Nanostructure of Magnesium for Hydrogen storage

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Due to its high hydrogen capacity, low specific weight and abundance, Magnesium, has been intensively studied as promising material for hydrogen storage even if slow reaction rate and high hydride stability are still open problems. Nanostructuring can provide a way to overcome the thermodynamic and kinetic barriers in order to tailor the sorption properties to the technological requirements.

In this work we study nanostructured magnesium powder produced by Inert Gas Condensation (IGC), that allows the formation of dispersed nanoparticles (NPs) with a core shell structure. The single crystal magnesium core in fact, is surrounded by a shell of magnesium oxide, produced directly by controlled oxidation in the synthesis chamber. The average particle size can be controlled by the pressure in the reaction chamber, so that this method can provide nanostructured model systems for the investigation of the basic aspects of the metal-hydride transformation (MHT). In addition, the decoration of surfaces with transition metals in order to assist the H_2 molecule dissociation/recombination can be carried out in the same reaction chamber by a post-synthesis vacuum deposition.

TEM (FEI Tecnai G2 30F, Schottky field emission source, 300kV), XRD and volumetric kinetics measurements are used in combination to correlate the morphological structure with the hydrogen sorption properties of IGC Mg NPs.

In particular, in this paper we report about the microstructure of Mg-MgO core shell NPs and the same NPs decorated with Pd nanocrystals deposited at the surface. This kind of material has in fact shown a fast hydrogen uptake and release kinetics.

In agreement with previous observation, the synthesized particles are single crystals, mostly with six-fold symmetry, arising from the coupling of two truncated pyramids whose basal planes coincide with a (0001) lattice plane. The average size of the Mg_Pd NPs (that is Mg-MgO NPs decorated with Pd clusters of 3-4nm in size) is about 450nm, as it can be observed in Fig 1. The image in Fig. 1(b) was recorded with the annular dark field detector in STEM mode. Since the image contrast arises from thermally diffuse scattering approximately proportional to the square of the average atomic number of the atomic column, the bright areas (marked by arrows in the figure) highlight the regions where Pd is present. Pd is present always at the particle surface and casts a shadow on a portion of the total surface, as expected from the experimental geometry adopted. In fact, in the IGC method, NPs are deposited by soft landing with random orientation, while Pd decoration occurs by evaporation from a point source and so, covering just the exposed surfaces. The selected thickness of the collected NPs film, corresponding to 1-2 NP monolayers, allowed for efficient decoration of practically all NPs.

Fig. 1(c) is a high resolution TEM image, taken along the [0001] orientation, of the Pd-decorated edge marked by the white arrow in Fig. 1(b). Going from left to right, the hexagonal lattice pertaining to the Mg core is followed by the cubic lattice having the interplanar spacing of MgO. The thickness of this nanostructured oxide layer is 4-5 nm.

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Finally, Pd clusters with of 3-4 nm size appear to constitute a non-continuous outer layer on top of the MgO shell. All these findings are supported by EDS microanalysis results.

In conclusion, we have analyzed the microstructure of Pd-decorated core shell Mg-MgO NPs produced by IGC. The careful description of the particles microstructure is of fundamental importance in the interpretation of the reaction kinetics with hydrogen in order to evidence the reaction rate limiting steps.

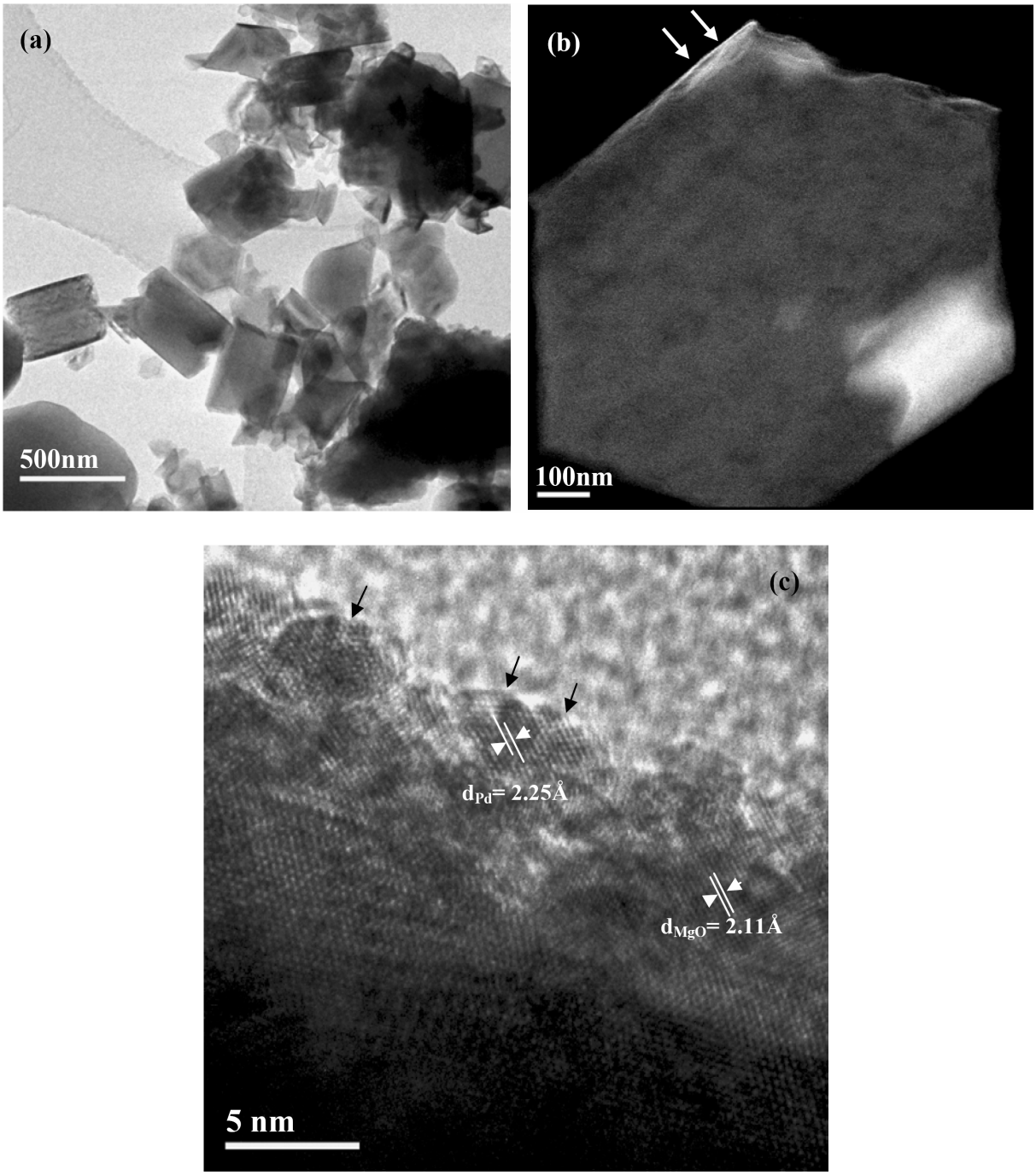

Figure 1. (a):Low magnification TEM image. (b): STEM image of as-prepared Mg_Pd NPs. Pd decoration appears in form of brighter and almost spherical regions (pointed by arrow) (c): HRTEM of the region marked by arrows in (b) taken along the same [0001] orientation. The Mg core is visible as hexagonal lattice to the left bottom of the image.

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