PREPARATION OF FE-TIO₂NANOCRYSTALS BY HYDROTHERMAL METHOD USED HIGH PRESSURES AND TEMPERATURES

M. MICLAU[1], I.GROZESCU[2], R. BAIES[3], C. LAZAU[4]

ABSTRACT

Iron–ion-doped anatase titanium dioxide (TiO_2) nanocrystalline samples were prepared by hydrothermal method used high pressures and temperatures. The samples were characterized by X-ray diffraction and TEM analyses. It was found that the amount of doped iron plays a signifificant role in affecting its photocatalytic activity and iron doped with optimum content can enhance photocatalytic activity, especially under visible light irradiation. Also, the dimension and shape of Fe-TiO_2 nanocrystals can be modified by the pressure and temperature chosen in during of the growth process.

KEYWORDS: titanium dioxide, photocatalitic, hydrothermal, high pressures

1. INTRODUCTION

In recent years there has been an extensive interest in the use of semiconductors as photocatalysts to initiate photocatalytic reaction at their interface [1]. As a popular catalyst, TiO_2 has been widely used because of its various merits,such as optical and electronic properties, low cost, high photocatalytic activity, chemical stability and non-toxicity [2]. However, its practical application seems limited for several reasons, among which one is the low photon utilization efficiency, another is the need to use an ultraviolet (UV) excitation source. To solve these problems, the modification of these catalysts has also been attempted by doping them with various metals such as Fe, Cr, Sn, Pt, V. The photocatalytic activities of the doped TiO_2 photocatalysts substantially depend on the dopant ion nature and concentration, besides the preparation methods, the thermal and reductive treatments [3,4].

Hydrothermal method has been applied to synthesize nanosized materials already, since products prepared by this method have well crystalline phase, which benefits to thermal stability of the nanosized materials.

In this paper, the preparation of TiO_2 anatase powders doped with $FeCl_3$ is reported. The samples have been characterized by X-ray diffractometry (XRD) and transmission electronic microscopy (TEM).

2. EXPERIMENTAL

2.1. Preparation of the iron-ion-doped TiO2 nanocrystalline powders

The iron-ion-doped TiO2 was synthesized by the hydrothermal method. TiO_2 amorphous powder, 2 g and the required amount of FeCl3 for 0.05%, 0.1%, 2%, 4%, 6% and 10% $FeCl_3$-TiO_2 were dissolved in NaOH solution then set in a 50 cm^3 autoclave. The degree of filling of autoclave was 70 %. The autoclave was heated to 473 K at a rate of 2.5 K/min, and kept at 273K for 2h, 5h and 10h. Autogenous pressure gradually increased as the temperature was raised. After the autoclave treatment, the resulting powders were rinsed repeatedly with acetone and deionized water, until the Cl– in the rinsing water could not be detected by 1M AgNO3 solution. The resulting powders were dried at 353K for 2 h under air atmosphere. All chemicals were of analytical grade and were used without further purification.

2.2. Characterization

The samples were characterized at RT by X-ray diffraction. The patterns were obtained using a Philips diffractometer using CuKα radiation, in the range $10° \leq 2\theta \leq 100°$ and the data were refined with the

Fullprof program [5], showing the single phase nature of the samples.

The crystallite sizes of samples were calculated from the half-height width of different diffraction peaks of anatase using the Scherrer equation.

The transmission electronic microscopy (TEM) has shown the shape and the size of the iron-ion-doped TiO2 nanocrystals.

3. RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction patterns for TiO2 doped with iron ion. All samples exhibit only patterns assigned to the well crystalline anatase phase showing the presence of a sharp peak at 25.0°which is the major peak for the anatase structure. Due to very low Fe content, any crystalline phase containing Fe could not be observed by XRD in Fe-doped TiO_2. For a coordination number of 6, Fe^{3+} and Ti^{4+} have similar ionic radii (0.79Å versus 0.75 Å), so Fe^{3+} can easily substitute Ti^{4+} into TiO_2 lattice. These results support that the current doping procedure allows uniform distribution of the dopants, forming stable solid solutions within TiO_2.

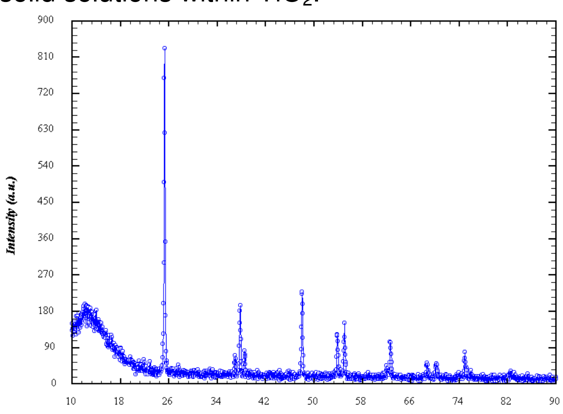

Fig. 1. X-ray diffraction pattern of iron-ion-doped TiO2 (2% $FeCl_3$-TiO_2).

The TiO2 particle was very spherical and regular form, and the size exhibited about 80–200 nm, depended by the growth conditions(time and the optimal Fe^{3+} concentration). For 2h and 0.1% $FeCl_3$-TiO_2, the nanocrystals have high specific surface areas and small crystal sizes, which are of benefit to efficient photocatalytic reactions.

The observed particle is showed in Fig. 2.

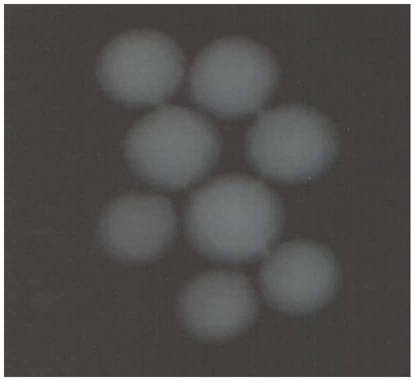

Fig. 2. TEM microphotograph of TiO2 anatase particles prepared by hydrothermal method

4. CONCLUSIONS

The hydrothermal method can be applied to dope TiO2 with metal ion deep and uniformly, which may effectively enhance photoactivity of TiO2. The properties of synthesized powders could be controlled by the hydrothermal conditions like Fe^{3+} concentration, temperature, duration of the synthesis and the degree of filling of autoclave.

REFERENCES

[1] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.

[2] A. Fujishima, T.N. Rao, D.A. Truk, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1.

[3] A. Di Paola, G. Marc`ı, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda, B. Ohtani, J. Phys. Chem. B 106 (2002) 637.

[4] D. Dvoranová, V. Brezová, M. Mazúr, M.A. Malati, Appl. Cat. B: Environ. 37 (2002) 91.

[5] J. Rodriguez-Carvajal, Physica B 192 (1993) 55.

AUTHORS

[1] PhD. M. Miclau, National Institute for Electro-Chemistry and Condensate Material, Timişoara, Romania

[2] PhD. I. Grozescu, National Institute for Electro-Chemistry and Condensate Material, Timişoara, Romania

[3] PhD. R. Baies, National Institute for Electro-Chemistry and Condensate Material, Timişoara, Romania

[4] PhD. C. Lazau, National Institute for Electro-Chemistry and Condensate Material, Timişoara, Romania