Quasi-atomic-scale platinum anchored on porous titanium nitride nanorod arrays for highly efficient hydrogen evolution

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ABSTRACT

Highly efficient electrocatalytic hydrogen evolution reaction (HER) is achieved by constructing uniformly dispersed quasi-atomic-scale Pt on porous conductive titanium nitride nanorod arrays (Pt–TiN NAs). The Pt–TiN NAs demonstrate high HER efficiencies both in acid (0.5 M H_2SO_4) and alkaline media (1 M KOH) with the overpotentials of 39.7 mV and 139 mV at the current density of 10 mA cm^{-2}, respectively, which is comparable to that of commercial 20 wt % Pt/C under the same experimental condition. In addition, the Tafel slopes of Pt–TiN NAs (38.6 mV dec^{-1} in acid and 98.3 mV dec^{-1} in alkaline media) are much lower than that of commercial Pt/C. More remarkably, the Pt–TiN NAs display a much higher current retention of 91.6% after continuous test for 60 h in 0.5 M H_2SO_4 comparing to 46.9% of Pt/C after 30 h cycling. The excellent HER performance of as-prepared Pt–TiN NAs are attributed to the abundant available reaction sites from the uniformly distributed quasi-atomic-scale Pt, the suppressed aggregation of Pt by the strong metal-substrate interaction between Pt and TiN, and the superior electron transfer caused by high electric conductivity TiN substrate. Our designed structure provides an ideal catalytic system for efficient HER, which may inspire the design and synthesis of other high efficiency electrocatalytic systems.

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1. Introduction

The ever increasing detrimental effects of traditional fossil fuels on energy and environment have triggered extensive urgency to explore environment friendly and renewable energy technologies [1–4]. Among all of the current green technologies, hydrogen generation through electrocatalytic water splitting and subsequently being used in fuel cell as a clean fuel have attracted wide attention [3–6]. Up to now, Pt-based catalysts are well-recognized as the most efficient electrocatalysts for hydrogen evolution reaction (HER) [7,8]. However, there are still great challenges to achieve

commercial applications of Pt-based catalysts due to the high cost and relative scarcity of Pt. So far, two dominant material systems were widely explored to overcome the inherent high cost of Pt-based electrocatalysts. The first one is replacing the expensive Pt with other low cost materials, mainly including transition metals (Fe, Co, Ni et al.) [9], the corresponding alloy compounds (NiFe, CoNi, FeCo) [10–12], phosphides (FeP, CoP, Ni_2P, MoP) [13–16], sulfides (Co_9S_8, NiS_2, FeS_2, MoS_2) [17–19] and nitrides (Ni_3N, CoN_x) [4,20]. Excepting for metal-based materials, the low cost non-metal heteroatom (N, P, B, S) doped carbon-based materials, such as carbon nanotubes [21], porous 3D carbon materials [22] and graphene [23], have also been proved to be the outstanding Pt-free HER electrocatalysts. Although lots of researchers are devoted into exploring various Pt-free electrocatalysts, their relative low current density and high overpotential in HER process are still far

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from replacing the commercial Pt-based catalyst [24,25]. Therefore, a large number of other promising strategies based on improving the utilization efficiency of Pt-based electrocatalysts are developed, including improving the electrocatalytic efficiency of Pt by exposing high reactive facets through crystal and structure engineering [26], reducing the amount of Pt through compounding Pt-based catalysts with other low cost metals in the forms of alloy [27–29] or core-shell structures [30], as well as reducing the size of Pt nanoparticles to sub-nanometer or atomic-scale to acquire available reactive sites as many as possible [31–37].

In past decade, quasi-atomic and single atomic scale Pt catalysts have triggered a new opportunity to achieve extremely high electrocatalytic efficiency of Pt-based catalysts by completely expose the whole available active sites of electrocatalysts. Lots of work has demonstrated that the catalytic properties of metal catalysts were dramatically enhanced as their size reduced to atomic scale. For example, Luo's group synthesized a single Pt atoms system for efficient HER, which exhibited an overpotential of 24 mV at the current density of 10 mA cm^{-2} in neutral media [38]. Zhang and coworkers demonstrated the oxidized Pt clusters as highly active and stable electrocatalyst for HER, which showed mass activities 42.66 and 100.58 A mg^{-1} at the overpotentials of 100 mV and 150 mV, respectively [39]. Stephenes et al. revealed that isolated atomic Pt was crucial for achieving high selectivity to hydrogen peroxide through a 2e$^-$ pathway from oxygen reduction reaction [40]. Lee et al. also proved the unique selectivity of single-atom Pt on the electrocatalytic oxidation of small organic molecules such as formic acid and methanol [31]. In spite of the excellent electrocatalytic activity, the natural tendency for diffusion and agglomeration of Pt atoms give rise to the most challenge for synthesizing long term stable atomic scale Pt-based catalysts. Fortunately, anchoring sub-nanometer/quasi-atomic-scale Pt on a series of substrates gives out a promising way to overcome the above shortcomings. The main advantages of substrate supported Pt-based electrocatalysts include: improving the stability of catalysts by decorating the atomic-scale Pt on substrates to prevent their agglomeration [31–33] and enhancing the electrocatalytic efficiency of whole system through the strong metal-substrate interaction (SMSI) [39,41–44]. To date, two typical substrates including metal oxides and carbon nanomaterials have been adopted for Pt-based electrocatalysts [45,46]. However, due to the insufficient interactions between carbon substrate and Pt catalyst, only low amount of atomic/quasi-atomic-scale Pt can be achieved in Pt-carbon system. The poor electrical conductivity of metal oxides greatly impedes the electrocatalytic efficiency of the atomic/quasi-atomic-scale Pt systems. Besides, binder-involved powder based electrocatalysts inevitably results in the limited effective reaction surface to some extent. Therefore, engineering and synthesizing Pt-based hybrid system with quasi-atomic/atomic scale Pt uniformly distributed on high conductivity substrate is of great importance in acquiring high HER performance.

In this work, we engineered a quasi-atomic-scale Pt anchored on porous titanium nitride nanorod arrays (Pt–TiN NAs) structure as a binder-free electrocatalytic system for high efficiency hydrogen evolution. The designed system is extremely beneficial to the electrocatalytic process because of the maximized catalytic reaction sites from the uniformly distributed quasi-atomic-scale Pt, the effectively suppressed aggregation and rearrangement of quasi-atomic-scale Pt due to the strong anchoring effect from the surface defects of TiN substrate, and the fast electrical transitions originated from the integration between high conductivity TiN NAs and carbon cloth (CC). The system demonstrated a quite low overpotential both in acid media (0.5 M H$_2$SO$_4$) and alkaline media (1 M KOH), which is comparable to that of current commercial 20 wt % Pt/C catalysts. More remarkably, the Tafel slopes in

0.5 M H$_2$SO$_4$ and 1 M KOH is better than those of commercial Pt/C. In addition, the designed system reveals excellent long-term stability and durability. Our Pt–TiN NAs exhibit an ideal candidate for binder-free electrocatalytic system with excellent HER performance, which provide a promising way to construct other high-performance Pt-based electrocatalytic systems.

2. Experiment section

2.1. Chemicals

All chemicals were of analytic grade and used without further purification, and the deionized water (18.25 MΩ) was used in all experiments. Typical chemicals include: ethanol (C$_2$H$_5$OH, Tianjin Chemicals), hydrochloric acid (HCl, 37%, Tianjin Chemicals), titanium butoxide (C$_{16}$H$_{36}$O$_4$Ti, ≥ 99%, Aladdin Industrial Co., Shanghai, China), metal magnesium powder (Mg, > 99%, Sigma Aldrich Co.), chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O, ≥ 37.0%, Tianjin Chemicals), high-purity nitrogen (N$_2$, 99.999%), hydrogen/argon (H$_2$/Ar, 30%/70%, by volume), carbon cloth (CC, WOS1002, Rocktek Co. Ltd, China), commercial platinum carbon (Pt/C, 20 wt %, JM/Johnson Matthey, HISPEC3000), nafion solution (Nafion, 5%, Dupont D-520).

2.2. Synthesis of TiN NAs on CC

The synthesis of TiN NAs on CC followed our previous work [47,48]. Firstly, about 3 nm amorphous TiO$_2$ layer was initially deposited on pre-cleaned CC (3 cm × 4 cm) by atomic layer deposition (ALD) and annealed in tube furnace at 400 °C for 30 min. Secondly, the yellowish transparent mixture solution including 1 mL of titanium butoxide, 22 mL of HCl and 10 mL of deionized water was transferred into a polytetrafluoroethylene (Teflon) lined stainless-steel autoclave (50 mL), and then the CC with TiO$_2$ seed layer was immersed into the solution for hydrothermal process at 180 °C for 10 h in a drying oven. After cooling down to room temperature naturally, the TiO$_2$ NAs was rinsed with deionized water and ethanol for several times and dried at 100 °C for 3 h in dry oven. Thirdly the as-synthesized TiO$_2$ NAs was covered with Mg powder in an uncovered cuboid aluminum oxide crucible and sent into a vacuum tube furnace. The pressure in vacuum tube furnace was kept at 800 mTorr under the N$_2$ flow rate of 50 sccm. The sample was annealed at 900 °C for 1.5 h with the heating rate of 3 °C min^{-1}. Fourthly, the magnesium oxide and other residuals were removed by 2 M HCl solution and rinsed with deionized water and ethanol for several times. Finally, the sample was dried in drying oven at 70 °C for 12 h.

2.3. Synthesis of quasi-atomic-scale Pt–TiN NAs

The quasi-atomic-scale Pt on TiN NAs was prepared by a simple physical adsorption process using H$_2$PtCl$_6$·6H$_2$O as the precursor. Different volumes (50 μL, 100 μL, 200 μL, 500 μL, and 1000 μL) of 100 mM H$_2$PtCl$_6$·6H$_2$O were firstly homogeneously dissolved in 30 mL of deionized water (solution 1). Secondly, the TiN NAs on CC with the area of 3 cm × 4 cm was fixed with a plastic clip and immersed into 100 mL of deionized water (solution 2). And then the solution 1 was slowly added into solution 2 by a constant flow pump. During the mixing process, the whole system was continuously stirred by a magnetic stirrer at the rate of 800 rad min^{-1}. After stirred for 1 h, turned the magnetic stirrer off and left the system for another 1 h. Thirdly, the sample was rinsed with deionized water for several times and dried at 60 °C for 24 h. Finally, the dried sample was annealed in a tube furnace at 100 °C for 2 h in a 30% H$_2$/Ar atmosphere with the flow of 50 sccm. According to the volumes