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ROOM TEMPERATURE FERROMAGNETISM IN Cu^{2+} DOPED TiO_2 NANOCRYSTALS

M. Vranješ [1], J. K. Jakovljević [1], Z. Konstantinović [2], T. Radetić [3], M. Stoiljković [1] and Z. Šaponjić [1]

[1]*Vinča Institute of Nuclear Sciences, University of Belgrade, P. O. Box 522, 11001 Belgrade, Serbia*
[2]*Institut de Ciéncia de Materials de Barselona, CSIC, Campus UAB, 08193 Bellaterra, Spain*
[3]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*

ABSTRACT

Hydrothermal synthesis of Cu^{2+} doped TiO_2 nanocrystals, using dispersion of titania nanotubes in the presence of Cu^{2+} ions as precursor, which showed room temperature ferromagnetism, is reported. Morphology of Cu^{2+} doped TiO_2 nanocrystals was characterized by transmission electron microscopy (TEM). An average size of polygonal nanocrystals mainly of square/rectangular shape was around 13 nm. The x-ray powder diffraction (XRPD) analysis of resultant powder confirmed the anatase crystal phase of Cu^{2+} doped TiO_2 nanocrystals. Room temperature ferromagnetic ordering with saturation magnetic moment of the order of 2×10^{-2} μ_B per Cu atom was observed.

INTRODUCTION

Great practical motivation for exploring doped semiconductors leis in the possibility of combining their semiconductor characteristics with magnetic properties. Diluted magnetic impurities in semiconductors produces materials that show ferromagnetic ordering at room temperature and therefore are appealing for spintonics in which simultaneous control of charge currents and spin polarized currents will be possible. Progress in the field of diluted magnetic semiconductors (DMS) has revealed a numerous new physical phenomena, including spin coherence, a new ferromagnetism and spin-polarized photoluminescence [1,2]. Wide band metal oxide semiconductors (TiO_2, ZnO) doped with Co, Cu and Ni [3-6] presents the class of diluted magnetic semiconductors that has been identified by theoretical considerations and proved as a good candidate for achieving room temperature ferromagnetism. In this paper we report on new synthetic procedure, structural and magnetic properties of Cu^{2+} doped TiO_2

nanocrystals. Using as a precursor titania nanotubes instead of molecular precursors we eliminated driving force problem that arises from the increase in the activation energy for nanocrystal nucleation in the presence of the dopant ions and consequent exclusion of the Cu^{2+} ions during nanocrystal growth.

EXPERIMENTAL

All chemicals were reagent-grade from Aldrich and used as received. Titania nanotubes were synthesized according to Kasuga et al. [7], using TiO_2 powder as a precursor. Cu^{2+}doped TiO_2 nanocrystals were synthesized using hydrothermal treatment (250 ^oC / 90 min) of a dispersion containing titania nanotubes (125 mg/50 ml) at pH=3 in the presence of 3,11 x 10^{-4} M $Cu(NO_3)_2$. In order to remove the excess of Cu^{2+} ions the dispersion of Cu^{2+} doped TiO_2 nanocrystals was dialyzed against acidified water (pH=3) at 4 ^oC for 3 days. Water was changed daily. Films for magnetic characterization were prepared by drop casting of dialyzed dispersions of Cu^{2+} doped TiO_2 nanocrystals onto pre-cleaned glass substrate. The films were annealed in air for 2 min at 150 ^oC after each drop. The shape and size of Cu^{2+} doped TiO_2 nanocrystals were characterized using JEOL 100 CX transmission electron microscope operating at 100 kV. The XRPD pattern was obtained on a Philips PW-1050 automated diffractometer. The percent of Cu^{2+} ions in TiO_2 nanocrystals was determined using ***inductively coupled plasma*** (ICP) emission spectrometry. The field dependence of the magnetic moment was measured using a superconducting quantum interference device magnetometer (SQUID). Hysteresis loop measurement has been performed up to 60 kOe.

RESULTS AND DISCUSSION

The XRPD analysis of Cu^{2+} doped TiO_2 nanocrystals revealed the existence of a homogeneous anatase crystal phase, Figure 1. Conventional TEM image of Cu^{2+} doped TiO_2 nanocrystals, Figure 1, inset, confirmed relatively uniform size distribution of faceted nanocrystals with average size of 13 nm.

The magnetic response for film made of 0.34 at% Cu^{2+} doped TiO_2 nanocrystals as a function of magnetic field strength (*H*) was followed at room temperature. The

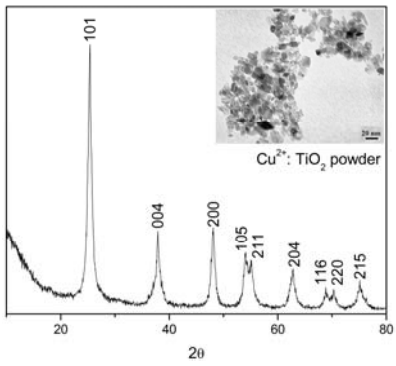

Figure 1. XRPD pattern of Cu^{2+} doped TiO_2 nanocrystals; Inset: TEM image of Cu^{2+} doped TiO_2 nanocrystals

magnetic field was applied parallel to the film surface. The diamagnetic contribution determined from the magnetic field dependence of magnetization at high field (for H > 10 kOe) was subtracted. The field dependent magnetization after diamagnetic correction is shown in Figure 2.

As can be seen from Figure 2, a weak room temperature ferromagnetic behaviour of Cu^{2+} doped TiO_2 nanocrystals was observed, with coercive field of *H*c ~ 200 Oe and saturation magnetization (M_s) of the order of 2 x 10^{-2} μ_B/Cu. Previous study indicated that the unexpected magnetism in such system could be the result of the interaction between the intrinsic defects and the doped ion [8]. There is couple of different carrier- mediated mechanisms that could provide an explanation for the influence of oxygen vacancies and structural defects on the ferromagnetic ordering in DMSs: carrier mediated interaction such as Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange, Zener double exchange or super exchange [5,8]. But, ferromagnetism in oxides with high electric resistance and low carrier densities such as the Cu^{2+} doped TiO_2 nanocrystals can be explained in terms of the noncarrier-mediated bound magnetic polaron (BMP) model [9]. When defects (oxygen vacancies) concentration increases they overlap many dopant ions to yield BMPs. This result in ferromagnetic coupling between Cu^{2+} ions mediated through oxygen vacancies. Li et al. proposed that substitutional Cu impurity binds easily with an oxygen vacancy (V_O) in TiO_2 to form the complex defect Cu_{Ti}-V_O, which relaxes to form the non-regular magnetic CuO_4 complex, in which the Cu ion is strongly magnetic [8]. This complex is similar to the magnetic one in other 3*d* transition metal-doped TiO_2 rutile films [10].

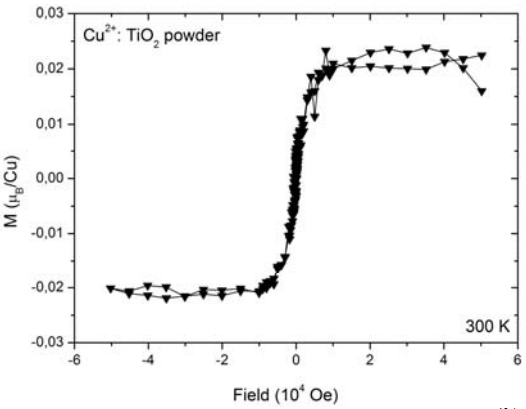

Figure 2. Magnetization curve for Cu^{2+} doped TiO_2 nanocrystals

CONCLUSION

The polygonal Cu^{2+} doped TiO_2 nanocrystals (d ~ 13 nm) were synthesized applying hydrothermal treatment on dispersion of titania nanotubes in the presence of Cu^{2+} ions at pH=3. XRPD study confirmed the anatase crystal structure of Cu^{2+} doped TiO_2 nanocrystals and absence of any impurity phases (CuO, Cu_2O) in the sample. The weak ferromagnetic ordering at

room temperature with almost closed loop (*Hc* ~ 200 Oe) and saturation magnetic moment of the order of 2 x 10^{-2} μ_B/Cu atom were observed in film made of Cu^{2+} doped TiO_2 nanocrystals. The reason for observed weak ferromagnetism could be found in the interaction between the oxygen vacancy and the substitutional Cu impurity.

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