One-step microwave synthesis and characterization of gadolinium-doped titania nanoparticles

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TiO_2 nanoparticles are widely used for applications such as photocatalysts, pigments, and cosmetic additives. In the last years, the relevance of different methods to synthesize titanium dioxide nanoparticles has been emphasized. An effective way to improve the TiO_2 photocatalytic efficiency is doping nanoparticles with different metals. There is not much literature about titanium oxide doped with gadolinium, usually; sol-gel synthesis or hydrothermal methods were used [1-4].

The homogeneity of the particle-size distribution is a critical factor for designing nanomaterials. The modification of the surface chemistry of TiO_2 particles is used to control the aggregation, but reduces the final properties of the nanomaterials. It has been found that the incorporation of trace-amount lanthanides into TiO_2 structure results in a reduction of the final aggregation in both solution and solid phases. Therefore, the main objective of the present work is obtaining Gd-doped TiO_2 nanoparticles with a narrow particle-size distribution and homogeneous shapes that prevent aggregation.

Microwave radiation has been applied to prepare different nanomaterials. Using microwave energy has many advantages as a rapid transfer of heat to medium and selective heating [5]. Synthetic methods that combine microwave and hydrothermal treatments have been developed to form different oxides [6, 7]. The synthesis procedure of Gd-TiO_2 nanoparticles combines a sol-gel processing followed by microwave treatment. This procedure leads to anatase nanoparticles avoiding the aggregation due to high temperature treatments.

Monodispersed Gd-doped anatase nanoparticles were prepared from titanium tetraisopropoxide. Several Gd(III) amounts were added using Gd(NO3)3 as precursor up to 0,5, 1, 3, 6 and 9% Gd/Ti atomic ratio. The precursors were heated to 120 ºC in a microwave oven during 15 min. The synthesized Gd-TiO_2 nanoparticles were analyzed by XRD, TEM, SEM, EDX, SQUID magnetometry, nitrogen adsorption, UV-VIS and DLS.

XRD patterns show the characteristic anatase diffraction peaks, regardless the amount of Gd doping amount no signals of Gd (III) or Gd (III) oxide were detected. Crystallite sizes calculated using the Scherrer equation were found between 6 to 7 nm. The morphology of Gd-TiO_2 samples can be seen in the TEM images of Figure 1, which show the homogenous particle shapes together with an average particle size about 15 nm.

Gadolinium doping was analyzed by using XPS and EDX. Gd3d XPS spectra of nanoparticles with 0.5, 1 and 3 % Gd/Ti atomic ratio are shown in Figure 2. The Gd/Ti atomic ratio calculated from XPS spectra was higher than the bulk concentration suggesting that Gd is mostly in the surface of the titanium dioxide nanoparticles..An SEM-EDX mapping was performed for 3% Gd sample indicating a homogeneous distribution of Gd in the particles. The 9 % Gd doped nanoparticles were found to have paramagnetic behavior when characterized using SQUID magnetometry.

The surface area of Gd-TiO_2 was determined by N2-Adsorption, giving a S_{BET} of 272 m^2/g. This surface area value is slightly larger than that for pure TiO_2 nanoparticles (239 m^2/g). Finally, the aggregation of Gd-TiO_2 nanoparticles aggregation was studied in aqueous dispersions by ζ-potential measurements at different pH. DLS measurements show good nanoparticles dispersion in aqueous acid solutions.

References

[1] J. Xu, Y. Ao, D. Fu, C. Yuan, Colloids and Surfaces A: Physicochemical and Engineering Aspects 334 (2009) 107-111.
[2] M. Zawadzki, L. Kepinski, Journal of Alloys and Compounds 380 (2004) 255-259.
[3] D. Zhao, T. Peng, M. Liu, L. Lu, P. Cai, Microporous and Mesoporous Materials 114 (2008) 166-174.
[4] W. Zhou, Y. Zhou, S. Tang, Materials Letters 59 (2005) 3115-3118.
[5] X. Chen, S.S. Mao, Chemical Reviews 107 (2007) 2891-2959.
[6] A.V. Murugan, V. Samuel, V. Ravi, Materials Letters 60 (2006) 479-480.
[7] Z. Chen, W. Li, W. Zeng, M. Li, J. Xiang, Z. Zhou, J. Huang, Materials Letters 62 (2008) 4343-4344.

Figures

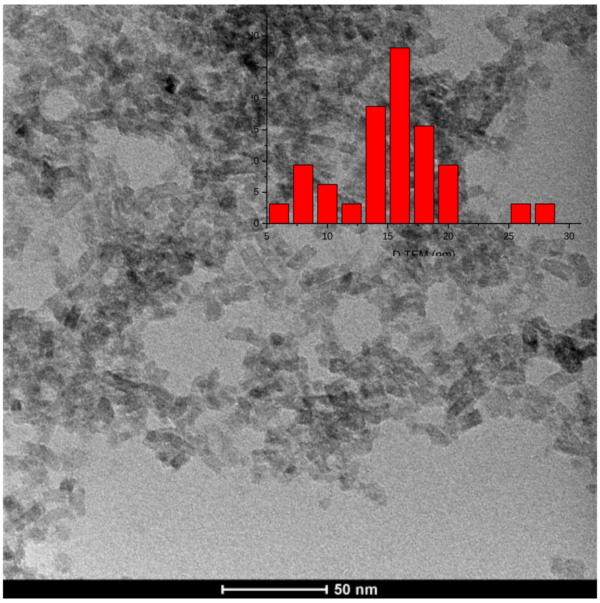

Fig 1. TEM image 3 % at gadolinium doped titania nanoparticles and histogram sizes calculated with imaQ Vision Builder.

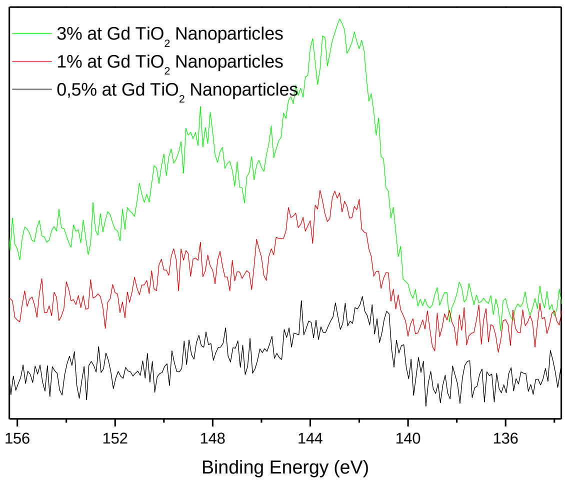

Fig. 2 Gadolinium 4d core level for nanoparticles with different amounts of gadolinium.