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PtRu nanoalloys loaded on graphene and TiO_2 nanotubes co-modified Ti wire as an active and stable methanol oxidation electrocatalyst

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ABSTRACT

Highly active, durable and scalable fuel cell electrocatalysts are highly desirable but challenging. Herein, we first develop a novel catalyst of PtRu nanoalloys loaded on graphene modified anodic TiO_2 nanotubes arrays (TNTs) grown on flexible Ti wires (denoted as PtRu/RGO/TNTs). Electrodeposited reduced graphene oxide (RGO) is used to improve the electric conductivity and facilitate the dispersion of PtRu nanoparticles. TiO_2 nanotubes arrays could guarantee the large surface area, and PtRu nanoalloys are well-dispersed on the inner and external walls of the TNTs as well as the RGO surface, which could facilitate the fast mass transport and enhanced electrocatalytic activity. PtRu nanoalloys with intimate contact between the two metals is conductive to remove the harmful CO-like byproduct, resulting in superior tolerance to CO poisoning. In addition, this work first design and use the spirally flexible Ti wire electrode configuration in direct methanol fuel cell, which shows a highly efficient catalytic performance. Moreover, this kind of catalytic support is a strong candidate for other electrochemical energy conversion devices.

Introduction

Driven by growing concerns for environmental and energy issues, direct methanol fuel cell (DMFC) as an alternative green and sustainable power source has attracted great attention due to its high energy conversion efficiency under ambient operating conditions [1–3]. Platinum (Pt) is traditionally used as electrocatalyst in fuel cells, however, the high-cost and easily-poison from the strong CO adsorption have hindered the wide commercial application. Consequently, Pt-based alloy (such as PtFe [4], PtRu [5], PtNi [6], PtCo [7], PtAg [8], PtPd [9], and PtAu [10,11]) have been widely explored as anode electrocatalysts in DMFCs. To obtain high catalytic efficiency, different conductive substrates (e.g., Vulcan XC-72 [12], carbon nanotubes [13], carbon fibers [14], carbon spheres [15] and graphene [16]) have been used to disperse these Pt-based bimetallic nanoparticles. An ideal support material should possess large surface area, good electrical conductivity and strong catalyst-support interaction, which could enhance electrocatalytic activity and stability as well as CO poison tolerance.

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Graphene as a two-dimensional sp^2-hybridized carbon sheet possesses ultrahigh electron mobility, large specific surface area, and high thermo-conductivity [17]. The surface functional groups such as carbonyls and hydroxyls facilitate the immobilization and uniform dispersion of the metal nanoparticles [3]. Another substrate is still necessary to support the soft graphene. Vertically oriented TiO_2 nanotube arrays (TNTs) with high surface-to-volume ratios, unidirectional electrical channels, and abundant active sites for particle nucleation could be a super catalyst supporter candidate [18–20]. Moreover, TiO_2 also possesses excellent anticorrosion property and strong metal-support interaction, which is favorable for enhancing the catalyst stability. However, the low electric conductivity of TiO_2 nanotube arrays limits its further application in electrocatalysis realm. Consequently, it is urgent to construct a self-ordered TiO_2 NTs-based composite with high electric conductivity for achieving high-performance fuel cell electrocatalysts.

Herein, we design and fabricate graphene and TNTs co-modified Ti wire as solid substrates and PtRu alloy nanoparticles were dispersed through pulsed electrodeposition method. Compared with the traditional Ti sheet, the stability of the TNTs on cylindrical Ti wires was higher due to the low internal stress. The conductive, solid, and soft Ti wires with TNTs possessing large and uniform surface provide facile ways for conjugating the RGO layers by electrodeposition technique. PtRu alloys are considered to be the optimum anode catalysts for fuel cells due to high electrocatalytic activity and perfect CO poison tolerance [21–23]. PtRu nanoalloys on the inner and outer space of the TNTs and on the RGO surface boosted the electrocatalytic efficiency in DMFC application. Although PtRu/graphene catalysts and their applications in methanol oxidation have been reported, the PtRu/RGO/TNTs grown on a soft Ti wire was constructed for the first time. As the PtRu/RGO/TNTs/Ti wire can act as both catalyst and electrode with soft, solid and conductive properties, it can be facilely incorporated in a DMFC.

Experimental

Preparation of RGO/TNTs

The spirally flexible Ti wire with 800 μm in diameter and 45 cm in length was used as titanium source. Anodization of the Ti wire was performed at 30 V in 40 mL DMSO electrolyte containing 2 w. t.% HF for 8 h in a two-electrode configuration with a platinum foil cathode. The as-anodized TNTs/Ti wire (Fig. 1a) was calcined under 500 °C for 4 h with a heating rate of 2 °C min^{-1} for crystallizing to anatase phase. Finally, the color of the TNTs changed from dark purple to blue (Fig. 1b).

Graphene oxide (GO) was obtained from natural graphite powders by a modified Hummers method [24]. The RGO was deposited on the TNTs through cyclic voltammetry in a solution containing 0.3 g L^{-1} GO and 0.1 M citric acid-sodium citric in the range from −1.5 V to 0.6 V at N_2 atmosphere [24,25]. The TNTs bearing RGO exhibit a color of deep blue, shown as in Fig. 1c.

Preparation of PtRu/RGO/TNTs

PtRu NPs were prepared on the surface of the RGO/TNTs support through a square pulsed electrodeposition method with a three-electrode system: the RGO/TNTs wire as the working electrode, a Pt foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. For each pulsed sequence, a potential of −4.0 V was applied for 0.2 s, followed by a potential of 0 V for 2 s, and the total sequence number is 100. The PtRu/RGO/TNTs is obtained by keeping the RGO/TNTs electrode in mixed solutions of 10 mM H_2PtCl_6 containing 5.0 mM $RuCl_3$. For comparison, the Ru/RGO/TNTs is obtained by firstly keeping the RGO/TNTs electrode in 5.0 mM $RuCl_3$ solution. The Pt-Ru/RGO/TNTs is obtained by secondly keeping the above Ru/RGO/TNTs in 10 mM H_2PtCl_6 solution using aforementioned square pulsed method. After the modification of metal NPs, the color of the Ti wire turned to black (Fig. 1d). Fig. 1e illustrates the three-dimensional simulation diagrams of the resulting TNTs arrays, showing the TNTs arrays were grown vertically on Ti wire with high order. Fig. 1f depicts the image of the PtRu nanoalloys particles attached on the TNTs. PtRu nanoalloys particles distribute on inside and outside of the TNTs uniformly. Detailed characterization is provided in TEM images in following.

Characterization

Scanning electron microscope (SEM) was performed using a Nova Nano SEM450. Transmission electron microscopy (TEM) analysis was performed using a JEOL 3010. X-ray photoelectron spectra (XPS) were recorded with a pressure 2×10^{-9} M bar using Al Kα irradiation (Thermo Fisher Scientific, ESCALAB 250).

Electrochemical measurements

The electrochemical properties of the prepared electrocatalysts were studied in a standard three-electrode electrolytic cell. Methanol oxidation reaction (MOR) was investigated through cyclic voltammetry (CV) and chronoamperometry in 0.5 M H_2SO_4 solution containing 1.0 M CH_3OH at a scan rate of 50 mV s^{-1}. All chronoamperometric analyses were performed at 0.65 V *vs.* SCE in an acid methanol electrolyte. All the geometric area of the effective working electrode is ca. 10 cm^2, which is calculated as $3.14 \times 0.08 \times 40$ cm^2 and used for current density calculation in the MOR.

Results and discussion

Physicochemical characterization

SEM images show the surface morphologies of Pt-Ru NPs (Fig. 2a and b) and PtRu alloy NPs (Fig. 2c and d) modified RGO/TNTs. TNTs are partly covered by RGO layers and all the metal NPs are uniformly dispersed on the RGO and TNTs. By the way, the particle size of Pt-Ru NPs is smaller than that of the PtRu alloy NPs, which may be caused by the fast growth of Pt and Ru nucleus under the same deposition voltage at the same