Palladium based nanomaterials for enhanced hydrogen spillover and storage

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Hydrogen storage remains one of the most challenging prerequisites to overcome toward the realization of a hydrogen based economy. The use of hydrogen as an energy carrier for fuel cell applications has been limited by the lack of safe and effective hydrogen storage materials. Palladium has high affinity for hydrogen sorption and has been extensively studied, both in the gas phase and under electrochemical conditions. In this review, recent advancements are highlighted and discussed in regard to palladium based nanomaterials for hydrogen storage, as well as the effects of hydrogen spillover on various adsorbents including carbons, metal organic frameworks, covalent organic frameworks, and other nanomaterials.

Introduction

Hydrogen has the potential to be a principal energy carrier. It has attracted significant attention not only because of its high energy density and light weight, but also because of the technological problems involved with its storage and release [1,2]. Since hydrogen is gaseous at ambient temperature and pressure, its confined storage is impractical. It is clear that the key challenge in developing this technology is centered on the viable storage of hydrogen. Presently hydrogen may be stored by different techniques such as within compressed tanks, in liquefied form, and as solid state hydrides. Currently, however, none of these storage methods have met the demands for onboard vehicular applications [3–7]. For transportation applications, the US Department of Energy (DOE) has set $\geq$7.5 wt% as the system capacity targets for onboard hydrogen storage in fuel cell applications in vehicles under ambient temperature and a maximum pressure of 12 bar [8,9]. Solid-state materials have been considered as potential candidates for hydrogen storage, over other storage techniques [10]. The hydrogen storage capacities of various solid state hydrides (including metal hydrides and adsorbents) are displayed in Fig. 1 [9]. Hydrogen may be stored as either molecular hydrogen (physisorption), or as atomic hydrogen (chemisorption). The storage of molecular hydrogen relies on weak physisorption, and results in lower hydrogen capacities under mild conditions, whereas chemisorption can occur under ambient conditions, but utilizes materials that are very expensive. In some cases, the hydrogen sorption phenomena are irreversible, albeit higher temperatures can facilitate the release of the adsorbed hydrogen [11,12].

Significant roles of Pd in hydrogen storage

Several exceptional properties are exhibited by Pd, which enable its integration into various hydrogen technologies. Pd is considered to be unique material with a strong affinity to hydrogen, owing to both its catalytic and hydrogen absorbing properties [13,14], and it plays important roles in a hydrogen economy [15]. Intensive investigations of Pd hydrides have been conducted in various fields of fundamental science and technology. In contrast to their bulk counterparts, nanostructured materials appear to exhibit more rapid charging and discharging kinetics, extended life cycles, and size tunable thermodynamics [16,17]. Many investigations of hydrogen storage employing bulk Pd or Pd based nanoparticles have been carried out recently [18]. In particular, Pd nanoparticles have been studied as an exemplar model for the elucidation of the hydrogen-storage properties of metallic nanoparticles. The absorption of hydrogen by Pd results in the formation of two phases. At low hydrogen concentrations (solid solution) the alpha phase appears, whereas at higher hydrogen concentrations (metal hydride) the beta phase appears. A schematic phase diagram of palladium hydride is depicted in Fig. 2 [19].

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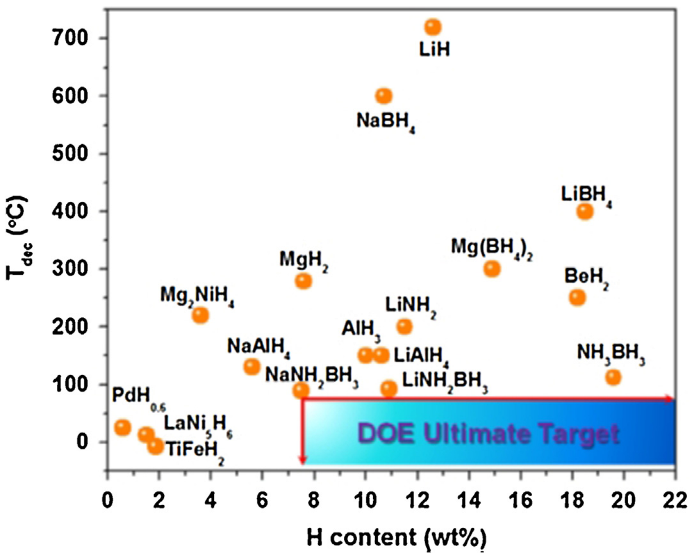

FIGURE 1

Overview of various solid-state hydrides, plot of decomposition temperatures (under 1 bar H_2 pressure) as function of heavy-metric hydrogen content. The ultimate DOE target is shown in the shadowed bar. (Reprinted with permission from [9]. © 2015 Elsevier).

Hydrogen concentrations and equilibrium pressures for the formation of Pd hydrides were reported to decrease with smaller nanoparticle dimensions [20]. In addition to size, the morphologies of metallic nanoparticles have also been critical to materials chemistry, in that their intrinsic properties are strongly correlated with their geometries [21,22]. Recent work by Li et al. has demonstrated that the morphology of Pd may play a critical role in the storage capacity of hydrogen, and that temperature plays a critical role in its uptake, absorption, and diffusion. Fig. 3 depicts the isothermal hydrogenation profiles of Pd octahedrons (red) and cubes (blue) at 303 K, under a hydrogen pressure of 101.3 kPa [23]. Phase transitions of individual palladium nanocrystals during hydrogen absorption and desorption were investigated using *in situ* electron energy-loss spectroscopy under an environmental transmission electron microscope. Palladium nanocrystals undergo extreme transitions between α and β phases, where surface effects dictate the size dependence of hydrogen absorption pressures [16]. In order to reduce hydrogen embrittlement, Pd is alloyed with other metals, which results in the expansion of the Pd lattice, thus Pd becomes less influenced by hydrogen. A number of studies were

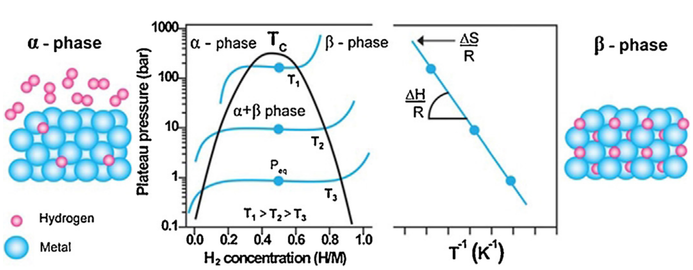

FIGURE 2

(Left) Pressure-composition isotherm plot of metal to metal hydride phase transition. (right) Van't Hoff plot related to the phase transition from metal to metal hydride. Schematic representation of alpha-phase (left) and beta-phase (right) of metal hydride are also shown. (Reprinted with permission from [19]. © 2011 Royal Society of Chemistry).

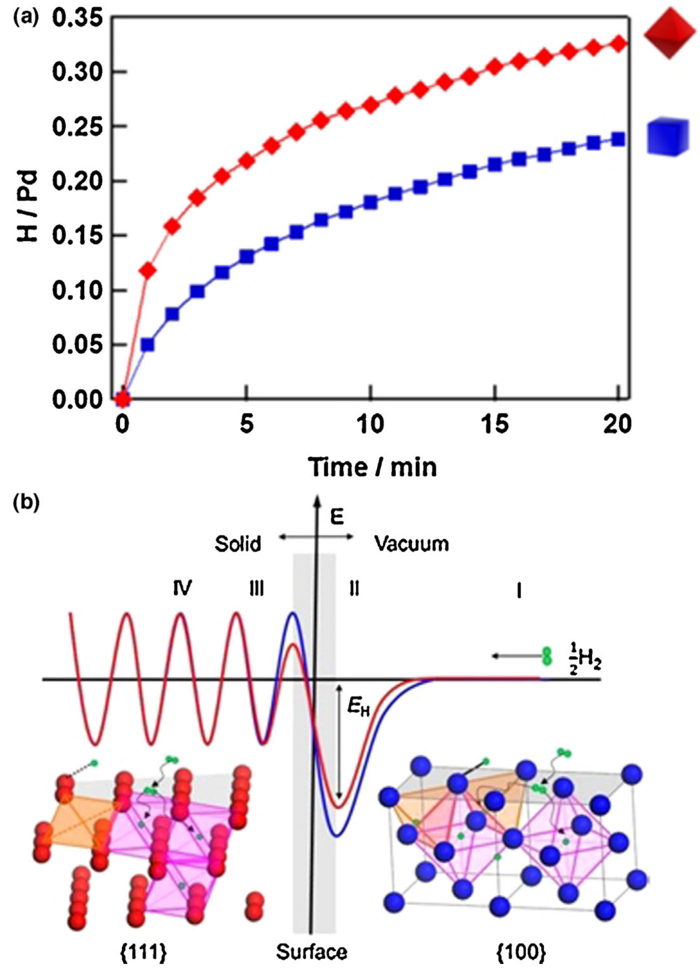

FIGURE 3

(a) Isothermal hydrogenation profiles of Pd octahedrons (red) and cubes (blue) at 303 K after introducing a hydrogen pressure of 101.3 kPa. (b) Schematic potential energy diagrams of the Pd octahedrons {1 1 1}/H (red) and the cubes {1 0 0}/H (blue) systems. (Reprinted with permission from [23]. © 2014 American Chemical Society).

carried out using a combination of Pd based alloys such as PdPt, PdCd, PdRu, PdRh, PdAg, PdCdAg to control hydrogen embrittlement [18,24–29]. In their work, T. Hango et al. investigated the effect of grain structure on hydrogen embrittlement using pure Pd (99.9%), which was processed by high pressure torsion (HPT) to form an ultrafine-grained (UFG) structure. Tensile tests revealed that, unlike coarse-grained samples in which hydrogen-induced embrittlement and hardening occurred, hydrogen-induced softening and elasticity occurred in the HPT-processed UFG sample [30].

Hydrogen spillover

It was observed by Khoobiar in 1964 that WO_3 was reduced by H_2 to blue WO_{3-x} when it came into contact with a platinum (Pt) catalyst. The presence of blue color was due to the chemisorptive dissociation of H_2 molecules on the surface of Pt particles that migrated to the yellow WO_3 particles, reducing them to blue WO_{3-x} particles [31]. Subsequently, Boudart et al. coined the term 'spillover' to describe the migration of H atoms from the metal particles to the substrate, explaining that H atoms spill over from hydrogen-rich to hydrogen-poor surfaces [32]. Extensive investigations as to the nature of hydrogen spillover were undertaken,