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Reduced TiO₂ nanotube array as an excellent cathode for hydrogen evolution reaction in alkaline solution

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ABSTRACT

Anodic TiO₂ nanotube (TNT) arrays have been intensively investigated as anodes in water splitting (WS) cells because of their excellent chemical stability. However, anodic TNT is seldom considered as a cathode for the hydrogen evolution reaction (HER) in an electrochemical WS cell. This study shows that a reduced TNT (R-TNT) sample prepared with a cathodic reduction technique without loading any co-catalyst can achieve remarkable HER performance. At -1.0 V vs reversible hydrogen electrode in 1 M NaOH in dark, R-TNT achieved a current of -221 mA, which is 17000-times of that achieved when using TNT and 5-times of that with Ti-foil as cathode. Chronopotentiometry tests were carried out sequentially at @ -100, -50 and -10 mA for 24 h and decay rates of 1.3%, 5.2% and 18.4% were measured, which indicate a good stability of the R-TNT sample.

1. Introduction

Electrochemical water splitting (ECWS) to store renewable electricity as hydrogen (H₂) through a hydrogen evolution reaction (HER) half-cell has attracted much attention [1]. The state-of-the-art cathode catalyst used for HER is still based on Pt [2]. Developing a durable, efficient and non-noble metal oxide cathode catalyst for green H₂ production is one of the key challenges ahead for ECWS [3–5]. Thus, an electrocatalyst for HER based on non-metallic materials has been actively explored [6,7].

Metal oxides are generally regarded as catalytically inert for HER, because of inappropriate hydrogen adsorption energies [6]. The metal oxide cathode catalyst works in an environment with formation of atomic H and release of gaseous H_2 , in some cases also with a cathodic reduction potential, which arises the corrosion problem [8]. However, metal oxides with semiconductor and quasi-metallic properties are of particular interests, because of their potential to incorporate other catalytic functions in the HER electrode [9]. Designing metal/metal oxide hybrid catalysts through incorporating a metal with a suitable work

function to a metal oxide cathode could be a path to enhance the HER performance. Markovic et al. [10] synthesized nanostructured metal/metal-oxide hybrid domains close to adjacent metal sites to enhance the overall HER performance. Recent works have provided evidence that metal/metal-oxide interaction is a promising approach to manipulate the HER behavior to enhance H_2 production [6,11,12].

Anodic TiO₂ nanotube (TNT) arrays are grown on Ti metal substrates, and are native metal oxide/metal hybrid structure. The advantages of anodic TNT are fast electron transfer and low charge carrier recombination rate due to the high specific surface area and restricted charge transportation pathways [13–15]. It has been intensively investigated as anode catalyst for the oxygen evolution reaction (OER) in photoelectrochemical WS cells [16–20]. However, the anodic TNT as HER catalyst is kinetically hampered due to the sluggish charge transfer between the semiconductor and the aqueous solution [21]. On the other hand, a monometallic Ti catalyst has a poor HER efficiency due to its large hydrogen-binding energy, i.e. 204.6 ± 8.8 kJ/mol or 1.06 ± 0.037 eV [22]. Recently, metallic Al and Cu atoms have been used to construct a cathode by forming a buried junction for enhancing the CO₂ reduction

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Fig. 1. Schematic diagram of the preparation process of the R-TNT sample.

reaction [23,24].

Herein, we demonstrate a novel metal oxide cathode for ECWS cell based on a reduced TNT (R-TNT), which functions exceptionally well as HER catalyst in aqueous solution. The R-TNT cathode exhibits high reaction rate and remarkable stability.

2. Experimental

2.1. Chemicals and materials

Titanium foil (Ti, purity 99.5%, thickness: 0.02 cm, Beijing Zhongnuo Advanced Material Technology Co., Ltd), ethylene glycol (C₂H₆O₂, EG, anhydrous 99.8%, Sigma Aldrich and Merck), ammonium fluoride (NH₄F, ACS reagent, \geq 98.0%, Sigma-Aldrich) and sodium hydroxide (NaOH, Merck KGaA, 64271 Darmstadt Germany, EMD Millipore Co.) were used in sample preparation and characterization.

2.2. Catalyst preparation

The R-TNT sample preparation procedure is illustrated in Fig. 1. The sample TNT was firstly prepared with the anodic oxidation method [16]. The as formed TNT was annealed at 450 °C in air for 30 min with a heating rate of 3 °C/min in a muffle oven (Nabertherm, Germany). The TNT sample was then blackened with a two-anode reduction (TAR) technique for 2 min [16]. R-TNT sample was obtained after four sequential cathodic reduction steps in 1 M NaOH. The active area of one side of R-TNT was 1 cm². Note: Anodic TNT array on Ti foil always grows symmetrically on both sides of the Ti foil and a native TiO₂ protective layer always forms on the Ti foils [25].

2.3. Characterization

The structure was characterized with X-ray diffraction (XRD) (PANalytical X'PertPro using Cu-K α ($\lambda = 1.540598$ Å) radiation. The morphology was observed with a field-emission scanning electron microscope (SEM, Tescan MIRA 3, Brno, Czech Republic). The high-resolution transmission electron micrographs were acquired with a transmission electron microscope (TEM, JEOL JEM-2200FS), equipped with a double aberration-corrected microscope. The X-ray photoelectron spectroscopy (XPS) analysis were detected with a surface science instrument SSX-100 ESCA spectrometer with an Al-K α X-ray excitation



Fig. 2. The LSV curves of Ti foil, TNT and R-TNT in 1 M NaOH.

source.

2.4. Electrochemical measurements

The electrochemical measurements were carried out with an electrochemical workstation (ZENNIUM pro, Zahner-Elektrik, Germany). The geometric area of the immersed Ti metal size was 1 cm². As the samples always have two sides, back and front, the overall measured area was 2 cm² for all the electrochemical measurements. All the measurement was done in the 1.0 M NaOH (pH = 13.6) electrolyte and the measured potential, *vs.* Ag/AgCl electrode, was converted into that versus reversible hydrogen electrode (RHE) with the Nernst equation [26]:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.196 \tag{1}$$

The HER performance was measured with a three-electrode system, where one of the three different samples (Ti, TNT and R-TNT) were used as the working electrode, a Pt sheet as the counter electrode, and an Ag/ AgCl as the reference electrode. The linear sweep voltammetry (LSV) curves were recorded with a scan rate of 10 mV/s in dark condition.



Fig. 3. (a) Durability tests of the R-TNT sample in chronopotentiometry mode at constant current of -100, -50 and -10 mA for 24 h. (b) LSV curves of R-TNT in 1 M NaOH before and after the durability tests.

Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 100 kHz to 10 mHz using an AC amplitude of 20 mV signal at open circuit potential (OCP) under dark. The durability test was carried out with chronopotentiometry (CP) mode sequentially at current (*J*) of -100, -50 and -10 mA for 24 h at every current. The NaOH solution was replaced with a fresh one after every 24 h CP test.

3. Results

3.1. Electrochemical performance

3.1.1. Current output and stability

The electrocatalytic activity of the three samples towards HER was evaluated with the LSV measurement in 1 M NaOH in dark and the results are illustrated in Fig. 2. The electrocatalytic activity of R-TNT shows a remarkably improvement in HER performance over both the Ti foil and TNT sample. The J of R-TNT is 0.59 mA at 0 V_{RHE} and 0 mA at - 0.108 V_{RHE}, respectively. It needs an overpotential, which is often used to compare the catalytic performance of different cathode catalysts [27], of -0.380 V_{RHE} to achieve an overall current of -10 mA. Under a bias of $-1.0 V_{RHE}$, the J of R-TNT achieves -221.08 mA. No surface corrosion was observed on the R-TNT sample during the LSV test. The Ti foil showed 0 mA at a bias of 0.195 V_{RHE} and a value of - 0.085 mA at 0 V_{RHE}. It required an overpotential of - 0.693 V_{RHE} to achieve a J of - 10 mA. The poor HER efficiency of Ti monometallic catalyst is due to the large hydrogen-binding energy value [22]. The TNT as cathode gave current in the range of -0.013-0.004 mA under the bias voltage in a range from -1.0 - 0.5 V_{RHF}. The current output of anodic TNT sample as cathode for HER is negligibly low [21]. During the LSV measurement, surface corrosion was observed in the TNT sample in the negative bias range, which is common to metal oxide cathodes [23], [28,29]. The

value of the current density of R-TNT at - 1.0 $V_{\rm RHE}$ is 17000 times that of the TNT sample and 5 times that of the Ti foil sample, exhibiting a dramatic improvement.

The CP test results of R-TNT are presented in Fig. 3(a). In the first stage, the current was kept at -100 mA for 24 h. The potential experienced a fast decay from -0.57 to -0.80 V_{RHE} during the first 50 s. During 1-24 h, the potential showed a slow and marginal, almost within the error margin, increase from -0.94 to -0.95 V_{RHE}, corresponding to a slow decay of 1.3%, suggesting a good stability of the sample. After the first 24 h test, the electrolyte was refreshed, and another 24 h CP test @ -50 mA was performed. The potential varied from - 0.61 to -0.93 V_{RHE}. Again, in the initial stage, the potential increased quickly, from -0.61 to -0.88 V_{RHE}, but in the period of 25–48 h, the potential decay was only 5.2%, from -0.88 to -0.93 V_{RHE}. After refreshing the electrolyte, the CP test was carried out @ -10 mA for another 24 h. In the initial stage, the potential was - $0.27 V_{RHE}$ and increased quickly to - 0.43 V_{RHE} within 6 min. In the period of 49–72 h, the potential decay was 18.3%, from - 0.49 to - 0.58 V_{RHE}. After a total of 72 h of three step CP tests, the LSV curve was measured again (Fig. 3b) and a slightly increased current density was observed as a cathodic shift of the curve, indicating an improvement of the HER activity during the test.

3.1.2. Electrochemical impedance spectroscopy analysis

EIS tests of the Ti, TNT and R-TNT samples were carried out at OCP for the measurement of the charge transfer resistances at the interface between electrode and electrolyte, which was presented as characteristic Nyquist plots in Fig. 4, including the overview plots and the zoomin parts at low resistance range of 1–5 ohm. In Fig. 4(a), the plot of the Ti foil exhibits only one arc of the single incomplete capacitive loop. In Fig. 4(b), the TNT sample in Nyquist plot also only has one arc, which is much larger than that of the Ti foil. The Nyquist plot of the R-TNT



Fig. 4. EIS presented as Nyquist plots of (a) Ti foil (b) TNT and (c) R-TNT.



Fig. 5. (a)-(b) The SEM cross-sectional views of the R-TNT sample after all electrochemical tests; (c) A TEM image of the TNT sample; (d) HR-TEM image of the TNT and the zoomed in image of lattice fringes; (e) A TEM image of the R-TNT sample, (f) HR-TEM image of the R-TNT and the zoomed in image of lattice fringes; (g) A TEM image showing formation of a smaller nanotube (h) HR-TEM image of the newly formed nanotube in (g).



Fig. 6. The XRD patterns of TNT and R-TNT.

sample in Fig. 4(c) gives two arcs, a smaller semi-arc (insert figure) and a comparatively larger one, indicating the R-TNT sample has two electroactive interfaces with different kinetics [30]. The smaller one gives a resistance value of *ca* 1 ohm, which is close to that of a metal. The larger one indicates the semiconductive behavior part of R-TNT, but the radius of curvature is ten times smaller than that of the TNT sample illustrated in Fig. 4(b). A small arc represents a low resistance at the electro-de/electrolyte interface, *viz*, the higher efficiency of the charge transfer [31]. An ideal cathode material should be characterized with the highest possible charge injection efficiency [9,32]. The radiuses of curvature of the arcs of the Ti and TNT sample as well as that of the larger arc of the R-TNT sample has a sequence of TNT > Ti > > R-TNT, indicating the R-TNT sample has the highest charge transfer efficiency.

3.2. Characterization

3.2.1. Morphology

The SEM micrographs of the R-TNT sample after the electrochemical tests are displayed in Fig. 5(a) and (b). All the nanotubes in Fig. 5(a) are still vertically aligned and arranged as a dense "forest" morphology, in consistency with the features of the TNT sample [16]. The average length of the nanotubes is $12.7 \pm 0.1 \mu$ m. An overview of the repeated rings is clearly observed on the outer walls and indicated by arrows in Fig. 5(b) [33]. The average length of the steps between two rings (Fig. S1) is 46.7 nm. Fig. 5(c) shows the TEM overview of a nanotube in the TNT sample. The zoom-in image inset of Fig. 5(d) shows that TNT is highly crystallized with a clear lattice [16]. A TEM overview of a nanotube in the R-TNT sample is presented in Fig. 5(e) and the HR-TEM image is given in Fig. 5(f). The lattice spacing of the R-TNT (Fig. 5(f)) is

smaller than that of TNT sample. In Fig. 5(f), a clear grain boundary is observed. Fig. 5(g) shows the TEM overview of two nanotubes. The bigger one has similar diameter and length with those of the original anodic TNT, while the smaller tube has a length of 465 nm and a diameter of 13 nm. Only a small number of tubes with a diameter of ca. 10 nm were observed during the TEM observation. These tubes are likely formed during the cathodic reduction steps in 1 M NaOH from the reconstruction of the TNT.

3.2.2. Structure

Both the TNT and R-TNT samples exhibit two phases in the XRD patterns, as shown in Fig. 6, a typical anatase phase (JCPDS no. 21–1272) and a Ti metal phase (JCPDS no. 44–1294) [33,34]. All the peaks of the R-TNT and TNT samples locate at the same positions, but the peak intensities all change significantly. The three largest characteristic peaks of R-TNT are not the A (101), A (004) and A (200) of anatase for TNT. In the XRD pattern of R-TNT, the intensities of T (101), the overlapping peak of A (112) and T (002), and the overlapping peak of A (220) and T (103) become much higher than those of the anatase phase.

3.2.3. Surface states

The surface chemical states of R-TNT sample after electrochemical tests were examined with the XPS technique and the results are shown in Fig. 7. The adventitious carbon peak locating at 284.8 eV was used as an internal standard to calibrate the location of the XPS curves. The high-resolution C1s spectrum is resolved into six components in Fig. 7(a). A C=C bond at 284.8 eV, together with the other carbon species of C-C, C-N, C-F, O-C=O and -CO₃ are observed [16], [35]. The Ti 2p core level spectrum is deconvoluted into four peaks [21]. Two peaks locating at 464.7 and 458.8 eV are ascribed to Ti $2p_{1/2}$ and Ti $2p_{3/2}$ of typical Ti-O bond, while the peaks at 463.9 and 458.4 eV belong to Ti³⁺. The typical Ti-O-H located at 530.24 eV and Ti-O-Ti located at 529.83 eV are observed in O 1s core level spectrum, *i.e.* Fig. 7(c) [36]. The peaks at 535.7 and 531.59 eV are assigned to C(O)OH and C=O, respectively [37]. The Ti³⁺-O shows a peak at a lower binding energy, 528.44 eV [34].

4. Discussion

4.1. Reduced TiO_2 nanotube as cathode

Ti metal as catalyst shows a poor HER activity due to the large hydrogen-binding energy value [22]. The LSV test result of the Ti foil sample in this work is in consistency with this remark. The Ti foils used in this work have been exposed in air and possess a native self-formed TiO₂ oxidation layer as a blocking surface[9], [32], which has a similar chemical composition with the TiO₂ thin layer formed during anodic oxidation [25]. However, the main characteristic peaks of Ti foil in the XRD pattern are consistent with the typical hexagonal closely



Fig. 7. XPS spectra of the R-TNT sample. (a) C 1s; (b) Ti 2p and (c) O 1s.



Fig. 8. A scheme illustrating the metallic component in R-TNT sample.

packed Ti metal (JCPDS no. 44-1294) in Fig. S2 [33,34]. The anodic TNT as cathode catalyst in ECWS cell has been rarely reported due to the low efficiency and instability as mentioned in aqueous solution [21]. The anodic TNT grows symmetrically on both sides of the Ti foil, and the annealing step has the effect to improve the mechanical attachment of the nanotube array on the Ti foil substrate [38]. The LSV result of the TNT sample in Fig. 2 gave the evidence for its negligibly low HER activity. Surface corrosion of the sample was also observed during the LSV test in the minus bias range, indicating the instability of the anodic TNT. However, TiO₂ has been often used as the protective layer for photocathode in the photoelectrochemical WS cell or as one of the components for the cathode in other cells [38,39]. The HER activity, measured as the current density output, of the R-TNT cathode is 17000 times that of the TNT and 5 times that of the Ti foil. The remarkably high HER performance of the R-TNT sample is attributed to the cathodic reduction treatments.

4.2. The metallic behavior

A small arc represents a low resistance at the electrode/electrolyte interface, *viz*, the higher efficiency of the charge transfer [31], [40]. The EIS curve of the TNT sample shows a big arc, which is in consistent with the behavior of a blocking surface [9], [32]. The EIS curve of the R-TNT in Fig. 4(c) has two arcs and indicates that the R-TNT sample has two electroactive interfaces with different kinetics [30]. Both the semiconductive and the quasi-metallic components of R-TNT sample have their own charge-transfer reactions during the EIS test and lead to a multi-time constant Nyquist plot of two semi-circles. The larger one is assigned to the semiconductor catalyst layer, and the smaller one is comparable with those of conductors, such as Pt/C based electrode [41]. The possible existence of the metallic behavior part in R-TNT is illustrated in Fig. 8.

One possible reason for the metallic part of R-TNT is due to the Ti metal substrate (pathway 1), which is exposed from the crack of the TNT film. However, from the SEM micrographs and the appearance of the R-TNT sample, no exposed Ti was found on the TNT film. Moreover, it is known that Ti is always covered with an oxidation layer when exposed to the air, and here the sample was exposed to air for ca 3 days before the EIS measurement. Another reason could be the formation of quasi-metallic titania TiOx (pathway2). Quasi-metallic reduced TiOx, such as the Magnéli phase, has been known for its low resistance comparable to conductors and exist in partially reduced Ti oxides [42-44]. The XRD pattern of R-TNT sample shows that the locations of all the peaks are the same with those in the pattern of TNT. However, the peak intensities are remarkably different with the anatase in TNT, but similar to those in the TNTs for instance in the Au-doped TNT and the TNT samples reported in the works also underwent modifications [45-49]. Even though the comparative intensity ratios of the peaks are very different from those of TNT, no new peaks indicate the formation of new phases in the R-TNT sample. Next, in this work, all reduction modifications and the HER processes were carried out for the sample as cathode under H₂ and H⁺ atmosphere, which raises the possibility of reducing TiO₂ to metallic Ti⁰ on the R-TNT top surface marked as

pathway ③ for the self-improving efficiency cathodic performance of the R-TNT sample. It is in agreement with the higher Ti peak intensity of R-TNT than that of the TNT in the XRD patterns. Moreover, in comparison with the Ti foil, besides T (002) and T (101), the T (103) and T (112) overlapped peaks of R-TNT show preferred orientation of the crystallites in the sample. This could be associated to the formation of a self-composite of a metal-metal oxide structure (Ti⁰/TNT@Ti). This would also be indicated by the smaller arc in the EIS curve of R-TNT in Fig. 4(c), and the faster electron transport in R-TNT for efficient HER performance. The hybridization of metallic Ti⁰ in Ti⁰/TNT@Ti structure forms a possible protective layer contributing to the good stability in the long-term CP tests. The XPS results give support to the existence of reduced species such as Ti³⁺ and oxygen vacancies in the R-TNT sample. However, metallic Ti⁰ peaks were not found in the Ti 2p core level XPS. TEM images and literature neither supports the existence of metallic Ti⁰ on top of R-TNT layer.

5. Conclusions

Reduced TiO₂ nanotubes with tubular array morphology were synthesized on a flexible Ti foil substrate to function as a cathode in a WS cell. It presents remarkably good HER performance in 1 M NaOH without loading any co-catalyst. The current density during HER of R-TNT sample at -1.0 V_{RHE} achieved - 221.1 mA showing a huge improvement of 17000-times of that of TNT and 5-times that of Ti foil sample. The R-TNT breaks the kinetic limitation of TiO2 and Ti as HER catalysts. Based on the XRD, XPS, TEM and electrochemical measurements, the remarkably good performance of R-TNT is attributed to the Ti⁰/TNT/Ti composite structure with a hybridization of metallic and semiconductive parts. Successful durability tests of R-TNT at @ -100, - 50 and - 10 mA were carried out for 24 h at each current, respectively. A decay of 1.3% under CP@ -100 mA for 24 h was observed indicating stable performance of the R-TNT at large cathodic voltage and current conditions. This work reports a novel useful material to design durable, flexible and efficient cathode catalyst for HER.

CRediT authorship contribution statement

Xuelan Hou: Experiment, analysis of the data and writing of the manuscript. **Kerttu Aitola:** Writing – review & editing of the manuscript. **Hua Jiang:** TEM characterization, and detailed analysis and discussion of the TEM. **Peter D. Lund:** Writing – review & editing of the manuscript, and supervision. **Yongdan Li:** Proposed the topic and contributed to writing – review & editing of the manuscript and CHEM lab facility.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2021.12.009.

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