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Controlled synthesis of mesoporous codoped titania nanoparticles and their photocatalytic activity

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Abstract. The photocatalytic (PC) activity of anatase titania nanoparticles can be improved through codoping with transition metals and nitrogen. In addition, the PC activity can also be improved by creating monodisperse, mesoporous nanoparticles of titania. The question naturally arose as to whether combining these two characteristics would result in further improvement in the PC activity or not. Herein, we describe the synthesis and photocatalytic characteristics of codoped, monodisperse anatase titania. The transition metals tested in the polydisperse and the monodisperse forms were Mn, Co, Ni, and Cu. In each case, it was found that the monodisperse version had a higher PC activity compared to the corresponding polydisperse version.

Keywords: titania; codoped; phototcatalysis; macro-spores; micro-spheres; hydrothermal method; hybrid method

1. Introduction

The poor conductivity of TiO_2 stands in the way of being more an efficient photocatalyst. In order for the photo-generated holes and electrons to be effective, they must reach the surface of the material before they recombine, the faster they can move, the less likely they will combine. Unfortunately, the electron mobility in TiO_2 is quite low, having a value of 0.1 cm^2/V.sec in mesoporous TiO_2 thin films (Tiwana *et al*. 2011). Using structures with nanometer-sized dimensions mitigate this somewhat by reducing the distance the charges through which the particles move, but on the other hand, the charges must then navigate across grain boundaries and particle interfaces. The higher the crystallinity of the material, the lower the barriers for the charges (Benko *et al*. 2003). It has also been shown that materials consisting of nano-sized beads of non-uniform size also suffer from poor charge mobility (Pascoe *et al*. 2014).

Adding metal ions to the TiO_2 structure through doping can increase conductivity. Among the metals used for doping TiO_2 that show significant increases in conductivity are Nb (Yamada *et al*. 2007, Liu *et al*. 2010, Wang *et al*. 2009), Sb (Wang *et al*. 2009), Ta (Wang *et al*. 2009), and Sn (Dorman *et al*. 2014). Doping with anions such as fluorine also increases conductivity *(*Seo *et al.*

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Park, Y.R. and Kim, K.J. (2005), "Structural and optical properties of rutile and anatase TiO_2 thin films: effects of Co doping", *Thin Solid Film*., **484,** 34-38.

Pascoe, A.R., Chen, D., Huang, F., Duffy, N.W., Caruso, R.A. and Cheng, Y.B. (2014), "Charge transport in photoanodes constructed with mesoporous TiO_2 beads for dye-sensitized solar cells", *J. Phys. Chem. C* **118**(30), 16635-16642.

Seo, H., Baker, L.R., Hervier, A., Kim, J., Whitten, J.L. and& Somorjai, G.A. (2011), "Generation of highly n-type titanium oxide using plasma fluorine insertion", *Nano Lett.*, **11**(2), 751-756.

Thompson, T.L. and Yates, J.T. (2006), "Surface science studies of the photoactivation of TiO_2-new photochemical processes", *Chem. Rev.*, **106**, 4428-4453.

Tiwana, P., Docampo, P., Johnston, M.B., Snaith, H.J. and Herz, L.M. (2011), "Electron mobility and injection dynamics in mesoporous ZnO, SnO_2, and TiO_2 films used in dye-sensitized solar cells", *ACS Nano*, **5**(6), 5158-5166.

Wang, X., Cao, L., Chen, D. and Caruso, R.A. (2013), "Engineering of monodisperse mesoporous titania beads for photocatalytic applications", *Appl. Mater. Interfac.*, **5**, 9421-9428.

Wang, Y., Brezesinski, T., Antonietti, M. and Smarsly, B. (2009), "Ordered mesoporous Sb-, Nb-, and Ta-doped SnO_2 thin films with adjustable doping levels and high electrical conductivity", *ACS Nano*, **3**(6), 1373-1378.

Yamada, N., Hitosugi, T., Hoang, N.L.H., Furubayashi, Y., Hirose, Y., Shimada, T. and Hasegawa, T. (2007), "Fabrication of low resistivity Nb-doped TiO_2 transparent conductive polycrystalline films on glass by reactive sputtering", *Jap. J. App. Phys.*, **46**(8R), 5275.

Zhu, W., Qiu, X., Iancu, V., Chen, X.Q., Pan, H., Wang, W., ... and Stocks, G.M. (2009), "Band gap narrowing of titanium oxide semiconductors by noncompensated anion-cation codoping for enhanced visible-light photoactivity", *Phys. Rev. Lett.*, **103**, 226401.

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