Porous and single-crystalline-like molybdenum nitride nanobelts as a non-noble electrocatalyst for alkaline fuel cells and electrode materials for supercapacitors

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ABSTRACT

Replacing precious and nondurable Pt catalysts with cheap materials is a key issue for commercialization of fuel cells. Intriguing transition metal nitrides (TMNs) have attracted great attentions as promising economic alternatives to Pt catalysts due to their noble metal-like properties. However, most of as-synthesized TMNs are nanoparticles until now. Clearly, the practical catalytic activities of such materials have hitherto been intrinsically restricted by the relatively small surface area and poor crystallinity of nanoparticles. Here, highly porous and "single-crystal-like" Mo_2N nanobelts with high density of nanopores have been synthesized on gram-scale. These novel Mo_2N nanobelts exhibited high electrocatalytic activity in alkaline electrolyte even better than that of other non-Pt materials and appear to be promising Pt-free cathodic electrocatalysts in alkaline fuel cells. This discovery reveals a new type of metal nitride ORR catalyst and appear to be promising Pt-free cathodic electrocatalysts in alkaline fuel cells.

Introduction

Increasing energy demands have stimulated intense research on alternative energy conversion and storage systems with high efficiency, low cost and environmental benignity. Fuel cells and supercapacitors as promising energy conversion and storage units have been widely studied for applications in stationary power sources and battery powered electric vehicles [1]. However, the fact that their performance requires

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continuous improvement, has encouraged ever greater scientific efforts toward the search for new materials that could replace the current state-of-the-art materials.

Catalysts for oxygen reduction reactions (ORR) are at the heart of key renewable-energy technologies for fuel cells [2,3]. Pt and its alloys remain the most efficient ORR catalysts, but the high cost and scarcity of Pt hamper further development of fuel cell technologies based on these materials. Although a broad range of alternative catalysts based on nonprecious metals (Fe, Co, etc.), metal oxides (Fe_2O_3, Fe_3O_4, Co_3O_4, IrO_2, etc.), nitrogen-coordinated metal on carbon, and metal-free doped carbon materials have been actively pursued [4], the development of novel non-noble catalysts which can substitute platinum-based catalysts are strongly required.

The most widely used active supercapacitor electrode materials are carbon, conducting polymers or transition metal oxides (TMOs) [5]. TMOs characterized by their low-cost and high specific capacitance (such as, MnO_2 generally with the capacitance of 100–160 F/g [6], MoO_2 with a capacitance of 140 F/g [7]), have attracted significant interest as active electrode materials for supercapacitors instead of carbon. However, their poor electrical conductivity and mechanical issues such as low structural stability exist for TMO electrodes [6], often resulting in degraded long-term electrochemical cyclability and limited rate capability.

Intriguing transition metal nitrides (TMNs) have been widely studied due to their scientific and technological importance [8]. The band structure of TMNs is qualitatively similar to those of fcc transition metals in the shape and relative ordering of the bands. For the transition metals, the d-band begins to fill from Ru and Os to Pd and Pt. This coincidence of the band structure seems responsible for the observed similarity in catalytic properties between Group 4–6 TMNs and the Group 8–10 transition metals [8]. The electronic structure strongly related with properties of TMNs studied by various spectroscopic techniques. Thus, the filled states of d-band were narrowed after formation of nitrides, resulting in the similar electronic structure of noble metals up to the Fermi level. On the other hand, at energies above the Fermi level, the width of the unfilled states of the metal was found to be broadened because of the TMNs formation, giving rise to a greater density of empty levels for TMNs than those of the parent metal. Due to the deficiency in the d-band occupation near the Fermi level, nitride surfaces could have a reduced ability to donate d-electrons to adsorbates. Therefore, high reactivities of early transition metals are explained by the formation of nitrides for reactions involving the donation of electrons from the metal catalysts to absorbate. The broadened unfilled portion of the d-band should make these nitrides better electronic acceptors than both the parent metals and the Pt Group metals. Thus for reactions that involve the donation of bonding electrons to the unfilled orbitals of the metal substrate, nitride catalysts might be more efficient than both parent metals and Pt Group metals, such as, Cu_3N nanocubes as promising Pt-free cathodic electrocatalysts for alkaline fuel cells (AFCs) [9], and Mo_2N/C as Pt-free cathodic electrocatalysts for proton exchange membrane fuel cells (PEMFCs) [10]. Some TMNs (such as, VN, MoN_x TiN, and WN) have been also attracted great attentions as replacements for MnO_2 and RuO_2 in supercapacitor electrodes because of their high conductivity, low cost and high chemical resistance [8].

As well known, material surfaces play an important role in the catalytic activity and capacitance. The effective integration of high surface areas and good crystallinity is expected to be very effective in promoting their catalytic activity and capacitance. However, unlike metal oxides and main group metal nitrides with rich nanostructure morphologies, most of as-synthesized TMNs are nanoparticles until now [8]. Clearly, the practical catalytic activity and capacitance of such materials have hitherto been intrinsically restricted by the relatively small surface area and poor crystallinity of nanoparticles. Therefore, it is highly desirable to accomplish TMN nanostructures with high surface area and good crystallinity to enhance their catalytic activities and improve their capacitances for supercapacitors.

Herein, we successfully synthesize gram-scale, highly porous and "single-crystal-like" [11] Mo_2N nanobelts with high density of ultra-fine nanopores by topotactic chemical transformation from single crystal MoO_3 nanobelts. Although traditional solid-state nitriding reaction using micrometer- or larger-sized powders is known to be a brute-force technique for the synthesis of many porous metal nitride materials [12], it has disadvantages: it requires diffusion over long distance; large strain nucleation barriers must be overcome; the pore sizes are large; and the microstructure of the final materials is difficult to control. However, these disadvantages might be ameliorated or eliminated by using nanocrystalline materials as starting reactants. For example, ZnO NWs have been converted into single-crystalline $ZnAl_2O_4$ spinel nanotubes via solid-state reaction [13]. In our work, single crystal MoO_3 nanobelts have been converted into highly porous and single-crystalline-like Mo_2N nanobelts via a slowly nitrided solid-state reaction. Such single-crystal-like Mo_2N nanobelts are here reported as promising Pt-free cathodic electrocatalysts in alkaline fuel cells for the first time, exhibiting high electrocatalytic activity toward oxygen reduction. Highly porous Mo_2N nanobelts also exhibited high rate capability, high specific capacitance of 160 F/g (higher than those of MnO_2 generally with the capacitance of 100–160 F/g [6], or MoO_2 with a capacitance of 140 F/g [7]), and good cycling stability, even at the high scanning rate of 100 mV s^{-1}, as supercapacitor electrode materials. The high catalytic activity and capacitance may result from its novel nanostructures with the effective integration of their high surface area and good crystallinity. This discovery reveals a new type of metal nitride ORR catalyst and appear to be promising Pt-free cathodic electrocatalysts in alkaline fuel cells.

Experimental

Single-crystal-like Mo_2N nanobelts with high density of ultra-fine nanopores were easily obtained by a two-step route. The first step is gram-scale synthesis of single-crystalline and uniform MoO_3 nanobelts. In a typical synthesis, MoO_3 powder (2 g, 99.99%, Sigma Aldrich) and 20 mL of 30% H_2O_2 (Sigma Aldrich) were mixed under vigorous magnetic stirring overnight until the solution was clear yellow, and then 20 mL H_2O was added to the solution before transferring to a 120 mL