

Turkish Journal of Chemistry http://journals.tubitak.gov.tr/chem/ Turk J Chem (2013) 37: 879 – 888 © TÜBİTAK doi:10.3906/kim-1204-19

# **Research Article**

# Synthesis of tetrakis(carboxyphenyl)porphyrin coated paramagnetic iron oxide nanoparticles via amino acid for photodegradation of methylene blue

# Rahmatolah RAHIMI,<sup>1,\*</sup> Azadeh TADJARODI,<sup>1</sup>Mina IMANI,<sup>1</sup> Mahboubeh RABBANI,<sup>1</sup> Samaneh SAFALOU MOGHADDAM<sup>1</sup>, Hamed KERDARI<sup>2</sup>

<sup>1</sup>Department of Chemistry, Iran University of Science and Technology, Narmak, Tehran, Iran <sup>2</sup>Department of Chemistry, Saveh Branch, Islamic Azad University, Saveh, Iran

Received: 08.04.2012	•	Accepted: 13.03.2013	٠	Published Online: 04.11.2013	•	<b>Printed:</b> 29.11.2013
----------------------	---	----------------------	---	------------------------------	---	----------------------------

Abstract: In this paper, synthesis of tetrakis(carboxyphenyl)porphyrin (TCPP) coated cadmium ferrite (CdFe<sub>2</sub>O<sub>4</sub>) nanoparticles by using L-lysine as an anchor is reported for the first time. The ferrimagnetic CdFe<sub>2</sub>O<sub>4</sub> nanoparticles were prepared via the facile self-assembly method of reflux followed by a heating treatment. The obtained magnetic nanoparticles were coated with TCPP in the presence of the amino acid L-lysine by sonication in ethanol and then refluxing for 12 h. The structural characteristics of the products were determined using FT-IR and XRD pattern. Scanning electron microscopy (SEM) images indicated uniform morphologies of the magnetic nanoparticles with an average size of 43 nm. The magnetic properties of the prepared samples were characterized on a vibrant sample magnetometer (VSM) with maximum saturation magnetization values of 65.09 and 46.80 emu/g for nanoparticles and nanoparticle/TCPP. The synthesized products were successfully employed to remove the methylene blue (MB) dye from aqueous solutions by using visible light irradiation. The magnetic CdFe<sub>2</sub>O<sub>4</sub> nanoparticles indicated an enhancement of 13% for photodegradation of MB dye after being sensitized by TCPP.

Key words: Magnetic nanoparticles, cadmium ferrite, photodegradation, amino acid

# 1. Introduction

Most synthetic dyes are toxic or mutagenic and carcinogenic, and it is an important environmental challenge to remove them from processing or waste effluents.<sup>1–3</sup> In recent years, transition metal oxides of the type MFe<sub>2</sub>O<sub>4</sub> nanostructures have attracted scientific and technological attention due to the fact that they possess interesting optical, magnetic, electrical, and heterogeneous catalytic properties.<sup>4–7</sup> These magnetic nanomaterials with excellent properties and cubic inverse spinel structure can be employed in the industrial photodegradation of organic dve pollutants.<sup>8–12</sup>

Synthetic porphyrins have been extensively used as catalysts for hydroxylation of organic compounds under mild conditions since 1979.<sup>13-15</sup> However, their use in homogeneous systems is limited by drawbacks: the porphyrin ring is liable to oxidative self-destruction and they are subject to aggregation through  $\pi - \pi$ interaction.<sup>16,17</sup>

Immobilization of porphyrins on magnetic nanoparticles as supports can offer several advantages over traditional solution-phase chemistry. For example, the solid-supported porphyrins have higher stability and increased selectivity.<sup>17-20</sup> In addition, electron transfers increase when they are adsorbed on nanomaterials.

<sup>\*</sup>Correspondence: rahimi\_rah@iust.ac.ir

The greatest advantage of magnetic nanoparticle-supported porphyrin is that it can be simply recycled and reused several times without significant loss of activity.  $^{21-30}$ 

The enhancement of accumulation of porphyrin photosynthesizers against biological substrates can be achieved by conjugate formation with biomolecules (e.g., amino acids, proteins).  $^{8,31,32}$ 

In the present paper, we describe the facile synthesis of lysine conjugated porphyrin and its coating on  $CdFe_2O_4$  nanoparticles. These nanoparticles were successfully synthesized by a self-assembly method of reflux reaction. Ethylenediaminetetraacetic acid (EDTA), a powerful complexing agent that is widely commercially available, was used as chelate agent during the reflux procedure. The phase structures, morphologies, particle size, and chemical compositions of the nanoparticles were characterized by FT-IR, XRD, VSM, SEM, and UV-Vis spectrophotometer. The photocatalytic activity of the as-prepared nanoparticles was measured by photodegradation of methylene blue (MB) as the dye model under visible illumination. The impetus for this is that the photocatalyst, utilized as a suspension, can be easily separated after the treatment. The photocatalyst, once separated, can be reused due to its regenerative property under the photocatalytic reaction.

#### 2. Experimental section

# 2.1. Materials of synthesis

Pure analytical iron(II) sulfate heptahydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O), cadmium nitrate tetrahydrate (Cd(NO<sub>3</sub>)<sub>2</sub>. 4H<sub>2</sub>O), EDTA, ammonia (NH<sub>3</sub>), L-lysine, and tetrakis(carboxyphenyl)porphyrin (TCPP) were supplied as initial reagents to synthesize porphyrin coated paramagnetic CdFe<sub>2</sub>O<sub>4</sub> nanoparticles. MB (3,7-bis(Dimethylamino)phenothiazin-5-ium chloride) was used as the model dye. Absolute ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and N,N dimethyleformadie (DMF) were applied as solvents in all reactions. All of the chemicals used in this work were purchased from Merck and used without further purification.

# 2.2. Synthesis of paramagnetic $CdFe_2O_4$ nanoparticles

Magnetic cadmium ferrite (CdFe<sub>2</sub>O<sub>4</sub>) nanoparticles were synthesized by self-assembly route. As a complexing agent, 1.1 g of EDTA was dissolved in 30 mL of deionized water. Stoichiometric weights of FeSO<sub>4</sub>.7H<sub>2</sub>O and Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O as starting materials were dissolved in sufficient amounts of deionized water and poured into the reflux flask. The solution was allowed to stir for 1.5 h at 90 °C. Subsequently, 20 mL of ammonia solution (5 M) was slowly dropped into the mixture of the reflux and the reaction continued at the same temperature for 3 h. The reaction was completely performed under nitrogen atmosphere to prevent further oxidation of the prepared nanoparticles. At the end, the obtained precipitation was collected, washed with distilled water, and then dried at 70 °C overnight. Following this step, the obtained precursor was heated at 550 °C for 2 h at a rate of 10 °C/h under nitrogen atmosphere to prepare the paramagnetic nanoparticles.

### 2.3. Synthesis of lysine conjugated tetrakis(carboxyphenyl)porphyrin (LTCPP)

In order to prepare this product, LTCPP, a stoichiometric amount of TCPP dissolved in 100 mL of absolute ethanol and DMF (1:1) mixture was slowly injected into 150 mL of solution of lysine in ethanol under continual stirring and nitrogen atmosphere. The reflux reaction was performed at 70 °C for 12 h. The synthesized sample was collected and washed with distilled water and subsequently ethanol to remove the excess reagents. The obtained precipitation was dried at 70 °C overnight and then was employed for coating on the prepared CdFe<sub>2</sub>O<sub>4</sub> nanoparticles.

### RAHIMI et al./Turk J Chem

# 2.4. Preparation of porphyrin coated magnetic nanoparticles (LTCPPNP)

Some 300 mg of cadmium ferrite nanoparticles dispersed by ultrasonic wave energy was added to 50 mg of LTCPP dissolved in 100 mL of ethanol. The mixture was sonicated for 1 h and then was transferred to a reflux container and the reflux reaction was performed at 70 °C for 12 h under continual stirring and N<sub>2</sub> atmosphere. Finally, the obtained product was collected and after washing with distilled water several times was dried at 70 °C overnight.

## 2.5. Photocatalytic activity

The photocatalytic activity of the synthesized paramagnetic  $CdFe_2O_4$  nanoparticles and TCPP coated  $CdFe_2O_4$ nanoparticles was measured by degradation of MB as a model dye in aqueous solution under visible light irradiation. In order to establish the adsorption–desorption equilibrium, each beaker containing magnetic products and related dye solution was left in the dark and magnetically stirred for 15 min before starting the photocatalytic reaction. In the photocatalytic experiments, a certain amount (0.01 g) of photocatalyst was separately poured into a 50-mL beaker containing 25 mL of related dye solution with an initial concentration (5 mg L<sup>-1</sup>) and magnetically stirred for 6 h under visible irradiation. At given intervals of irradiation (1 h), portions of the suspension were taken out of the reaction vessel and easily separated using a permanent magnet and then analyzed by UV-Vis spectrophotometer. Next, the remaining concentration of MB solution was studied by a UV-Vis spectrophotometer at a wavelength of 668 nm.

### 2.6. Characterization

The powder X-ray diffraction (XRD) measurements were carried out using a Jeoljdx-8030 diffractometer with monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å, 40.0 kV, 30.0 mA). Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu-8400S spectrometer in the range of 400–4000 cm<sup>-1</sup> using KBr pellets. The magnetic properties of the sample were recorded by using a vibrating sample magnetometer (VSM, MDK6, Magnetis Daghigh Kavir Co., Iran). Scanning electron microscopy (SEM) images were obtained on a Philips XL-30 with gold coating to prove the presence of elements. Diffuse reflectance spectra (DRS) were prepared via a Shimadzu (MPC-2200) spectrophotometer to investigate the photocatalytic ability of magnetic nanoparticles. The UV-Vis absorption study was performed at room temperature in the wavelength range of 190–800 nm on a UV-Vis spectrometer (Shimadzu UV-1700).

#### 3. Results and discussion

# 3.1. The study of FT-IR spectra

Figure 1 shows the FT-IR spectra of the prepared cadmium ferrite nanoparticles. The FT-IR spectrum of cadmium ferrite before calcination obtained from the reflux reaction is indicated in Figure 1a. The observed peaks in this spectrum are related to the organic groups of synthesized precursor. The broad peak observed at  $3442 \text{ cm}^{-1}$  is attributed to the O-H stretching vibration bands of the EDTA compound overlapped with the vibration bands of H<sub>2</sub>O molecules. The signified peaks at 1620 and 1118 cm<sup>-1</sup> belong to the ionized and coordinated C=O and C-O stretching vibration bands of EDTA molecule, respectively, which were used in the formation of precursor. These frequencies are less than those of the free functional group due to coordination with the metal ions in the intermediate molecule. The observed frequency at 592 cm<sup>-1</sup> is assigned to Fe-O vibration, which is broadened due to overlapping with the Cd-O vibration band. The organic groups of

#### RAHIMI et al./Turk J Chem

synthesized precursor after heating at 550 °C are completely removed and only the peak of Fe-O remains (Figure 1b). Figure 2a indicates the FT-IR spectrum of LTCPP covered on  $CdFe_2O_4$  nanoparticles. The metal oxygen vibration band is also observed at about 568 cm<sup>-1</sup>. Figures 2b and 2c indicate the FT-IR spectra of pure magnetic nanoparticles and pure TCPP, respectively, which are given for comparison. The FT-IR spectrum of LTCPPNP (Figure 2a) revealed peaks at 1680 and 1527 cm<sup>-1</sup>. These peaks were assigned to the C-O stretching vibration of TCPP and the NH<sub>2</sub> deformation of the amide group, respectively. The amide group is formed when the carboxyl acid group of TCPP conjugates with the amino group of amino acid. The presence of these peaks proves the LTCPP coated magnetic nanoparticles.





Figure 1. The FT-IR spectra of the prepared cadmium ferrite nanoparticles (a) before calcinations and (b) after calcinations at 550  $^{\circ}$ C for 2 h.

Figure 2. The FT-IR spectra of (a) LTCPP coated  $CdFe_2O_4$  nanoparticles, (b) pure  $CdFe_2O_4$ , and (c) pure TCPP.

# 3.2. X-ray diffraction pattern

Figure 3 displays the XRD pattern of prepared magnetic nanoparticles calcined at 550 °C for 2 h. The marked peaks in the pattern reveal the spinal phase of CdFe<sub>2</sub>O<sub>4</sub> with identified peaks according to the JCPDS card no. 22-1063. The major peaks at  $2\theta$  values of  $29.00^{\circ}$ ,  $34.12^{\circ}$ ,  $35.68^{\circ}$ ,  $41.46^{\circ}$ ,  $45.37^{\circ}$ ,  $51.39^{\circ}$ ,  $54.76^{\circ}$ ,  $60.06^{\circ}$ ,  $68.07^{\circ}$ ,  $70.96^{\circ}$ ,  $71.92^{\circ}$ , and  $78.44^{\circ}$  are very compatible with the planes of 220, 311, 222, 400, 331, 422, 511, 440, 620, 533, 622, and 551, respectively. The space group of Fd3m with lattice constant 8.699 Å is also assigned to cadmium ferrite. Although this pattern is compatible with the cadmium ferrite X-ray diffraction pattern, there are partial diffraction signals at  $2\theta$  values of  $12.74^{\circ}$ ,  $33.95^{\circ}$ , and  $57.40^{\circ}$ , which may belong to the slight residual phase of Fe<sub>2</sub>O<sub>3</sub> (JCPDS card no. 025-1402).

# 3.3. Morphology study

The SEM images of the obtained cadmium ferrite nanoparticles are indicated in Figures 4a and b. The low magnification image of SEM (Figure 4a) shows the accumulated magnetic particle shape. The high magnification of SEM images (Figure 4b) clearly indicates the uniform morphology of nanoparticles with an average particle



Figure 3. The XRD pattern of prepared magnetic  $\mathrm{CdFe}_{2}\mathrm{O}_{4}$  nanoparticles.



Figure 4. (a, b) The SEM images and (c) the histogram of the particles size distribution of  $CdFe_2O_4$  nanoparticles.

size of 43 nm and standard deviation of 3.10. A histogram of the particle size distribution for the obtained product (shown in Figure 4c) was determined by microstructure measurement program and Minitab statistical software. The observed agglomeration can be a result of high magnetization of samples. In fact, due to the large surface area-to-volume ratio and magnetic dipole–dipole interactions between the synthesized particles, these nanoparticles are prone to aggregate.<sup>33</sup>

# 3.4. Magnetic properties

Magnetic properties of the obtained samples were analyzed by vibrating sample magnetometer with an applied field of  $-10 \text{ kOe} \leq \text{H} \leq 10 \text{ kOe}$  at room temperature; Figures 5a and 5b exhibit the magnetization (M) versus the applied magnetic field (H) for synthesized CdFe<sub>2</sub>O<sub>4</sub> nanoparticles and TCPP coated nanoparticles, respectively. The measured maximum values of saturation magnetization (Ms) for ferrite nanoparticles and LTCPP/nanoparticles are 65.09 and 46.80 emu/g, respectively. The LTCPP/magnetic nanoparticles indicate low saturation magnetization, which is attributed to the nonmagnetic contribution of the LTCPP shell covering the cadmium ferrite nanoparticles. Moreover, the observed high saturation magnetizations of both prepared samples can be assigned to the size of particles and well developed crystallinity of structures.<sup>34,35</sup> Despite the high saturation magnetization, all specimens indicated relatively small coercivity. The remnant magnetizations (Mr) of mentioned samples are 4.2 and 4.5 emu/g, respectively. Spinel ferrites with the nanosized particles indicate different magnetic properties from their bulk counterparts. Cadmium ferrite is a normal spinel having an antiferromagnetic property in bulk form in which cadmium ions have occupied the tetrahedral sites. It has been shown to be ferrimagnetically ordered when the grain size is reduced to nanometer size.



Figure 5. The magnetization (M) versus the applied magnetic field (H) for (a) synthesized  $CdFe_2O_4$  nanoparticles and (b) TCPP coated nanoparticles.

Therefore, the as-prepared nanosized sample exhibits the ferrimagnetic characteristic. The hysteresis loop of an S-shaped curve having the slight remanence effect can be indicative of the ferrimagnetical nature of the product. Thus, the magnetization curves of the samples show strong magnetic behavior with high saturation magnetization and slender hysteresis.<sup>34-36</sup> The resulting values of saturation magnetization are considerable in comparison with the reported values for this material so far.<sup>34,37-39</sup> Substitution of cadmium ions into crystalline structure causes the soft magnetic properties. It is found that the magnetic properties of samples

improve owing to reduction in particle size so that the sample of pure cadmium ferrite nanoparticles indicates higher Ms than another one.

#### 3.5. Photodegradation activity

The possibility of using  $CdFe_2O_4$  and LTCPP coated  $CdFe_2O_4$  nanoparticles for the photodegradation of dyes such as MB was evaluated by examining the degradation efficiency of MB in the presence of visible light irradiation. Photocatalytic efficiency was evaluated based on the absorption intensity of MB solutions at different times. In addition, the decolorizing efficiency was inferred from Eq. (1):

Decolorozing efficiency = 
$$\frac{C_0 - C_i}{C_0} \times 100\%$$
, (1)

where  $C_0$  is the initial concentration of dye before the reaction happens, and  $C_i$  is the concentration of dye after the treatment with prepared products at various illumination times. Figures 6 and 7 illustrate the changes in MB absorbance versus wavelength (nm) in the presence of pure  $CdFe_2O_4$  nanoparticles and porphyrin coated  $CdFe_2O_4$  nanoparticles, respectively, for 2 h at room temperature. In the absence of light irradiation, the slight value of MB on both resulting samples is adsorbed. In fact, when no nanoparticles are present, the light irradiation leads to negligible degradation of MB. It was found that the degradation values increased with the introduction of prepared magnetic products into colored aqueous solution. Figure 8 represents the decolorizing efficiency of MB by employing both products. It is observed that the photodegradation was increased from 76% (Figure 8a) to 89% (Figure 8b) by replacing  $CdFe_2O_4$  nanoparticles with LTCPP/CdFe\_2O\_4 nanoparticles. This result revealed that such a modest enhancement can be attributed to the slight difference in the band gap energies. Figure 9 shows the band gap energy curves of the pure nanoparticles (Figure 9a) and porphyrin coated nanoparticles (Figure 9b) based on UV-Vis spectrum and using the Tauc equation as follows:

$$(\alpha h\vartheta)^n = B(h\vartheta - E_g),\tag{2}$$

where  $h\nu$  is the photon energy,  $\alpha$  is the absorption coefficient, B is a constant value,  $E_g$  represents the band gap energy, and n is related to direct and indirect transitions. By plotting of  $(\alpha h\nu)^2$  vs.  $h\nu$  in eV and by determining the extrapolation point, the band gap energies are calculated. However, the resulting nanomaterials have the appropriate photocatalytic behavior, which can be explained by the injection of electrons to the conduction band by porphyrin molecules coated nanoparticles. Likewise, it is concluded that the coating of nanoparticles by porphyrin molecules leads to better dispersion of magnetic nanoparticles in the solution and to a higher degradation of the pollutant.

A suggested mechanism of photodegradation behavior is shown in the Scheme. When the visible light is irradiated on the surface of LTCPP coated  $CdFe_2O_4$ , the sum of the electrons is excited from valence band (VB) to conduction band (CB). Subsequently, these electrons in the CB reduce  $O_2$  molecule adsorbed on the surface of the catalyst and transform into singlet  $O_2$  and then  $H_2O_2$  and OH radical, which oxidize the dye molecules to  $CO_2$  and  $H_2O$ .<sup>40</sup>





Figure 6. The absorbance changes vs. wavelength (nm) for MB on the surface of pure  $CdFe_2O_4$  nanoparticles for 2 h at room temperature.

Figure 7. The absorbance changes vs. wavelength (nm) for MB on the surface of LTCPP/CdFe $_2O_4$  nanoparticles for 2 h at room temperature.



Figure 8. The photodegradation efficiency of dye solution (MB) using synthesized pure  $CdFe_2O_4$  and (b) LTCPP coated  $CdFe_2O_4$  nanoparticles.



Figure 9. The plots of  $(\alpha h\nu)^2$  vs.  $h\nu$  (eV) of (a) the pure CdFe<sub>2</sub>O<sub>4</sub> nanoparticles and (b) LTCPP/CdFe<sub>2</sub>O<sub>4</sub> nanoparticles.

886



Scheme. The proposed mechanism of photodegradation of MB dye solution by using porphyrin coated  $CdFe_2O_4$  nanoparticles.

# 4. Conclusion

Uniform  $CdFe_2O_4$  nanoparticles with an average size of 43 nm and saturation magnetization (Ms) of 65.09 were synthesized by using a facile reflux reaction followed by heating treatment. Then the obtained magnetic ferrimagnetic nanoparticles were successfully coated by lysine conjugated porphyrin to improve the photocatalytic activity in the visible domain. This process was evaluated using MB as a dye model. The dye removal efficiency on the pure cadmium ferrite after 2 h of visible light was improved from 76% to 89% due to sensitizing of the nanoparticles with porphyrin molecules. This performance is explained by improved flow of the excited electrons to the conduction band and high dispersion of the particles by covering the surface of cadmium ferrite nanoparticles with a thin layer of LTCPP molecules. The good efficiency and simple separation of catalyst after photocatalytic treatment by a permanent magnet make these products suitable for many applications in this field.

# Acknowledgment

The financial support of this study by Iran University of Science and Technology is gratefully acknowledged.

#### References

- 1. Chen, K.-C.; Wu, J.-Y.; Huang, C.-C.; Liang, Y.-M.; Hwang, S.-C. J. J. Biotechnol. 2003, 101, 241–252.
- 2. Gong, R.; Ding, Y.; Li, M.; Yang, C.; Liu, H.; Sun, Y. Dyes Pigments 2005, 64, 187–192.
- 3. Tor, A.; Cengeloglu, Y. J. Hazard. Mater. 2006, 138, 409-415.
- 4. Shifu, C.; Wei, Z.; Wei, L.; Huaye, Z.; Xiaoling, Y. Chem. Eng. J. 2009, 155, 466-473.
- 5. Nghia, N. D.; Tung, N. T. Synthetic Met. 2009, 159, 831-834.
- 6. Farea, A. M. M.; Kumar, S.; Mujasam Batoo, K.; Yousef, A.; Alimuddin. Physica B 2008, 403, 684-701.
- Albuquerque, A. S.; Tolentino, M. V. C.; Ardisson, J. D.; Moura, F. C. C.; de Mendonça, R.; Macedo, W. A. A. Ceram. Int. 2012, 38, 2225–2231.
- 8. Kemikli, N.; Kavas, H.; Kazan, S.; Baykal, A.; Ozturk, R. J. Alloy. Compd. 2010, 502, 439-444.
- 9. Cornell, R. M.; Schwertmann, U. The Iron Oxides: Structure, Properties, Reactions Occurrence and Uses. VCH, New York: 1996.

- 10. Niu, X.; Li, H.; Liu, G. J. Mol. Catal. A: Chem. 2005, 232, 89-93.
- 11. Meng, W.; Li, F.; Evans, D. G.; Duan, X. J. Porous Mat. 2005, 11, 97-105.
- 12. Fan, G.; Gu, Z.; Yang, L.; Li, F. Chem. Eng. J. 2009, 155, 534-541.
- 13. Meunier, B. Chem. Rev. 1992, 92, 1411-1456.
- 14. Groves, J. T.; Nemo, T. E.; Myers, R. S. J. Am. Chem. Soc. 1979, 101, 1032–1033.
- 15. Nam, W.; Park, S.-E.; Lim, I. K.; Lim, M. H.; Hong, J.; Kim, J. J. Am. Chem. Soc. 2003, 125, 14674–14675.
- 16. Berner, S.; Biela, S.; Ledung, G.; Gogoll, A.; Bäckvall, J.-E.; Puglia, C.; Oscarsson, S. J. Catal. 2006, 244, 86–91.
- 17. Fu, B.; Yu, H.-C.; Huang, J.-W.; Zhao, P.; Liu, J.; Ji, L.-N. J. Mol. Catal. A: Chem. 2009, 298, 74-80.
- 18. Bai, D.; Wang, Q.; Song, Y.; Li, B.; Jing, H. Catal. Commun. 2011, 12, 684-688.
- 19. Topoglidis, E.; Campbell, C. J.; Cass, A. E. G.; Durrant, J. R. Electroanal. 2006, 18, 882–887.
- 20. Tang, T.; Fan, H.; Ai, S.; Han, R.; Qiu, Y. Chemosphere 2011, 83, 255-264.
- 21. Cao, D.; He, P.; Hu, N. Analyst 2003, 128, 1268-1274
- 22. Luque, G. L.; Rodríguez, M. C.; Rivas, G. A. Talanta 2005, 66, 467-471.
- 23. Zhao, G.; Feng, J.-J.; Xu, J.-J.; Chen, H.-Y. Electrochem. Commun. 2005, 7, 724-729.
- 24. Mehta, R. V.; Upadhyay, R. V.; Charles, S. W.; Ramchand, C. N. Biotechnol. Tech. 1997, 11, 493–496.
- Koneracká, M.; Kopčanský, P.; Antaliğk, M.; Timko, M.; Ramchand, C. N.; Lobo, D.; Mehta, R. V.; Upadhyay, R. V. J. Magn. Magn. Mater. 1999, 201, 427–430.
- 26. Polshettiwar, V.; Varma, R. S. Chem.-Eur. J. 2009, 15, 1582–1586.
- 27. Shokouhimehr, M.; Piao, Y.; Kim, J.; Jang, Y.; Hyeon, T. Angew. Chem. Int. Edit. 2007, 46, 7039-7043.
- 28. Kawamura, M.; Sato, K. Magnetically separable phase-transfer catalysts. Chem. Commun. 2006, 4718–4719.
- 29. Hu, A.; Yee, G. T.; Lin, W. J. Am. Chem. Soc. 2005, 127, 12486-12487.
- 30. Zheng, N.; Zhou, X.; Yang, W.; Li, X.; Yuan, Z. Talanta 2009, 79, 780-786.
- Sol, V.; Branland, P.; Chaleix, V.; Granet, R.; Guilloton, M.; Lamarche, F.; Verneuil, B.; Krausz, P. Bioorg. Med. Chem. Lett. 2004, 14, 4207–4211.
- Kwitniewski, M.; Kunikowska, D.; Dera-Tomaszewska, B.; Tokarska-Pietrzak, E.; Dziadziuszko, H.; Graczyk, A.; Glosnicka, R. J. Photoch. Photobiol. B 2005, 81, 129–135.
- 33. Zhang, H.; Zhu, G. Appl. Surf. Sci. 2012, 258, 4952-4959.
- 34. Nayak, P. K. Mater. Chem. Phys. 2008, 112, 24-26.
- Chinnasamy, C. N.; Narayanasamy, A.; Ponpandian, N.; Joseyphus, R. J.; Chattopadhyay, K.; Shinoda, K.; Jeyadevan, B.; Tohji, K.; Nakatsuka, K.; Guérault, H.; Greneche, J. M. Scripta Mater. 2001, 44, 1411–1415.
- 36. Berbenni, V.; Milanese, C.; Bruni, G.; Marini, A.; Pallecchi, I. Thermochim. Acta 2006, 447, 184–189.
- 37. Shelar, M. B.; Jadhav, P. A.; Patil, D. R.; Chougule, B. K.; Puri, V. J. Magn. Magn. Mater. 2010, 322, 3355–3358.
- Rai, R.; Verma, K.; Sharma, S.; Nair, S. S.; Valente, M. A.; Kholkin, A. L.; Sobolev, N. A. J. Alloy. Compd. 2011, 509, 7585–7590.
- 39. Vasanthi, V.; Shanmugavani, A.; Sanjeeviraja, C.; Kalai Selvan, R. J. Magn. Magn. Mater. 2012, 324, 2100-2107.
- 40. Choi, K.-H.; Wang, K.-K.; Shin, E. P.; Oh, S.-L.; Jung, J.-S.; Kim, H.-K.; Kim, Y.-R. J. Phys. Chem. C 2011, 115, 3212–3219.

Copyright of Turkish Journal of Chemistry is the property of Scientific and Technical Research Council of Turkey and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.