Solution based routes to energy materials; Oxide semiconductors and metal-in-ceramic composites

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Introduction

Sol-gel type processing routes receive much attention due to the possibilities of preparing very unique and high quality materials of various shapes and complexities. They also offer direct and simple processes allowing for easy technological exploitation without the use of complex and size limiting vacuum chambers.

Here we describe solution based synthesis routes to important energy materials: (i) wide band-gap semiconductors such as doped TiO_2, ZnO and WO_3, as thin films, core-shell, mixed phased and wire oxides, and (ii) metal in ceramic composites in thin film and sponge structures. The former systems were investigated as photo-catalysts decomposing gas-phase organic compounds and water into hydrogen fuel and oxygen, but also as magnetic semiconductors. The latter materials were investigated as spectrally selective solar heat absorber and dry reforming catalyst, converting the greenhouse gases; methane and carbondioxide into a mixture of hydrogen and carbon monoxide according to: $CO_2 + CH_4 \rightarrow CO + 2H_2$ which can used as fuel or synthesis of more complex organic molecules.

Oxide semiconductors

The preparation of transition metal-ion doped, nano-mixed phase and, core-shell and wire nano-structured oxide semi-conductors based on TiO_2, WO_3 and ZnO is described with a focus on the processing and the strong influence of the precursors and heat-treatment on the materials structures, contents and properties. Elucidation of the phase development on heating to yield the target materials was made with a combination of techniques such as; TGA, DSC/DTA, SEM, TEM, XRD, XAS, XPS, IR-, Raman and UV-Vis-NIR spectroscopy. The photo-catalytic and magnetic properties were investigated in some detail. Different TiO_2 phases, particle sizes and surface facets were compared, and from these studies, a TiO_2 photo-catalyst with ca 15 times higher decomposition rate of organic molecules than P25 was obtained. In addition, doped titania catalysts showed a high and sustained photo-catalytic activity which is well known not to be the case for pure titania (1-3).

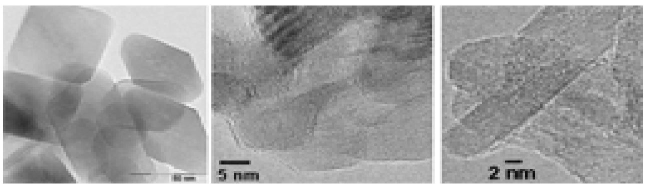

Figure 1. TEM images of TiO_2 nano-particles prepared by solution routes; anatase (left); brookite (mid), and rutile (right), prepared by solution routes.

A salt based route to WO_3 was developed and used for formation of mixed nano-phase, core-shell structures of TiO_2-WO_3, as well as WO_3 wires.

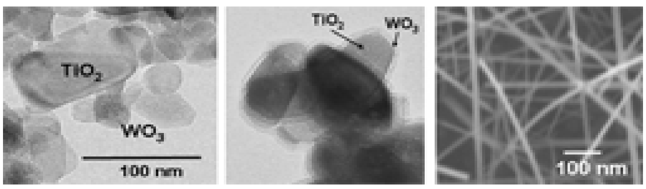

Figure 2. TEM images of WO_3-TiO_2 as; mixed phase (left) and core-shell structure (mid) and WO_3 wires (right).

ZnO:CoO films and powders were obtained with up to 15-20 mol% Co via a purely alkoxide based route, while conventional metal-organic routes allow only for a doping concentration of up to 6% CoO. However, even with such high Co^{2+} doping levels we did not observe any high temperature ferromagnetism (4-7).

Metal-in-ceramic matrix composites

Metal-in-ceramic composites containing nano-sized metal inclusions are expected to become the leading materials for a wide range of technological applications, such as catalysis, carbon nano-tube growth, magnetic response materials, resistors, memories, light-weight structural ceramics, durable coatings and spectrally selective solar heat-absorbers. The research focus in this case is on low cost salt-based solution based routes to homo- and heterometallic nano-inclusion materials of M-Al_2O_3 with metals from the d- and p-blocks. Besides alumina, matrix ceramics were made with metals taken from the s, d and p-blocks. The metal particle sizes could be controlled down to below 5 nm and the metal particle loadings could be achieved up to over 80% without particle coalescence. The materials could be prepared both as dense, thin films and porous sponge and foam-like structures.

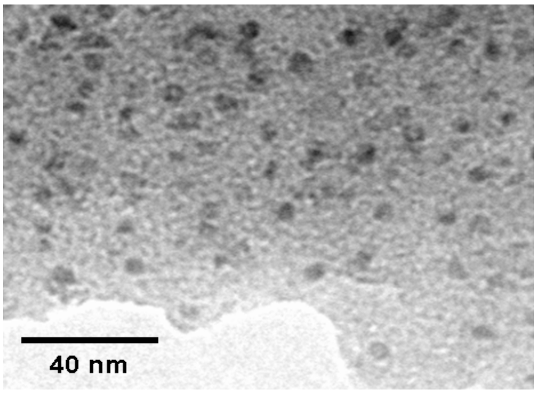

Figure 2. TEM image of 10 mol% Ni-$AlO_{1.5}$ nano-composite.

Spectrally selective solar heat absorbers with a record high efficiency of; absorptance of 0.97 and emittance of 0.05 at 100°C, were obtained with a three layer stack consisting of; Ni(80%)-Al_2O_3/Ni(40%)-Al_2O_3/SiO_2 on aluminum (8-12). The deposition could be done by spin-, spray- or roll-coating. The latter technique was exploited in industrial up-scaling for roll-to-roll deposition of 50 m bands. The glossy black coatings are appealing and mechanically and chemically very durable which allows for unprotected architectural applications with is currently explored. In addition, highly porous composites were successfully tried out for catalysis of the methane reforming reaction: $CH_4 + CO_2$ to $2H_2 + CO$, producing carbon-free hydrogen.

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