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Nanostructured palladium/polypyrrole composite paper for enhanced catalytic hydrogen generation from ammonia borane

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ABSTRACT

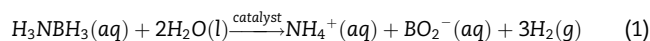
“Mass transfer in catalyst supports” and “reactive sites” are two critical factors for supported thin film catalysts. Based on such considerations, paper composed of cellulose fibers (CFs) is chosen as a competent nano-catalyst carrier because its broad porous structure is conducive to mass transfer. Then a facile aquatic synergistic synthesis is developed to decorate polypyrrole (PPy) encapsulated palladium nano-composites onto the CF paper structures. The pyrrole monomers (Py) reduce Pd²⁺ to Pd nanoparticles in aqueous solution, and meanwhile the Pd²⁺ initiates the polymerization of Py to PPy. In the as-prepared composite paper catalysts, the broad pores constructed by the microfibers facilitate the reactant diffusion and the Pd/PPy nanoparticles supported on the fibers provide more reactive sites for catalysis. As a result, the catalytic activity for hydrolysis of ammonia borane is improved. The H₂ turnover frequency is 21.1 mol H₂ mol Pd⁻¹ min⁻¹, surpassed most other Pd based film catalysts. Importantly, excellent stability and reproducibility are also realized by the immobilization of Pd NPs by PPy layers onto fibers.

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Introduction

With the growing threat of energy exhaustion, global warming and environmental pollution, the developments of sustainable, clean and environmentally friendly energy become extremely urgent. Hydrogen has been regarded as one of the most qualified candidates for future energy crisis [1,2]. However, the widespread application of hydrogen is strictly limited by the deficiencies in reliable H₂ generation, storage and transportation [3]. Recently, Ammonia borane (NH₃BH₃,

AB) attracts increasing attention as a solid competent hydrogen resource owing to its high hydrogen content (19.6 wt %), nontoxicity, good stability at room temperature and easy storage [4–6]. It is capable of releasing hydrogen at room temperature by hydrolysis in the presence of suitable catalysts according to this Equation (1): [7].



Recent studies have revealed that there are numerous nanoparticle (NP) catalysts, including noble metals, non-

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noble metals, multicomponent metallic systems, etc [8–15], were developed to enhance the dehydrogenation of AB. Additionally, in order to avoid the aggregation of high-efficiency NPs and improve the stability, many stabilizers were employed, such as carbon [16,17], metal oxides [18,19] and polymers [7,10,20]. However, until now, most catalysts for AB dehydrogenation are homogeneous powders [19], and the separation of powders from the reaction solution is challenging, which incurs poor reproducibility. Moreover, the powdered catalysts are difficult to be used in continuous flow systems. On the other hand, the film catalysts, as an alternative, can overcome the above problems [21–24]. And in addition to easy recovery and reusability, supported thin film catalysts can also act as a suitable On/Off switch for H₂ production [23,24].

In recent years, the products composed of 1D microstructures or nano-structures, are regarded as one of the most promising candidates for construction of film catalysts, due to their open structures, large surface area, high aspect ratio, flexibility and good stability [25–29]. For example, Lu and his co-workers prepared nanofiber membranes by electrospinning, and then decorated with Pd and Ag–Pd NPs for fabricating recyclable catalysts [28,29]. But many recent efforts are focus on increasing reactive sites by refining nanostructures (e.g. reducing the diameter of the 1D structures), which are at the cost of suppressing mass transport paths in the inner region of catalyst carriers [30], so as to reduce catalytic performances. As such, “reactive sites” and “mass transfer” should be both taken into account for fabricating high-performance supported catalysts.

Paper, an often used material in life, is playing more and more important role in improving the performances in flexible electronics, energy devices and so on [31–33]. It is composed of rough cellulose fibers (CFs) and exhibits ideal open porous structure, which is expected to promote the mass transfer of reactants. Additionally, a large number of surface functional groups on the CFs is beneficial for binding additional functional materials [33]. Therefore, in this work we used CF paper as a substrate to construct high-efficiency catalyst by the incorporation of Pd/polypyrrole (PPy) nanocomposites. An one-pot synergistic synthesis in aqueous solution was developed to simultaneously decorate Pd nanoparticles (NPs) and PPy onto the surface of the CF papers (Fig. S1). The pyrrole monomers (Py) reduced Pd²⁺ to Pd NPs in aqueous solution, and at the same time the Pd²⁺ initiated the polymerization of Py to PPy. As a result, Pd/PPy nanocomposites were assembled onto the paper fibers. In the as-prepared composite papers, the big porous structure constructed by the microfibers could extend the paths of mass transportation for reactants. Meanwhile, the secondary structure based on the Pd/PPy composite nanostructures on the CFs provided more reactive sites for catalysis. As a result, the catalytic activity of the materials for hydrogen generation from the hydrolysis of ammonia borane was enhanced, exhibiting low activation energy, higher turnover frequency, easy separation, excellent stability and reproducibility.

Experiment section

Materials

The CF papers were brought from Kimberly-Clark Kimwipes Company. AB (technical grade, 90%) was obtained from Sigma–Aldrich (St. Louis, Missouri, USA). Pyrrole (99%) and disodium tetrachloropalladate (Na₂PdCl₄) were purchased from Aladdin, China. Ethanol was provided by Xilong Chemical Co., Ltd, China. All the chemicals were of analytical grade and used as received without further purification.

The aquatic one-pot synthesis for the preparation of Pd/PPy composite papers

30 mg of CF paper without other processing were immersed in 35 mL of deionized (DI) water. Then, 100 μL of pyrrole monomer was added to the solution and shaken for 30 min by a shaking table to obtain a homogeneous solution. 750 μL of Na₂PdCl₄ (0.1 M) was added into the above solution to start the polymerization. The Pd/PPy composite papers were washed with DI water and ethanol three times respectively after polymerization (for 24 h) at 25 °C. Finally, the obtained composite papers were dried in air at 40 °C.

The control sample of Pd/PPy polyacrylonitrile (Pd/PPy/PAN) composite nanofiber mat was prepared by the same method, except using the electrospun PAN nanofibers as substrates [22]. Another control sample of Pd/PPy composite paper (Pd/PPy paper-EG) with smooth surface (Fig. 6d) was fabricated by a reported oil-phase method in ethylene glycol, also using CF paper as substrates [22]. The thickness of all the three thin film samples was 60 μm approximately.

Catalyst characterization

The morphology of composite papers was observed by scanning electron microscope (SEM, Helios Nanolab600i, FEI Co., USA) and transmission electron microscope (TEM, JEOL JEM-1400). Energy dispersive X-ray (EDX) analysis was carried out on the scanning electron microscope. The BET surface area measurement was performed by a Micromeritics ASAP2020 instrument. High resolution transmission electron microscope (HRTEM) imaging analysis and EDX-mapping were performed with a FEI Tecnai G2 F30. The FTIR spectra were recorded on a Perkin–Elmer Spectrum One B spectrometer. The chemical composition of the sample surface was identified by using X-ray photoelectron spectroscopy (XPS; PHI 5700 ESCA System, Physical Electronics, U.S.). The amount of Pd in the composite papers was determined using an inductive coupled plasma emission spectrometer (ICP, PerkinElmer Optima 5300DV) after the sample was digested (details of digestion is provided in Supporting Information). A dead-end filtration module (Millipore 8200, Millipore Corp., Bedford, MA) was used to measure the pure water flux of the samples by the gravity

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