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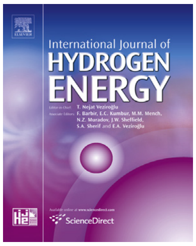

Short Communication

# Palladium nanoparticle and decorated carbon nanotube for electrochemical hydrogen storage

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ABSTRACT

This study proposes a multicomponent system for hydrogen storage. An electrochemical evaluation was used as a simple and accurate technique to assess the storage capacity. A porous silicon substrate was fabricated using an electrochemical anodization process and decorated with palladium nanoparticles using the electroless method. The hybrid substrate underwent chemical vapor deposition for 45 min. Since the deposited palladium nanoparticles could act as potential catalysts, carbon nanotubes grew properly over hybrid structure. The final sample was obtained through post-treatment by palladium nanoparticles using the same electroless method. This triplet sample was characterized using field emission scanning electron microscopy and X-ray diffraction. Galvanostatic charge/discharge experiments were used to conduct electrochemical evaluations of proposed electrode. A maximum hydrogen storage capacity of 537 mAh/g (~2.05 wt.%) was achieved for the triple-structure sample. The measurements demonstrate that the storage capacity of the triple-structure sample was reduced by a factor of 0.05% after 100 cycles. Although the obtained storage capacity is far from DOE targets, optimized structures based on the proposed electrode may be further developed as an efficient storage system.

## Introduction

These days, depletion and negative environmental impacts of fossil fuels have prompted scientists to research alternative energy resources. As a high-content energy resource, hydrogen has the potential to play an important role in sustainable development. Unlike fossil fuels, it is a clean energy resource and does not emit pollution during combustion operation. Hydrogen is also a renewable energy resource, and there is no concern regarding depletion. While several hydrogen production methods have been investigated to harness this potential [1,2], storage remains the primary obstacle to its practical application as an energy resource.

Recently, several structures and materials have been developed to address this problem. Among these, porous medias have demonstrated a high potential; in fact, the

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presence of pores in the substrate could offer large surface area and empty volume [3]. Porous silicon (PS) has received considerable attention in practical and theoretical studies [4,5]. Due to the medium affinity of PS and hydrogen [6], the presence of catalyst species associated with PS could improve storage capacity. For example, transitional metals could contribute to the efficient atomization process of hydrogen molecules [4,7], thereby facilitating the diffusion of hydrogen atoms into PS's nanoscale pores and channels. Moreover, the catalysts could improve the strength of interactions through chemisorption. Ghorbani Shiraz et al. demonstrated a high hydrogen storage capacity (HSC) for palladium (Pd)-decorated PS [8], observing that Pd nanoparticles selectively absorb hydrogen molecules [9] and improve storage capacity through atomization and chemisorption. Javan et al. studied hydrogen's interactions with a graphene-like silicon carbide (SiC) sheet doped with Pd using density functional theory [10]. They reported that hydrogen is absorbed chemically over either Pd or a silicon carbide sheet. However, some of the bonding may be attributable to the Kubas interaction, which is the hybridization of the hydrogen molecule's anti-bonding orbital with the d-orbital of the transition metal. Although Kubas interaction is one of the efficient hydrogenation process, its shortcoming is the tendency of metal species to clustering phenomenon [11]. Javan et al. reported that, in the absence of Pd, most of the interactions are physisorption.

Carbonaceous nanomaterials have recently exhibited a high potential for hydrogen storage applications. According to the literature, these nanomaterials could be hydrogenated through physisorption [12,13] and spillover [14,15]. Ren et al. documented that hydrogen's interaction (physisorption) with carbon nanomaterials possesses very low binding energy, which indicates a low HSC [16]. However, high surface areas, in the case of these materials, present the potential for numerous physisorption. Absolutely, decoration of carbonaceous nanomaterials with the transition metals could strongly create numerous physisorption and chemisorption interactions [11,17]. Faye et al. used the first principle method to calculate the HSC of Pd-functionalized graphene [4]. They reported an HSC of 3.622 wt.% for double-sided Pd-functionalized graphene and demonstrated that the active hydrogenation mechanisms were polarization and orbital hybridization. In fact, the polarization process could contribute to hydrogenation through the electric field enhancement caused by the interaction of cations with multiwall carbon nanotubes (MWCNT) and graphene.

One of the simplest and most accurate methods to evaluate hydrogen storage is electrochemical hydrogenation [18]. During this process, hydrogen is produced by splitting water on the surface of a polarized electrode that then absorbs it [19]. Oberoi et al. measured the HSC of an active carbon electrode made of brown coal using the electrochemical method. They reported an HSC of 1.29 wt.% [20]. Visintin et al. reported that, in presence of Pd, electrochemical hydrogenation demonstrated a longer cycle lifetime and a higher rate of electrode discharge [21].

In this study, the triple-structure of Pd-CNT/Pd/PS/Si is introduced to improve HSC through a synergic effect.

## Experimental

Electrochemical anodization employs an electrochemical cell to advance the etching process through chemical reactions. An ethanol-based solution was used as an electrolyte for electrochemical anodization, in a given volume ratio (35% HF: EtOH: DI $H_2O$; 2: 1: 2). Electrochemical anodization was conducted using direct current at a constant density of 10 $mAcm^{-2}$ for 10 min.

Immediately after electrochemical anodization, Pd nanoparticles were deposited on the porous polysilicon using the electroless technique. This process used an aqueous solution of palladium dichloride ($PdCl_2$) in the presence of trace amounts of hydrogen chloride (HCl) at room temperature.

Following this, carbon nanotubes (CNTs) were grown over the decorated-porous substrate (Pd/PS/Si) using Chemical vapor deposition (CVD), which was performed using methane ($CH_4$) as a feed gas with a flow rate of 80 sccm for 45 min at 980 °C. Finally, the prepared samples (CNT/Pd/PS/Si) were decorated with Pd nanoparticles using the same electroless process (post-treatment).

### *Characterization*

The surface morphology was carried out by Field emission scanning electron microscopy (FESEM, Mira 3-XMU). The crystalline structure of the samples was characterized using X-ray diffraction (Philips X'pert operating with CuK$\alpha$ radiation ($\lambda = 1.54178$ Å) at 40 kV/40 mA). The chemical composition of the Pd-CNT/Pd/PS/Si sample was characterized by Energy dispersive X-ray spectroscopy (EDS).

The electrochemical measurement was carried out with a three-electrode system, using 3 M $H_2SO_4$ as an aqueous electrolyte; where working electrodes were PS, Pd/PS, and Pd-CNT/Pd/PS/Si. Platinum foil was assigned as the counter and Ag/AgCl electrode (Metrohm AG 9101 Herisau, 3 M KCl, 0.207 V versus, SHE at 25 °C) was chosen as reference electrode. The reference electrode was fixed near the working electrode to minimize the ohmic drop of electrolyte. Also, the working electrode potential vs. reference electrode was monitored during this process. CP analysis was carried out using a potentiostat/galvanostat (PGSTAT204, Autolab, Echo Chemie) in a three-electrode glass cell. Galvanostatic characterizations for charge/discharge process were carried out under the current density of 500 mA/g; meanwhile, the cut-off potential of 0.5 V was adjusted. The charge operation was followed by15 min rest. Also, the discharge process was performed under current density of 500 mA/g with the cut-off potential of 0.6 V.

## Results and discussion

### *Surface morphology*

The microstructure and surface morphology of fabricated samples were characterized using FESEM, Figs. 1 and 2. Fig. 1 (a) shows Pd nanoparticles decorated the PS substrate before CVD: A large number of Pd nanoparticles have clearly been