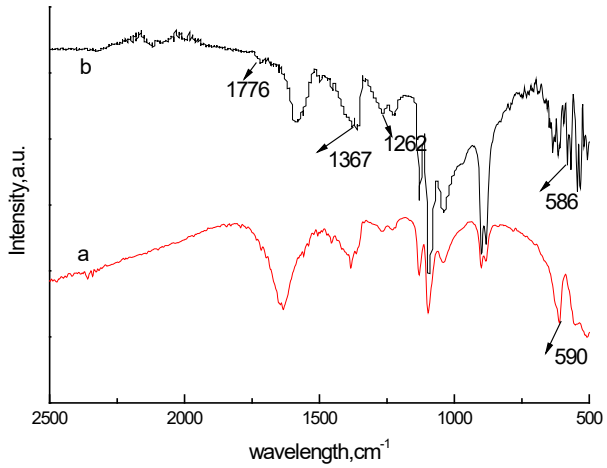
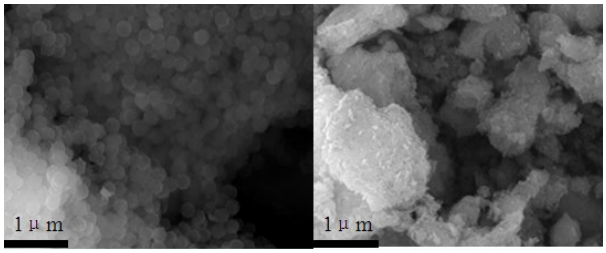


Fig. 2. Infrared spectra of composites: a – Fe_3O_4; b – Fe_3O_4/PI

At the same time, the stretching vibration peak of Fe–O also appeared at 590 cm^{-1}, and the characteristic absorption peak of polyimide and Fe_3O_4 coexisted on curve b. It can be seen that PI has successfully interacted with Fe_3O_4. Combined, it shows that the preparation of Fe_3O_4/PI composites is completed.

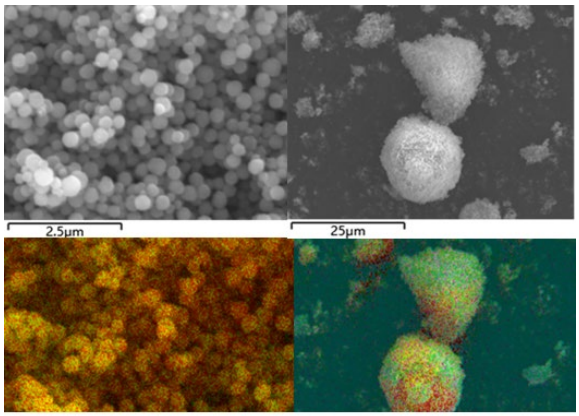


a b

Fig. 3. SEM images of composites: a – Fe_3O_4; b – Fe_3O_4/PI

Fig. 3 a is a scanning electron microscope picture of pure Fe_3O_4 particles. It can be seen from the picture that the particles are spherical and the particle size is about 200 nm. Fig. 3 b is the SEM photo of PI/Fe_3O_4 composites. Comparing the pictures of pure Fe_3O_4 particles and composite microspheres, it can be seen that there are polymer fibers on the surface, but the PI/Fe_3O_4 composites are no longer spherical. This is since PI is wrapped on Fe_3O_4, but the composite microspheres are stuck together due to the excessive concentration of triethylamine salt of polyamic acid, so the synthesized PI/Fe_3O_4 composites do not present a spherical structure.

The EDS analysis in Fig. 4 a shows that oxygen accounts for 35.5 % and iron 64.5 %. Fig. 4 b shows that carbon accounts for 68.3 %, nitrogen 1.2 %, oxygen 23.8 % and iron 6.7 %. Fe_3O_4 composite microspheres have a wide range of applications. Due to the variety of polymers and the fact that the polymer itself has functional groups, the PI/Fe_3O_4 composite microspheres can have functional groups without further modification to make them functional. Fe_3O_4 composite microspheres have received extensive attention. However, most polymers have low thermal decomposition temperature, which limits their application in some fields. Therefore, the high temperature resistant polyimide material can break this temperature limit well [23, 24].



a b

Fig. 4. EDS images of composites: a – Fe_3O_4; b – Fe_3O_4/PI

Thermogravimetric analysis (TGA) measurements were carried out with Fe_3O_4 microspheres and PI/Fe_3O_4 composites in the air. The corresponding TGA curves are shown in Fig. 5. Due to the oxidization of magnetite in air, the curve a of the pure Fe_3O_4 curve shown in Fig. 5, the weight loss is partly due to the loss of oxygen of metal oxides at high temperature, and it may also be due to some residual solvent and some hydroxyl groups on the surface of Fe_3O_4 during the preparation of Fe_3O_4. Mass loss due to solvent volatilization and radical removal.

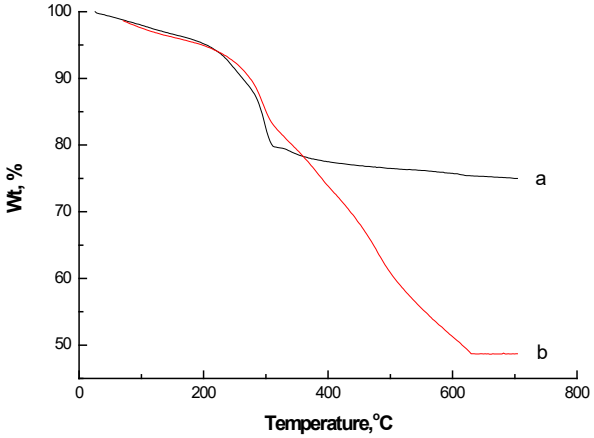


Fig. 5. Thermogravimetric curves of composites: a – Fe_3O_4; b – Fe_3O_4/PI

The DSC test was performed on the Fe_3O_4/PI composites to investigate whether the PI in the Fe_3O_4/PI composites has been completely imidized. The corresponding DSC curve is shown in Fig. 6. From the DSC curve of the Fe_3O_4/PI composites, it can be seen that the Fe_3O_4/PI composites have no reaction peak between room temperature and 500 °C, so it can be recognized that the polyimide in the Fe_3O_4/PI composites is in the reaction kettle has been completely imidized. Magnetism is an important physical parameter of all ferrite magnetic materials. For Fe_3O_4 particles, people were most concerned about their magnetic response intensity (saturation magnetization, *Ms*).

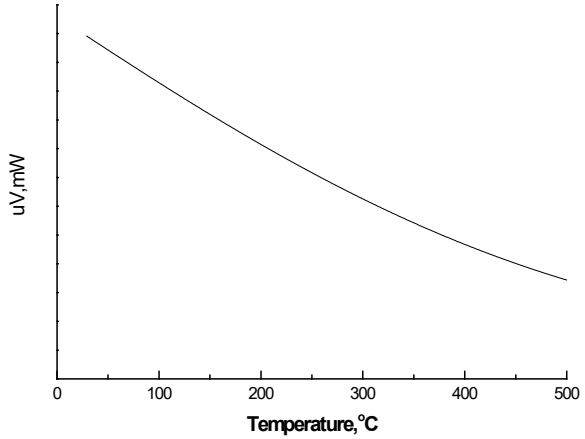


Fig. 6. DSC curve of Fe_3O_4/PI composites

The saturation magnetization meant that the magnetic moment of the magnetic domain tends to the same direction as the external magnetic field under the action of the external magnetic field, and thus forms a magnetization vector. When the external magnetic field gradually increased, its magnetization also increased until it reached the maximum value, the higher the saturation magnetization, the better the performance as a permanent magnet material. The magnetization behavior was investigated by applying a magnetic field to pure Fe_3O_4 as well as PI/Fe_3O_4 composites microsphere powder samples with a vibrating sample magnetometer (VMS) [25].

The reason for this phenomenon was that the PI coating on the surface of Fe_3O_4 made Fe_3O_4 in the composite microspheres. The proportion of PI decreased, the proportion of PI increased, and PI did not respond to the magnetic field; and during the resynthesis of PI/Fe_3O_4 composite microspheres, Fe^{3+} was first complexed to the main chain of PAAS, which hindered the formation of Fe_3O_4 crystals. It may make the Fe_3O_4 crystallization not perfect. The Fe_3O_4 content and saturation magnetic field strength of the PI/Fe_3O_4 composite microspheres were presented in Fig. 7.

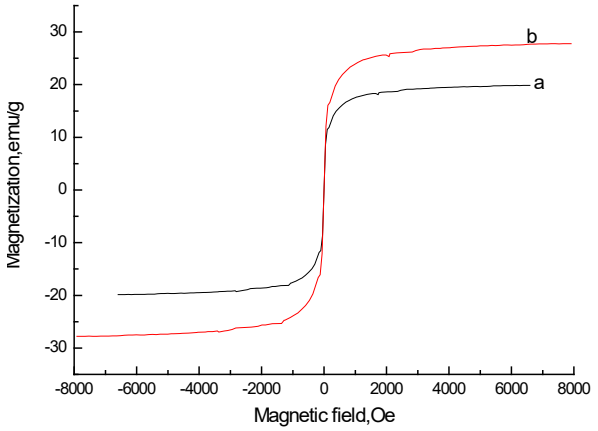


Fig. 7. VSM curves of PI@Fe_3O_4 composites: a – pure; b – Fe_3O_4

It can be seen from Fig. 7 that the saturation magnetization of PI/Fe_3O_4 composite microspheres with higher Fe_3O_4 content was also higher, indicating that the saturation magnetic field strength of PI/Fe_3O_4 composite microspheres is positively correlated with the Fe_3O_4 content [26]. This phenomenon can be attributed to the nonmagnetic polyimide coated on the Fe_3O_4 surface as well as the incomplete crystallization caused by the polyimide permeated throughout the crystals. The saturation magnetization decreases gradually, increasing the polyimide content, with a saturation magnetization of PI/Fe_3O_4 determined to be 20.29 emu/g.

To observe the magnetic response of the Fe_3O_4/PI composites more intuitively, the samples were dispersed in ethanol, and the photos before and after applying the magnetic field were taken as shown in Fig. 8. It can be seen from Fig. 8 a that the composites are uniformly dispersed in the ethanol solution before applying the magnetic field, and it can be seen from the Fig. 8 b that the sample aggregates to the side close to the magnet after applying the magnetic field, which can intuitively show that the synthesized Fe_3O_4/PI composites have a certain magnetic response.

a b

Fig. 8. Photographs of the Fe_3O_4/PI composites ethanol dispersion before and after applying a magnetic field: a – without an applied magnetic field; b – with an applied magnetic field

4. CONCLUSIONS

Compared with other methods, the preparation process of polymer Fe_3O_4 composite microspheres does not require pre-preparation of Fe_3O_4 particles, but a one-step solvothermal method to prepare Fe_3O_4/PI composite powder. One-step synthesis of Fe_3O_4/PI composite powder. Not only the method is simple and the conditions are mild, but also the experimental loss of first generating Fe_3O_4 and then coating its surface is avoided. The results show that the surface of Fe_3O_4 can be successfully combined with PI, and PI penetrates into the whole crystal through the self-assembly process. The Fe_3O_4/PI composites exhibit certain magnetic properties and excellent thermal properties and have the potential to be used as high-performance absorbing materials and other applications. The morphology and structure of the samples were both characterized by scanning electron microscopy (SEM) and infrared spectroscopy (IR). The thermal properties of the composite microspheres were studied via thermogravimetric analysis (TGA) and the magnetic properties were determined by a vibrating sample magnetometer (VSM). The saturation magnetization decreases gradually, increasing the

polyimide content, with a saturation magnetization of PI/Fe_3O_4 determined to be 20.29 emu/g.

REFERENCES

1. **Yao, T.J., Cui, T.Y., Fang, X., Yu, J., Cui, F., Wu, J.** Preparation of Yolk/shell Fe_3O_4@polypyrrole Composites and Their Applications as Catalyst Supports *Chemical Engineering Journal* 225 2013: pp. 230 – 236. https://doi.org/10.1016/j.cej.2013.02.026
2. **Murray, R.W.** Nanoelectrochemistry: Metal Nanoparticles, Nanoelectrodes, and Nanopores *Journal of Chemical Research* 108 (11) 2008: pp. 2688 – 2720. http://link.springer.com/article/10.1007%2Fs11595-0110163-y
3. **Crooks, R.M., Zhao, M.Q., Sun, L., Chechik, L., Yeung, L.K.** Dendrimer-encapsulated Metal Nanoparticles: Synthesis, Characterization, and Applications to Catalysis *Journal of Chemical Research* 34 (3) 2001: pp. 181 – 190. https://doi.org/10.1002/(SICI)15214095(199903)11:33.0.CO;2-7
4. **Reddy, L.H., Arias, J.L., Nicolas, J.P.** Magnetic Nanoparticles: Design and Characterization, Toxicity and Biocompatibility, Pharmaceutical and Biomedical Applications *Chemical Reviews* 112 2012: pp. 5818 – 5878. https://doi.org/10.25772/A8X1-8G20
5. **Gawande, M.B., Branco, P.S., Varma, R.S.** Carbothermally Synthesized Core–shell Carbon–magnetite Porous Nanorods for High-performance Electromagnetic Wave Absorption and the Effect of the Heterointerface *Chemical Society Reviews* 42 2013: pp. 3371 – 3393. https://doi.org/10.1016/j.jallcom.2013.03.160
6. **Qiu, P.P., Thokchom, B., Park, B., Cui, M.C., Zhao, D.Y.** Uniform Core–shell Structured Magnetic Mesoporous TiO2 Nanospheres as A Highly Efficient and Stable Sonocatalyst for the Degradation of Bisphenol-A *Journal of Chemistry Materials* 3 2015: pp. 6492 – 6500. https://doi.org/10.1039/C4TA06891B
7. **Qu, C.Y., Liu, C.W., Zhou, H.R., Yu, W.M., Wang, D.Z., Wang, D.X.** One-step Synthesis of PI@Fe_3O_4 Composite Microspheres and Practical Applications in Cu(II) Ion Adsorption *RSC Advances* 5 2015: pp. 88943 – 88949. https://doi.org/10.1039/C5RA18756G
8. **Fang, X., Su, G.M., Song, M.H., Jiang, H.J., Cui, X.H., Zhang, X.C., Chen, M.Y.** Preparation of Polyimide@Polypyrrole/Palladium Hollow Composites with Applications in Catalysis *Materials Science (Medžiagotyra)* 27 (2) 2021: pp. 192 – 196. https://doi.org/10.5755/j02.ms.23144
9. **Yin, Y., Suto, Y., Sakabe, T., Chen, S.W., Hayashi, S., Mishima, T., Yamada, O., Tanaka, K.H.** Water Stability of Sulfonated Polyimide Membranes *Macromolecules* 39 2006: pp. 1189 – 1198. https://doi.org/10.1021/ma0523769
10. **Shang, Y.W., Cui, G.H., Liu, W., Wu, D.Z., Wu, Z.P., Guo, W.L.** Catalytic Synthesis and Structural Characterizations of a Highly Crystalline Polyphenylacetylene Nanobelt Array *Materials Letters* 136 2014: pp. 71 – 73. https://doi.org/10.1021/ja075540b
11. **Han, E.L., Wu, D.Z., Qi, S.L., Tian, H.Q., Niu, G.P., Yan, X.N., Yang, X.P.** Structure Evolutions Involved in the Carbonization of Polyimide Fibers with Different Chemical Constitution *Advanced Materials Interfaces* 4 2012: pp. 2583 – 2590. https://doi.org/10.1016/j.mtcomm.2014.08.001
12. **Zhang, L., Wu, J.T., Sun, N., Zhang, X.M., Jiang, L.** A Novel Self-healing Poly(amic acid) ammonium Salt Hydrogel with Temperature-responsivity and Robust Mechanical Properties *Journal of Chemistry Materials* 2 2014: pp. 7666 – 7668. https://doi.org/10.1021/la0155799
13. **Meng, F.B., Zhao, R., Zhan, Y.Q., Lei, Y.J., Zhong, J.C., Liu, X.B.** One-step Synthesis of Fe-phthalocyanine/Fe_3O_4 Hybrid Microspheres *Materials Letters* 65 2011: pp. 264 – 267. https://doi.org/10.1016/j.matlet.2010.09.075
14. **Lu, J.J., Chen, L., Liu, M.Q., Yan, Y.D., Zhao, X.B.** Preparation of Poly(amic acid) Particles by Precipition Polymerization and Study on the Imidization of Poly(amic acid) *Journal of Shanxi Chemical Industry* 31 (4) 2011: pp. 18 – 23. https://doi.org/10.1016/j.polymer.2011.07.008
15. **Zhang, Y., Jiang, L., Li, H., Fan, L.Z., Hu, W.P., Wang, C.R., Li, Y.F., Yang, S.H.** Single-crystalline C60 Nanostructures by Sonophysical Preparation: Tuning Hollow Nanobowls as Catalyst Supports for Methanol Oxidation *Chemistry-A European Journal* 17 2011: pp. 4921 – 4926. https://doi.org/10.1002/chem.201002719
16. **Yu, X.L., Liang, F.X., Liu, J.G., Lu, Y.F., Yang, Z.Z.** Simultaneous Adsorption of Atrazine and Cu (II) from Wastewater by Magnetic Multi-walled Carbon Nanotube *Journal of Colloid and Interface Science* 367 2012: pp. 531 – 536. https://doi.org/10.1016/j.cej.2012.09.102
17. **Jiang, W., Wang, W.F., Pan, B.C., Zhang, Q.X., Zhang, W.M., Lv, L.** Facile Fabrication of Magnetic Chitosan Beads of Fast Kinetics and High Capacity for Copper Removal *ACS Applied Materials & Interfaces* 6 2014: pp. 3421 – 3426. https://doi.org/10.1007/s00396-010-2254-2
18. **Shao, M.F., Ning, F.Y., Zhao, J.W., Wei, M., Evans, D.G., Duan, X.** Hierarchical Layered Double Hydroxide Microspheres with Largely Enhanced Performance for Ethanol Electrooxidation *Chemical Society Reviews Journal* 134 2012: pp. 1071 – 1077. https://doi.org/10.1002/adfm.201202825
19. **Zhang, X.F., Mansouri, S., Clime, L., Ly, H.Q., Yahi, L.H., Veres, T.** Fe_3O_4–silica Core–shell Nanoporous Particles for High-capacity PH-triggered Drug Delivery *Journal of Chemistry Materials* 22 2012: pp. 14450 – 14457. https://doi.org/10.1039/C2JM31749D
20. **Graeser, M., Pippel, E., Greiner, A.** Polymer Core-shell Fibers with Metal Nanoparticles as Nanoreactor for Catalysis *Macromolecules* 40 (17) 2007: pp. 6032 – 6039. https://doi.org/10.1021/ma070898d
21. **Yao, W., Shen, C., Lu, Y.** Silica Coating onto Graphene for Improving Thermal Conductivity and Electrical Insulation of Graphene/polydimethylsiloxane Nanocomposites *Chemical Society Reviews Journal* 87 2013: pp. 8 – 13. https://doi.org/10.1016/j.jmst.2018.09.016
22. **Ziegler-Borowsk, M., Chełminiak, D., Kaczmarek, H.** Thermal Stability of Magnetic Nanoparticles Coated by Blends of Modified Chitosan and Poly(quaternary ammonium) Salt *Journal of Thermal Analysis and Calorimetry* 119 2015: pp. 499 – 506. https://doi.org/10.1007/s10973-014-4122-7
23. **Trchová, M., Šeděnková, I., Konyushenko, E.N.** Evolution

of PANI Nanotubes: Oxidation of Aniline in Water *Journal of Physical Chemistry B* 110 (19) 2016: pp. 9461 – 9468. https://doi.org/10.1021/jp057528g

24. **Liu, X.G., Wu, N.D., Cui, C.Y., Bia, N.N., Sun, Y.P.** Geochemical Characteristics of Gaseous Hydrocarbons and Hydrate Resource Prediction in the Qiong-dongnan Basin of the South China Sea *RSC Advances* 5 2015: pp. 24016 – 24022. https://doi.org/10.1016/S1872-5813(07)60034-6
25. **Ran, F, Yang, Y.L., Zhao, L., Niu, X.Q., Zhang, D.J., Kong, L.B., Luo, Y.C., Kang, L.** Preparation of Nano-PANI@MnO_2 by Surface Initiated Polymerization Method Using as A Nano-tubular Electrode Material: The Amount Effect of Aniline on the Microstructure and Electrochemical Performance *Journal of Energy Chemistry* 24 (4) 2015: pp. 388 – 393. https://doi.org/10.1016/j.jechem.2015.07.003
26. **Todorov, R., Lozanova, V., Knotek, P., Cernoskova, E., Vicek, M.** Microstructure and Ellipsometric Modelling of the Optical Properties of Very Thin Silver Films for Application in Plasmonics *Thin Solid Films* 628 (30) 2017: pp. 22 – 30. https://doi.org/10.1016/j.tsf.2017.03.009