

Synthesis and characterization of magnetite - titanium dioxide - 4-Benzene-azo- α -naphthylamine and methylene blue composites

V. I. LUNTRARU^a, O. GALES^a, L. IARCA^a, E. VASILE^b, S. I. VOICU^{a,*}, A. C. NECHIFOR^{a, b}

^aFaculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, 011061 Bucharest, Romania

^bNational Institute for Research and Development in Microtechnologies, Bucharest, Romania

This paper presents the synthesis and characterization of magnetite particles covered with titanium dioxide and with two dyes adsorbed on the TiO₂ coated surface of the particles. The synthesized materials were structurally characterized using Scanning Electron Microscopy, FT-IR spectroscopy and Energy-Dispersive X-ray spectroscopy.

(Received August 8, 2011; accepted November 23, 2011)

Keywords: Magnetite, Titanium dioxide, Magnetic particles, Dyes

1. Introduction

In the last decades there was an explosion regarding the research and development in the field of materials and nanomaterials [1-3]. Magnetic particles have been intensively studied in the past 40 years, because they have unique physicochemical, magnetic and optical properties. Due to their properties, the magnetic particles have a wide range of uses in many diverse applications like: ferrofluids, magnetic recording media and data storage, targeted drug delivery, magnetic resonance imaging (MRI) contrast enhancement and hyperthermia treatment of cancer [4-11]. The most used and accessible magnetic particle is magnetite (Fe₃O₄). Titanium dioxide (TiO₂) is a well known inorganic material with many uses (pigments, photocatalysis and others). For environmental applications TiO₂, a semiconductor photocatalyst, has been proven to be very suitable due to its biological and chemical inertness, strong oxidizing power, low cost, and long-term stability against photo and chemical corrosion [12-15]. By combining magnetite particles with titanium dioxide we obtain a new material which combines the properties of the magnetic particles with the properties of titanium dioxide. By adding a dye to a titanium dioxide coated magnetic particle we obtain a new material with potential applications in magnetic inks, optical sensors and photovoltaic cells. The main advantage of these materials is given by the fact that using a red and a blue dye the optical properties of the final composite particles cover a wide band of visible spectrum. The materials obtained in this study were structurally characterized using Scanning Electron Microscopy (SEM), FT-IR spectroscopy and Energy-Dispersive X-ray spectroscopy (EDAX).

2. Experimental

2.1 Materials

Mohr salt (Fe₂(NH₄)₃•(NH₄)₂SO₄), ferri sulfuric alum salt (FeSO₄•(NH₄)₂SO₄) from Merk. Potassium hydroxide (KOH, Fluka), Titanium tetrabutoxide (Ti(OBu)₄, Fluka), 5,5-Dimethyl-1,3-cyclohexanedione (Dimedone, Fluka), 4-Benzene-azo- α -naphthylamine (Sigma-Aldrich), methylene blue (Sigma-Aldrich). The solvents, ethanol, acetone, methanol, tributyl phosphate (TBP) and dimethylacetamide (DMAc) were purchased from Merk.

2.2 Magnetic particles synthesis

Magnetic nanoparticles are obtained by a variant of Massart method [16, 17], which consists of ferric ions coprecipitation into a potassium hydroxide solution. 250 cm³ of Mohr salt solution 0.1 M and 250 cm³ of ferri-ammonium sulfuricum (ferri alum) are mixed under stirring. 1.5 L of potassium hydroxide 1M is added in three portions. After 4 hours, the black suspension is separated in magnetic field. The entire quantity of suspension is dialyzed until pH \approx 9 value is achieved. The magnetic particles are washed with methanol, ethanol and then with acetone.

2.3 Titanium dioxide coated magnetic particles synthesis

The TiO₂ coated magnetite particles were obtained by a sol-gel method. The starting materials are magnetite nanoparticles (obtained above) and titanium tetrabutoxide (Ti(OBu)₄). There are two ways to obtain this material: a) by using titanium tetrabutoxide and dimedone (5,5-Dimethyl-1,3-cyclohexanedione) as a chelating agent, or b) by activating the magnetic particles with potassium

hydroxide in ethanol. We preferred the first method because the chelating agent stabilizes the alkoxide this resulting in a better control of the sol-gel reactions. The experimental procedure is as follows: 1 gram of magnetite nanoparticles dispersed in 100 mL mixture of absolute ethanol and TBP (1:1) are milled together with 50 grams of glass spheres (for grinding), in a Retch mill at 250 rpm. After 1 hour a sol, obtained by mixing $\text{Ti}(\text{OBU})_4$ (1.11 mmol, 0.33 mL) and dimedone (2.4 mmol, 0.22 mL) in 3 mL dimethylacetamide (DMAc) at 0 °C, is added and the mixture was milled at room temperature for 2 hours at 250 rpm. Fig. 1 shows the reaction scheme. The obtained TiO_2 -magnetite particles were separated in magnetic field, dried and washed with ethanol. These particles were analyzed using FT-IR, SEM and EDAX.

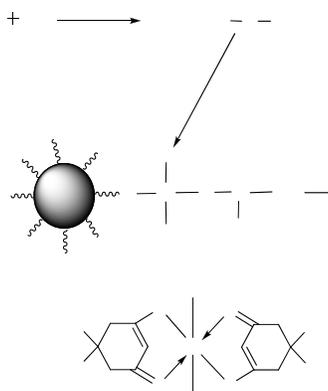


Fig. 1. The synthesis of $\text{TiO}_2\text{-Fe}_3\text{O}_4$ particles.

2.4. Adsorption of dyes onto TiO_2 coated magnetic particles

The selected dyes were 4-Benzene-azo- α -naphthylamine (Fig. 2a.) and Methylene blue (Fig. 2b). These dyes were dissolved in diethyl ether to form a 5% concentration solution. The TiO_2 -magnetite particles were added to these solutions. After 24 hours the solvent was evaporated and the particles were washed with distilled water. These particles were analyzed by FT-IR analysis.

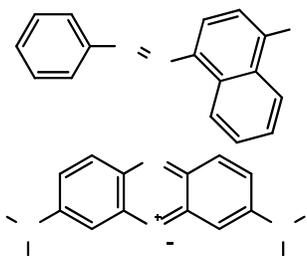
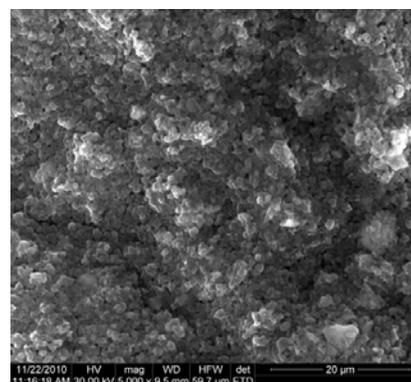


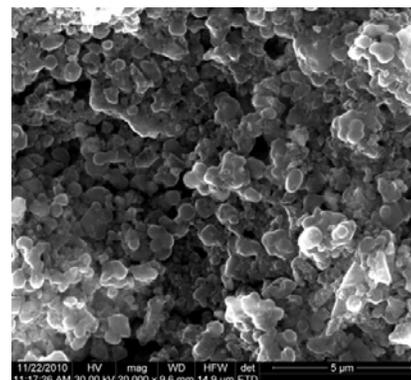
Fig. 2. The structures of 4-Benzene-azo- α -naphthylamine (a) and methylen bleu (b).

3. Results and discussion

The Scanning Electron Microscopy, performed with a FEI instrument, reveals the formation of homogeneous spherical aggregates (Fig. 3a), with the approximately diameter of the aggregates between 1 and 4 μm . By increasing the magnification (Fig. 3b) the titanium dioxide sphere particles can be observed. The diameter of these particles varies between 100 and 800 nm.



a



b

Fig 3. SEM images of covered magnetite particles at x5000 (a) and x20000 (b).

The EDAX mapping shows a uniform distribution of iron and titanium across the surface of the particle (Fig 4.a). Fig. 4b shows the EDAX elemental composition of magnetite-titanium dioxide particles. As it can be seen the highest peaks are for titanium and iron in accord with the EDAX mapping. The presence of phosphorus is due to the use of tributyl phosphate in the synthesis process. This solvent has a high boiling point (289 °C) and it couldn't be totally eliminated by evaporation.

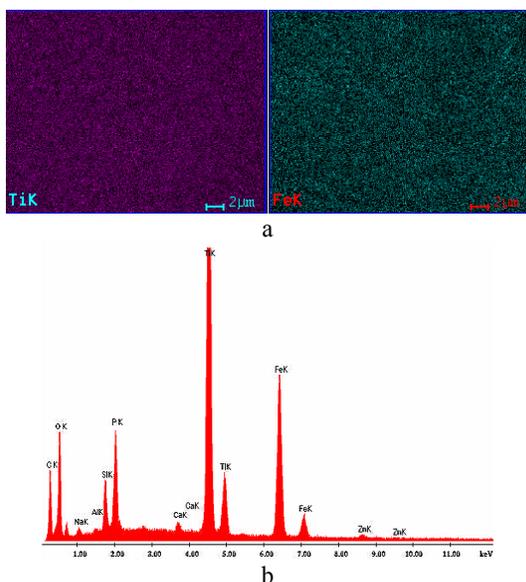


Fig. 4. EDAX mapping of Fe and Ti (a) and EDAX elemental composition (b).

The FT-IR analysis was conducted using a Bruker Tensor 27 instrument with diamond ATR annex. In Fig. 5a we can observe some characteristic peaks for TiO_2 . The first peak is very wide and it is situated in the range $2700\text{--}3600\text{ cm}^{-1}$ (it is attributed to Ti-OH and Ti-O bonds) and the second one is situated in the range $2300\text{--}2400\text{ cm}^{-1}$ (attributed to the absorption of carbon dioxide). In Fig. 5b and 5c we can see that the IR spectra is changed. The intensity of the wide peak decreases while the peak assigned to CO_2 absorption increases (probably because of an increase of the absorbed carbon dioxide quantity). For the IR spectra of the particles with methylen bleu dye (Fig. 5b) the attributed values are: 1640 cm^{-1} the stretching vibration for C=N bond, $1360\text{--}1320\text{ cm}^{-1}$ stretching vibration for C-N aromatic tertiary amine bond and 1385 cm^{-1} for methyl group.

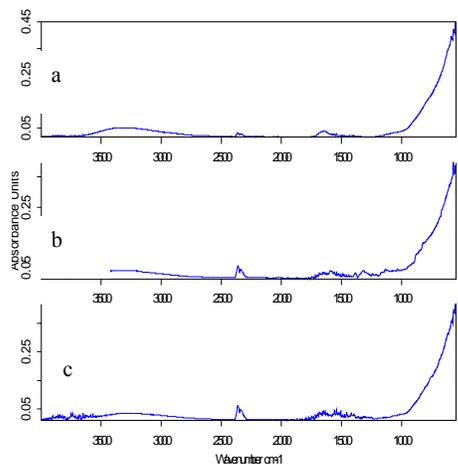


Fig. 5. IR spectra of TiO_2 covered particles (a), TiO_2 covered particles with adsorbed methylen bleu (b) and TiO_2 covered particles with adsorbed of 4-Benzene-azo- α -naphthylamine (c).

For the 4-Benzene-azo- α -naphthylamine dye (Fig. 5c) the attributed values are: 1615 cm^{-1} the bending vibrations for N-H bonds, 1570 cm^{-1} the stretching vibrations for azo (N=N) bond and $1250\text{--}1340\text{ cm}^{-1}$ the stretching vibration for C-N aromatic primary amine bond.

4. Conclusions

The magnetite particles covered with titanium dioxide were obtained by a simple and accessible technique. SEM and EDAX analysis shows that the Fe_3O_4 particles are uniformly covered with titanium dioxide. By adding the two dyes onto the TiO_2 surface we have obtained a new material with potential applications in magnetic inks, optical sensors and photovoltaic cells. The adsorption of these dyes was proved by FT-IR analysis.

Acknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/61178 (project that financed Vlad Ionut Luntraru from University Politehnica). The authors also recognize the financial support from project POSDRU/89/1.5/S/63700, 2010-2013, „Human Resource Development by Postdoctoral Research on Micro and Nanotechnologies” (project that financed Aurelia Cristina Nechifor and Eugeniu Vasile from National Institute for Microtechnologies).

References

- [1] F. Miculescu, I. Jepu, C. P. Lungu, M. Miculescu, M. Bane, Digest Journal of Nanomaterials and Biostructures **6**(2), 769 (2011).
- [2] G. Nechifor, S. I. Voicu, A. C. Nechifor, S. Garea, Desalination, **241**, 342 (2009).
- [3] F. Miculescu, I. Jepu, C. Porosnicu, C. P. Lungu, M. Miculescu, B. Burhala, Digest Journal of Nanomaterials and Biostructures **6**(1), 307 (2011).
- [4] M. A. Willard, L. K. Kurihara, E. E. Carpenter, S. Calvin, V. G. Harris, International Materials Reviews, **49** (3-4), 125 (2004).
- [5] Yu. V. Kulvelisa, V. A. Trounova, V. T. Lebedeva, D. N. Orlova, M. L. Gelfond, Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques, **3**(3), 379 (2009).
- [6] P. Tartaj, M. del P. Morales, S. Veintemillas-Verdaguer, T. Gonzalez-Carreno, Carlos J Serna, J. Phys. D: Appl. Phys., **36**, R182 (2003).
- [7] Q. A. Pankhurst, J. Connolly, S. K. Jones, J. Dobson, J. Phys. D: Appl. Phys. **36**, R167 (2003).
- [8] K. Gupta, M. Gupta, Biomaterials **26**(18), 3995 (2005).

- [9] N. Nitin, L. E. W. LaConte, O. Zurkiya, X. Hu, G. Bao, *J. Bio. Inorg. Chem.* **9**(6), 706 (2004).
- [10] R. Muller, R. Hergt, M. Zeisberger, W. Gawalek, *J. Magn. Magn. Mater.* **289**, 13 (2005).
- [11] A. Jordan, R. Scholz, P. Wust, H. Fahling, R. Felix, *J. Magn. Magn. Mater.* **201**, 413 (1999).
- [12] S. Tawkaew, S. Supothina, *Materials Chemistry and Physics*, **108**, 147 (2008).
- [13] F. Miculescu, M. Miculescu, L. T. Ciocan, A. Ernuteanu, I. Antoniac, I. Pencea, E. Matei, *Digest Journal of Nanomaterials and Biostructures* **6**(3), 1117 (2011).
- [14] S. I. Voicu, F. Aldea, A. C. Nechifor, *Revista de Chimie* **61**(9), 817 (2010).
- [15] S. I. Voicu, A. C. Nechifor, B. Serban, G. Nechifor, M. Miculescu, *J. Optoelectron. Adv. Mater.* **9**(11), 3423 (2007).
- [16] A. C. Nechifor, M. G. Stoian, S. I. Voicu, G. Nechifor, *Optoelectron. Adv. Mater. – Rapid Commun.* **4**(8), 1118 (2010).
- [17] F. D. Balacianu, A. C. Nechifor, R. Bartos, S. I. Voicu, G. Nechifor, *Optoelectron. Adv. Mater. – Rapid Commun.* **3**(3), 219 (2009).

*Corresponding author: svoicu@gmail.com