



Synthesis, characterization, and hydrogen uptake studies of magnesium nanoparticles by solution reduction method



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ABSTRACT

Facile and simple, surfactant-mediated solution reduction method was used to synthesize monodisperse magnesium nanoparticles. Little amount of magnesium oxide nanoparticles were also formed due to the presence of TOPO and easy oxidation of magnesium, eventhough, all precautions were taken to avoid oxidation of the sample. Precise size control of particles was achieved by carefully varying the concentration ratio of two different types of surfactants, – trioctylphosphine oxide and hexadecylamine. Recrystallized magnesium nanoparticle samples with and without TOPO were analyzed by X-ray diffraction, scanning electron microscope, field emission scanning electron microscope, and transmission electron microscope. The peak diameters of particles were estimated from size distribution analysis of the morphological data. The particles synthesized in the presence and absence of TOPO found to have diameters 46.5 and 34.8 nm, respectively. This observed dependence of particle size on the presence of TOPO offers a convenient method to control the particle size by simply using appropriate surfactant concentrations. Exceptional enhancement in hydrogen uptake and kinetics in synthesized magnesium nanoparticles as compared to commercial magnesium sample was due to the smaller particle size and improved morphology. Overall hydrogen uptake not affected by the little variation in particle size with and without TOPO.

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1. Introduction

Magnesium plays a key role in the development of high density solid-state hydrogen storage devices because of its high gravimetric hydrogen storage capacity (7.6 wt%) [1,2]. However, the practical application of the bulk-magnesium as a hydrogen storage material is limited due to its extremely slow hydrogen sorption kinetics at ambient conditions. The slow hydrogen sorption kinetics exhibited by bulk-magnesium is ascribed to kinetically limited surface-to-bulk diffusion and poor hydrogen recombination rates, as suggested by the density functional modeling studies of the bulk-magnesium potential energy surfaces [3,4]. Nevertheless, the ambient temperature, hydrogen adsorption, and release kinetics in magnesium can be significantly accelerated by reducing the bulk-magnesium to nanoscopic dimensions [5–8]. A remarkable 40 times enhancement in the hydrogen absorption rate was benchmarked by Zaluksa et al., by reducing the particle size of magnesium from 1 μm to 20–30 nm [7,8]. A theoretical footing for this enhanced kinetics has been recently provided by comparing

the Hartree–Fock derived the relative stability of Mg and MgH_2 in the bulk and the nanoscopic dimensional regimes [9]. Additionally, it has been suggested that increased defects and the reduced diffusion length in nano-sized magnesium particles also contribute to the enhanced sorption kinetics when compared to the bulk-samples [10]. The evaluation of the energy (hydrogen) storage in nano-sized magnesium is typically hindered by the difficulty associated with its synthesis. Presently, most synthesis of nano-sized magnesium particles is performed using high energy ball milling and hydrogen plasma-metal reaction (HPMR) [5–8,11,12]. However, the size control of magnesium nanoparticles fabricated in a ball-milling setup is extremely difficult due to the high ductility of the metal [13]. Furthermore, the complex experimental parameters of these processes depend on the particular experimental setup and have to be developed and optimized individually. Yet again, the highest energy processes involved in the HPMR or ball-milling typically results in the partial oxidation of surface magnesium to the metal oxide, – which is not transparent to the hydrogen sorption [11,14]. Not too surprisingly, the synthesis of magnesium nanostructures appears rare in the literature. This, demands the formulation of simple and size-controllable magnesium nanoparticle synthesis techniques, if the magnesium-based solid state hydrogen storage devices are to be developed. On the

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other hand, a number of methods have been developed for the preparation of metal nanoparticles, mostly for transition metals, which includes photolytic reduction, sonochemical method, microemulsion technique, and chemical reduction method [15–20]. Amongst these, reduction synthesis of metal nanoparticles in the presence of surfactants: alkyl phosphine oxide-alkyl phosphine has received considerable attention recently, as it provides very good control on the dispersion and the size of the synthesized nanoparticles [19,20]. This method is simple, inexpensive, and efficient, when compared with the high energy complex processes, such as HPMP and ball milling.

The present study is undertaken to report preparation of magnesium nanoparticles using the reduction of the magnesium salt in the presence of surfactants, – trioctylphosphine oxide and hexadecylamine. The reduction of $\text{Mg}(\text{acac})_2$ is performed using sodium borohydride in an aqueous medium. Different ratios of surfactant concentrations are used to control the growth of nanoparticles and to protect them from oxidation and aggregation. Hydrogen uptake studies of commercial magnesium powder and synthesized magnesium nanoparticles were performed using Sievert's volumetric apparatus at 323, 573, 623, 673 K and hydrogen pressure of 4.5 MPa.

2. Experimental

2.1. Chemical synthesis of magnesium nanoparticles

Sodium borohydride (98%), trioctylphosphine oxide (99%), magnesium acetylacetonate dihydrate (98%), *o*-dichlorobenzene (99%), and hexadecylamine (98%) were purchased from Sigma–Aldrich. All of them were used without further purification. The nanoparticle synthesis using the standard Schlenk technique was carried out under nitrogen atmosphere throughout the experiment. The synthesis involved the reduction of magnesium acetylacetonate [$\text{Mg}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$] in the presence of TOPO and HDA using NaBH_4 as the reducing agent. In a typical nanoparticle synthesis, 0.2 g of the [$\text{Mg}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$] in a RB flask was dissolved in 10 ml of *o*-dichlorobenzene at 100 °C, and quickly injected into a mixture containing 40 ml of *o*-dichlorobenzene, 0–1 g TOPO, 1 g HDA, and 0.15 g of NaBH_4 at 100–140 °C under vigorously stirring condition. The amount of TOPO was varied in order to control the dimension of the nanoparticles. The mixture was slowly heated to 180 °C and aged at this temperature for nearly 30 min. During this process, the solution became slightly whitish-gray indicating the formation of magnesium nanoparticles. The obtained solution was allowed to cool to room temperature. The magnesium nanoparticles were extracted from the solution by addition of ethanol. The product was re-dispersed in hexane and was filtered and dried in a vacuum oven.

2.2. Characterization

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and field emission scanning electron microscopy (Hitachi, S4700) studies were performed to evaluate morphology and particle size. The samples for TEM were prepared by depositing a drop of magnesium nanoparticles dispersed in ethanol onto a coated-carbon Cu grid, followed by evaporation of the solvent. Powder X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/MAX 2500 X-ray diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.1541 \text{ nm}$)

2.3. Hydrogen storage

Hydrogen storage studies of synthesized magnesium nanoparticles and commercial magnesium powder were carried out on

a Sievert's volumetric device at 323, 573, 623, 673 K and hydrogen equilibrium pressure of 4.5 MPa. Sievert's volumetric apparatus consists of a hydrogen buffer-tank, a reactor, and a high sensitivity and calibrated pressure transducer (0.05% error at full scale) connected to PC via RS-232 device. Prior to the storage experiments, we performed the iterative dead-volume determination of the system using the Redlich–Kwong equation of the state of helium gas. The determined volume was additionally cross-checked using the density and the hydrogen adsorption data of a known amount of the intermetallic alloy LaNi_5 . Nearly 0.5 g of magnesium nanoparticles was used in each hydrogen storage study. Prior to each adsorption experiment, the samples were outgassed for nearly 2 h under continuous evacuation up to 10^{-4} Torr. Re-adsorption studies were typically performed by outgassing the samples at 200 °C under evacuation up to 10^{-4} Torr. For adsorption experiments, high purity hydrogen gas (99.9999%) initially at equilibrium vented into the reactor and the pressure drop in the hydrogen gas was measured as a function of time. The storage capacity of the samples was determined from the pressure drop of hydrogen gas using the ideal gas equation. After each experiment, the corresponding sample was degassed under aforementioned conditions and was subjected to repeated storage experiments to understand if the maximum hydrogen storage capacity diminishes with the hydrogenation–dehydrogenation cycles. Further hydrogen storage experimental details can be obtained from elsewhere [21,22].

3. Results and discussions

In Fig. 1(a) and (b), XRD pattern of magnesium nanoparticles synthesized with and without TOPO is displayed, respectively. The XRD spectra are characterized by several intense peaks between the diffraction angle 5 and 70°. The peaks that appear above the diffraction angle 30° can be indexed to the reflection from (201), (100), (202), (004), (104), and (203) planes of the bulk-metallic magnesium with hexagonal structure. Both spectra shows characteristic low angle diffraction peaks ($2\theta < 5\text{--}15^\circ$) suggesting the existence of larger unit cells, in addition to the metallic-magnesium unit cells. These larger unit cells or so-called superlattices are typically formed when a periodic arrangement of surfactant-capped metal clusters occurs [23]. By comparing the XRD pattern (a) and (b), we infer that the formation of superlattices predominantly takes place when the magnesium nanoparticles are prepared in the absence of TOPO. Previously, it was known that

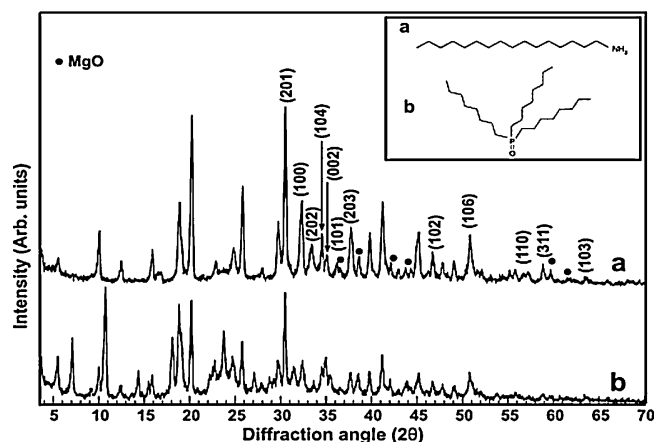


Fig. 1. X-ray diffraction (XRD) pattern of magnesium nanoparticles synthesized by solution reduction method. Profile 'a' corresponds to the sample prepared with TOPO, while the profile 'b' corresponds to the sample prepared without TOPO. Peaks arising from the MgO are indicated using (●).

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