Scalable solution based processes to energy materials

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Introduction

Complex hetero-phase nano-structures including metals and ceramics are required for optimised energy materials including batteries, solar cells, solar assisted fuel generation and high efficiency solar thermal applications. This to include a number of different functions working in concerted manner, such as a photon absorber for hole-electron formation and catalysis of one or more reactions, Li insertion and transport etc. But nevertheless the materials need to be prepared at low cost and high throughput, which is partly achieved through the use of low cost abundant elements, but perhaps to an equally large degree through the use of highly efficient materials synthesis routes. In this respect the wide spectrum of solution based techniques are the most promising. Therefore there is a great need for development of efficient, low cost, reliable synthesis routes for complex multi-element multi-phase materials. Both the elemental composition and detailed nano/microstructure need to be controlled at a very high degree with few processing steps. Here different processes to complex metal-ceramic composite materials will be presented and discussed; (i) metallic nano-particles in an oxide matrix (ii) metallic coatings on oxide nano-structures. A solution based route that yields homogeneous distributions of Cobalt, Nickel or Copper nano-particles in sizes down to 1-2 nanometres and metal loadings of up to ca 85-90% in alumina is was developed. The metal in ceramic composites can be deposited on various substrates to yield thin films on flat surfaces, such as Si/SiO_2, but also on various kinds of oxide nano-structures such as porous films TiO_2, Fe_2O_3 or ZnO particles. The metal-in-ceramic materials are of interest for their magnetic, catalytic and optical properties. The optical absorption properties of flat films was investigated and optimised for solar thermal applications. Further on the combination of the composites with photo-active oxide nano-particles and wires may result in enhanced photo-catalytic properties due to the catalytic properties of well dispersed metal nano-particles, where Ni nano-particles are known to often be beneficial for activation of hydrocarbons.

A second process was developed yielding nano-structured metal thin films, coatings and sponges of e.g. Ni, Cu and Cu. The nano-structured thin films and sponges are described. In addition, metal coatings on nano-structured oxide particles and wires were achieved with metal coating thicknesses down to 1-2 nm (Fig 1.).

Experimental

Two solution based routes are described using simple metal-ion precursors such as nitrates and acetates complex bound by organic molecules. They are capable of (i) producing composites of well distributed metal nano-particles of cobalt, nickel or copper metal particles within an amorphous alumina matrix, and (ii) nano-structured metal films, sponges and coatings.

The conversion of the metal-organic complex solutions to composite or metal is achieved at temperatures up to 500^{o}C. No or very short annealing times were used for any of the routes [1-5].

Films were prepared by depositing the solutions on different substrates by spin- or dip-coating. After subsequent heat-treatment dense glossy films were obtained. A wide range of substrates were successfully tried out for deposition of both the metal-oxide composites and metals, including Si/SiO_2, aluminium, steel, alumina, quartz and window glass. Various kinds of nano-structured oxide films were prepared on Si/SiO_2 substrates, such as porous films of 20-25 nm sized ZnO nano-particles or ZnO wires, and then composite or metal films a few nano-metres were deposited on the structures. The microstructures and elemental composition were obtained with transmission and scanning electron-microscopes; TEM-EDS/ED (Jeol 2100F or Jeol 2000FXII-Link 10000AN) and SEM-EDS (Leo 1550 and 440, and Jeol 820). The crystalline contents were obtained by X-ray diffraction using Guiner–Hägg geometry cameras ($K\alpha_1$ radiation) or Siemens D5000 diffractometers ($K\alpha$ radiation), the organic and amorphous contents were acquired with IR spectroscopy (Bruker IFS-55) and the decomposition by thermo-gravimetry (TG, Perkin-Elmer TGA7).

Results and discussion

Composites with a very even distribution of the metal particles being in sizes down to 1-2 nm were obtained in these systems. Loadings of up to 85% metal were successfully achieved with retained narrow size distribution and with the particles still being isolated by alumina.

The films were investigated on their optical properties for solar thermal applications. The Ni metal particle sizes and refractive index of the composites were used as input for optimising a three layer graded film structure on aluminium; from the bottom: 80% Ni, 40% Ni and a top layer of SiO_2 [2-6]. The optimised structure yielded record high efficiency at 100^{o}C (97% absorptance and 5% emittance). The process has been scaled to semi-continuous pilot process.

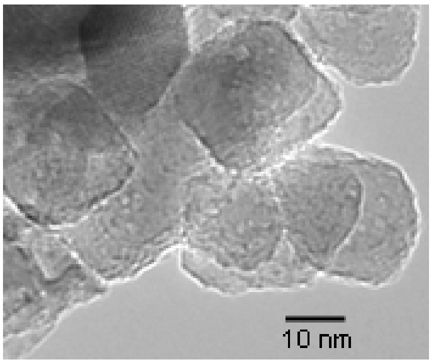

Figure 1. TEM image of 1-2 nm thick nickel coating of a TiO_2 anatase porous electrode..

Conclusions

Solution based processes provide efficient routes to highly nickel nano-particle loaded M-Al_2O_3 composite materials, as well as metals, showing a wide range of interesting optic and catalytic properties, including record high efficiency solar thermal absorbers. The processes can be efficiently deposited on many kinds of complex shape substrates and be used to build highly complex and precise functional metal-oxide materials.

References

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