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# Embedded CuO nanoparticles@TiO<sub>2</sub>-nanotube arrays for photoelectrocatalytic reduction of CO<sub>2</sub> to methanol

Liqiang Zhang, Huazhen Cao\*, Qiuyuan Pen, Liankui Wu, Guangya Hou, Yiping

Tang,

Guoqu Zheng\*

(College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, China)

#### ABSTRACT

Herein, we report a simple approach to synthesize high-performance and structurally stable CuO nanoparticles catalyst embedded in TiO<sub>2</sub> nanotube arrays for CO<sub>2</sub> reduction. To summarize, anodic TiO<sub>2</sub> nanotube arrays (TNTs) were electrochemical reductive doped in 1 mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution to form an activated surface. Then CuO nanoparticles were successfully filled into the pores pace of TNTs by electrodeposition and heat treatment. The effects of Ti(III) reduction doping were discussed by means of electrochemical impedance spectroscopy (EIS) and X ray photoelectron spectroscopy (XPS). Results show that partial Ti(IV) in TNTs can be reduced to Ti(III) by electrochemical reduction, which leads to an significant improvement in TNTs surfactivity and then benefits the deposition of Cu nanoparticles to form a stable embedded structure. As a consequence, the composite electrodes showed higher photoelectrocatalytic performance for CO<sub>2</sub> reduction. The maximum current of CuO-TNTs composite electrodes is up to -1.37 mA/cm<sup>2</sup> at -0.5 V and high selectivity for methanol synthesis is also obtained in this case. At the same time, the amount of methanol produced by the CuO/self-doped TNTs composite electrode is about 15% higher than that by the CuO/TNTs electrode without reductive doping.

Keywords: CuO catalyst, TNTs reductive doping, Photoelectrocatalysis, CO2

reduction

#### **1** Introduction

Global warming and energy shortage are becoming two big problems in the 21th century. The problems caused by the increasing CO<sub>2</sub> concentration in the atmosphere are damaging our living environment and bringing negative effects to sustainable development. Many researchers have proposed the use of photocatalytic reduction of CO<sub>2</sub> to organics (such as methanol, formaldehyde, methane, etc.) to solve these problems. Cu and its oxides [1-4] have attracted extensive research interest in photocatalytic or photoelectrocatalytic reduction of CO<sub>2</sub> due to the narrow band gap, relative negative conduct band, low cost and non-toxicity. For example, CuO with band gap of  $1.3\sim1.6$  eV shows high visible light response. Its relative negative conduct band is about -0.78 V vs. NHE, far below the reduction potential of CO<sub>2</sub> to CH<sub>3</sub>OH (-0.38 V vs. NHE) and CO<sub>2</sub> to HCHO (-0.48 V vs. NHE) [5, 6], which means a strong ability for CO<sub>2</sub> reduction.

Some studies have reported the excellent photocatalytic activity of CuO nanoparticles [7, 8]. As we known, the agglomeration of CuO nanoparticles and the charge recombination are the important factors leading to the decrease of their photocatalytic activities. In order to solve these issues, various strategies have been tried, for example, the use of dispersant [7] and constructing heterojunction semiconductors system to promote electron-hole separation [9]. TNTs is a favorable substrate in nanometer material synthesis [10-15] owing to its distinctive nanostructure and high chemical stability [16, 17]. Furthermore, TNTs in itself is a kind of photocatalyst responding to only UV light because of its broad bandgap [18]. Thus, the combination of CuO with TNTs may bring out some expected results, i.e. the visible light response and the p-n junction arising from the p type CuO and the n type TiO<sub>2</sub>, which can efficiently promoted the separation of photoelectrons from vacancies.

However, CuO nanoparticles are easy to accumulate on the surface of TNTs,

and few can be deposited into the pore space of TNTs, which is mainly caused by the poor conductivity and the inert surface of  $TiO_2$  nanotubes [19]. The loose crumb structure usually leads to a rapid depletion of CuO nanoparticles, accompanied by fast decay in photocurrent and low efficiency. In the prior studies [20], it has been discovered that partial Ti(IV) can be reduced to Ti(III) by reductive doping, and the conductivity and surficial characteristics of TNTs can be improved remarkably, thus facilitating the deposition of nanoparticles. Based on this, we synthesized CuO-TNTs composite electrode with a stable embedded structure via using reductive doped TNTs as substrate, in order to obtain high-performance and structurally stable CuO composite catalyst.

#### 2 Experimental

#### 2.1 Preparation of CuO/TNTs.

TNTs are prepared by anodic oxidation on Ti sheets (25 mm×15 mm×1 mm, >99.5%) in 1% HF aqueous solution at constant potential (20V) and room temperature (20°C). Before anodization, the Ti sheets were polished with metallographic sandpaper and ultrasonically degreased in ethanol, followed by chemical polishing in solution with 50 g/L CrO<sub>3</sub> and 3% HF at 50°C. All TNTs were heat treated under 450°C for two hours in a tube furnace with heating and cooling rate of 5°C per minute, by which the amorphous TNTs can be transformed into anatase [21, 22].

Reductive doping of TNTs was conducted in 1 mol/L  $(NH_4)_2SO_4$  solution at different applied potentials with different reduction times using CHI660C electrochemical workstation. A conventional three-electrode system was used by employing the TNTs, Pt sheet and a saturated calomel electrode (SCE) as working electrode, counter electrode and reference electrode, respectively. Cu was electrodeposited on the reductive doped TNTs in 1 mol/L CuSO<sub>4</sub> via pulse mode with a cathodic pulse (-0.07A, 0.01s), an anodic pulse (+0.07A, 0.002s) and rest time (0A, 1s). Finally, all samples were calcined at 450°C for 1 h.

#### 2.2 Characterization

Cyclic voltammetry curves and electrochemical impedance spectroscopy were measured on CHI660C electrochemical workstation using platinum sheet and saturated calomel electrode (SCE) as auxiliary electrode and referring electrode, respectively. The frequency range of 100 kHz to 10 mHz and the modulation amplitude of 10 mV were employed for impedance measurements. Microstructural observation and elemental analysis were performed by TEM (Tecnai G2 F30) and SEM (ZEISS SUPRA55) equipped with the GENENIS-4000 energy dispersive spectrometry (EDS). XRD patterns of TNTs and CuO/TNTs were recorded on a Panalytical X'Pert PRO equipped with Cu K $\alpha$  radiation ( $\lambda$ =0.154056 nm) at 40 kV and 40 mA. And the valence states of Ti in TNTs were analyzed by XPS (Kratos Axis ultra DLD, Al K $\alpha$  X-ray source, hv=1486.6 eV).

#### 2.3 Photoelectrocatalytic reaction

The photoelectrocatalytic reduction of CO<sub>2</sub> was carried out in a homemade 100 ml gas tight dual-chamber cell with 0.1 mol/L NaHCO<sub>3</sub> solution, in which the CuO/TNTs electrode with an exposed area of 1 cm×1 cm and a Pt foil were served as photocathode and counter electrode. The chamber was irradiated from the side by a 250 W xenon lamp and the light intensity reaching the surface of sample was about 100 mW/cm<sup>2</sup>. CO<sub>2</sub> was kept bubbling into the solution to remove oxygen completely and saturate  $CO_2$  in solution. The photocurrent curves were recorded at -0.5 V (vs SCE) with an interval of 60 s for light on/off. The total yield of methanol and formaldehyde in the liquid phase from the photoelectrocatalytic reduction of CO<sub>2</sub> in the period of 5h was detected by headspace gas chromatograph (Fuli GC9720) equipped with a flame ionization detector (GC-FID) and capillary column (30m, inner diameter 0.25mm, DB-23). The column and detector temperatures were kept at 60 and 180 °C, respectively. The carrier gas of high-purity N<sub>2</sub> was flowing at a rate of 30 mL/min. The amount of formaldehyde was detected by UV-vis spectroscopy (HACH DR6000). In detail, 10 mL liquid product was directly mixed with 2.5 ml of color agent which consists of 50 g ammonium acetate, 6 ml acetic acid and 1ml

acetylacetone in 100 mL deionized water. After mixing, the final solution was heated at 50°C for 20 min and analyzed by UV–vis spectroscopy.

#### **3. Results and discussion**

#### 3.1 Ti(III) reductive doping

Redox behavior of TNTs in  $(NH_4)_2SO_4$  aqueous solution is studied and the characteristic CV curve is shown in Fig. 1. A cathodic peak is clearly seen at -1.46 V during negative potential scanning, which denotes to the reduction of Ti((IV) to Ti(III) [20]. On the reverse scanning, an oxidation peak corresponding to the reduction of Ti(III) appears at -1.30 V. The CV curve indicates that the self-doping of TNTs can be conducted by electrochemical reduction under certain potentials.

Naturally, the reductive doping potential is a major factor to be considered. Low overpotential is insufficient to drive the reduction of Ti(IV) and under too negative potential serve hydrogen evolution will occur. In order to reveal the exact influence of doping potential on the surface reactivity of TNTs for Cu electrodeposition, a series of electrochemical impedance curves are measured for various reductive-doped TNTs, as shown in Fig. 2. It is found that all curves show a slightly depressed semicircular shape. The different radius indicates different surfactivity in medium. It is obvious that the reductive doped TNTs is more active than the sample without reductive doping, as evidenced by the shrunken capacitive loops. An equivalent circuit model  $R_s(R_{ct}Q)$  is employed to analyze the EIS data. In this circuit,  $R_s$  stands for electrolyte resistance, R<sub>ct</sub> parallel accounts for the charge transfer resistance of Cu reduction on TNTs and Q is constant phase angle component. Table. 1 shows the fitting results by using the equivalent circuit model  $R_s(R_{ct}Q)$ . It is found that the charge transfer resistance is as high as 10.8 k $\Omega$  cm<sup>2</sup> for the undoped TNTs, which reduces obviously when the TNTs is reductive doped. Moreover, along with the reductive potential turning negative the charge transfer resistance decreases and then reaches a minimum at potential of -1.5 V, after which it changes little.

In order to further illustrate the exact effects of reductive doping, XPS analysis is adopted to reveal the variation of Ti valence state in TNTs. From the XPS patterns in

Fig. 3, it is noted that the characteristic peak of Ti2p XPS for undoped TNTs appears at 458.8 eV [21, 23], which shifts slightly toward low binding energy after reductive doping at -1.2, -1.5 and -1.7 V. The negative shift of Ti2p peak is an evidence of Ti(III) existence [24-26]. By comparison, it is also found that the doping amount of Ti(III) reaches saturation at -1.5 V and the further decreasing of doping potential is bootless. This result agrees well with the electrochemical impedance analysis.

#### 3.2 Characteristic of CuO/TNTs

Fig. 4 shows the XRD patterns of TNTs and CuO/TNTs composite electrode, in which the TNTs support is reductive doped at -1.5 V. The diffraction peaks of Ti substrate is clearly seen as the CuO/TNTs film is only several hundred nanometers thick. The weak diffraction peaks at 25.28° denotes the presence of TNTs (JCPDS 00-001–0562) [27], and the peaks emerging at 35.59° and 38.78° are attributed to (0 0 2) and (1 1 1) reflections of face-centered cube CuO. There is no obvious Cu<sub>2</sub>O diffraction peak, indicating that the heat treatment at 450°C enables a complete transformation of the electrodeposited Cu to CuO. It must be noted that the Ti(III) will also be oxidized to Ti(IV) during the heat treatment because of the unstable surface doping [28].

Fig. 5 shows the top and cross-section views of CuO nanoparticles loaded on the TNTs support with or without reductive doping. It can be seen that the TiO<sub>2</sub> nanotubes exhibit an average diameter of 80 nm with tube length of 300~400 nm. The deposits, i.e. CuO nanoparticles, are clearly seen while their filling position are much different. For the case of undoped TNTs (Fig. 5a, b), lots of large-grained CuO particles accumulate on the surface of TNTs and only few are filled into the pore space of TNTs, so many nanotubes are empty. However, when using the TNTs reductive doped at -1.5 V as support (Fig. 5c, d), it is readily to find that numerous CuO nanoparticles are deposited in the pore space of TNTs and their particle size becomes smaller. Obviously, the deposition of CuO on TNTs support is facilitated by the reductive doping of TNTs. A CuO/TNTs composite electrode with an embedded structure is then synthesized, which seems more stable than the one with CuO particles

accumulating on the surface of TNTs due to the space limitation by TiO<sub>2</sub> nanotubes.

The corresponding TEM images of CuO/TNTs with reductive doping are shown in Fig. 6a. Similarly to the above SEM observations, the TEM image also demonstrates that the CuO nanoparticles are well-deposited in the pose space of TNTs, which locate at not only the inner side of nanotubes but also the interstice between nanotubes (Fig. 6a). In addition, most CuO nanoparticles grow along the tubes wall and so some tubes are empty at the center, i.e. forming a hollow structure. In Fig. 6b, the HRTEM image exhibits two different set of atomic lattice fringes, and they match well with the (1 0 3) crystallographic plane of anatase  $TiO_2$  and (-1 1 1) crystallographic plane of CuO. This result is consistent with the XRD analysis in Fig. 4. By contrast, the deposition of Cu nanoparticles in undoped TNTs is unsatisfactory (Fig. 6c).

Based on the above analysis, a schematic illustration of the growth of Cu nanoparticles on different TNTs is presented in Fig. 7. By reductive doping treatment, partial Ti(IV) can be reduced to Ti(III) at the presence of H<sup>+</sup> ( $Ti^{4+} + e^- + H^+ \rightarrow Ti^{3+}H^+$ ) [19]. Both the bottom and the wall of TiO<sub>2</sub> tubes is then activated due to existence of these active sites. The enhancement in surfactivity is bound to bring convenience for the deposition of Cu nanoparticles. As a result, Cu nanoparticles will grow from the bottom and the tube wall, leading to form an embedded structure. However, for the case of bare TNTs without any treatment, it is difficult for Cu nanoparticles to deposit inside the nanotubes due to its inert state. In this way, abundant of Cu nanoparticles can only grow on the surface of TNTs and form loose crumb structure.

#### 3.3 Photoelectrocatalytic activities of CuO/TNTs

The linear sweep voltammetry of CuO/TNTs in  $CO_2/N_2$  saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution was shown in Fig. 8. In the medium without carbon source (N<sub>2</sub>-saturated), the cathodic current increases sharply when the scanning potential reaches -0.6 V, which denotes hydrogen evolution. It is found that the cathodic current in CO<sub>2</sub>-saturated medium is much higher than that in N<sub>2</sub>-saturated medium, indicating that the electrode

has excellent electrocatalytic/photoelectrocatalytic activity for CO<sub>2</sub> reduction.

Fig. 9a shows a series of transient photocurrent curves of CuO/TNTs electrodes using different TNTs support, in order to understand the effects of reductive doping potential on their photoelectrocatalytic properties for CO<sub>2</sub> reduction. For comparison, the transient photocurrent curve of the sample prepared on titanium plate is also presented. It can be seen that TNTs play a significant role in photoelectrocatalysis, the photocurrent on a CuO/TNTs electrode is much higher than that on a CuO/Ti electrode. From these curves, the effects of reductive doping potential of TNTs on electrode's photoelectrocatalytic property are evident. The initial photocurrent of composite electrode is only around -1.21 mA/cm<sup>2</sup> when using undoped TNTs as support. However, for the case of using doped TNTs as support, the initial photocurrent rises obviously, which is about -1.28 mA/cm<sup>2</sup>, -1.37 mA/cm<sup>2</sup> and -1.37 mA/cm<sup>2</sup> respectively at doping potential of -1.2 V, -1.5 V and -1.7 V. Also, it is found that when the doping potential of TNTs is not negative enough (i.e. -1.2 V), the effects of reductive doping is not obvious. With the increasing of doping potentials, the photocurrent rises and reaches the maximum at potential of -1.5 V. Obviously, Overnegative doping potential won't improve the performance of CuO/TNTs electrode any more, which is in agreement with the results in EIS and XPS analysis (Fig. 2 and Fig. 3).

The influence of reductive doping time at same reduction potential is also investigated and the corresponding transient photocurrent curves of  $CO_2$  reduction are presented in Fig. 9b. There is an obvious increasing tendency in photocurrent with the extension of doping time. When the doping time of TNTs is 5 s, an obvious current growth is observed, which indicates a fast transformation of Ti(IV) to Ti(III) during doping process. And it is found that the photocurrent reaches the highest at reductive doping time of 10 s after which the current keeps constant, that is to say, the reductive doping of TNTs reaches saturation state quickly.

Furthermore, it is worth noting that whether Ti(III) is doped or not, there is severe current fluctuation between light on and off, up to 1mA, which indicates a strong photoresponse of CuO/TNTs in visible light. In addition, the current of

as-prepared CuO/TNTs can reach a high level at the moment light on, which is contributed to the fast separation and transmission of electron-hole pairs.

3.4 Photoelectrocatalytic reduction of CO<sub>2</sub>

Photoelectrocatalytic properties of CuO/TNTs electrodes toward CO<sub>2</sub> reduction is investigated at -0.5 V under visible light. The product contains methanol and formaldehyde in the liquid phase and very few methane is detected in the gas phase. The methanol yield by using the synthesized CuO/TNTs electrode is displayed in Fig. 10. It is found that the methanol yields of the two samples synthesized on different TNTs vary greatly with time. For instance, after one hour of reaction, the methanol yield on CuO/self-doped TNTs and CuO/undoped TNTs are 8.3  $\mu$ mol/cm<sup>2</sup> and 7.6  $\mu$ mol/cm<sup>2</sup>, respectively. In spite of the subtle difference in the initial stage, however, after two hours of reaction, the amount of methanol produced by a CuO/self-doped TNTs electrode is about 15% higher than that by a CuO/undoped TNTs electrode. And after five hours of reaction, the amount of methanol reaches 30  $\mu$ mol/cm<sup>2</sup> on CuO/self-doped TNTs electrode, far more than that with a CuO/undoped TNTs electrode (26  $\mu$ mol/cm<sup>2</sup>). The enhancement of methanol yield after long-term reaction is closely related with the higher activity and the excellent stability of CuO/self-doped TNTs electrode.

Effect of applied potentials on the products selectivity was also studied and shown in Fig. 11. It can be seen clearly that in the range of -0.2 V to -0.5 V, the yield of methanol on CuO/self-doped TNTs electrode increases with the negative shift of potentials, while the yield of formaldehyde decreases gradually. However, when the applied potential reaches -0.6 V, the outputs of both methanol and formaldehyde will decrease. Obviously, formaldehyde is easier to produce during CO<sub>2</sub> reduction at low applied potential (-0.2 V) [29], while methanol is incline to generate at more negative potentials (>-0.3 V). However, when the applied potential is too negative (>-0.6 V), the hydrogen evolution reaction began to take place [2, 30], as shown in Fig. 8. As a result, the competition between CO<sub>2</sub> reduction and hydrogen evolution reaction becomes serious, which finally lead to the decrease of catalytic efficiency for CO<sub>2</sub>

reduction. i.e. the reduction of methanol and formaldehyde yields.

#### 3.5 The reaction mechanism

Fig. 12 shows the diagram of p-n junction of CuO-TNTs. P-type CuO and n-type TiO<sub>2</sub> are combined to form Z-Scheme p-n junction [31, 32]. Some photo generated electrons in TiO<sub>2</sub> with a lower conduction band could recombine with the holes in CuO as the valence band of CuO is close to the conduction band of TiO<sub>2</sub>. More powerful photo generated electrons and holes can be retained on different counterparts, the isolated powerful oxidative holes and reductive electrons generated on TiO<sub>2</sub> and CuO respectively result in a strong photoelectrocatalytic ability [32], as shown in Fig. 9. A possible reaction mechanism is that CO<sub>2</sub> can be reduced to methanol and formaldehyde during the reaction because of the powerful reductive electrons generated by CuO, and formaldehyde will be further reduced to methanol at a relatively negative potential.

#### **4** conclusion

In conclusion, CuO/TNTs composite electrodes were successfully synthesized by using reductive doped TNTs as support. Various tests show that the surfactivity of TNTs doped with Ti(III) is greatly improved so that Cu nanoparticles can be better deposited inside the TiO<sub>2</sub> nanotubes. The optimum condition for TNTs doping is to conduct at potential of -1.5 V for 60 s. The corresponding CuO/reductive doped TNTs electrode shows a strong photocurrent of -1.37 mA/cm<sup>2</sup>, which means a high photoelectrocatalytic reduction ability for CO<sub>2</sub> reduction. The appropriate potential for methanol synthesis is around -0.5 V due to the higher yield and the better selectivity.

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## Tables

Table 1 The parameters obtained by simulation with the equivalent circuit model  $R_{s}(R_{ct}Q)$ 

Table 1

Reduction potential /V	$R_s/\Omegacm^2$	$R_{ct}/\Omega \ cm^2$	$Q/\Omega^{-1} \cdot cm^{-2} \cdot s^{-n}$	n
0	8.60	1.08E4	2.19E-5	0.895
-1.2	8.72	0.54E4	2.02E-4	0.931
-1.5	11.18	0.41E4	2.42E-4	0.925
-1.7	10.13	0.46E4	2.60E-4	0.922

S.P.MA

#### Figures

- Fig. 1 CV curve of TNTs in 1mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at scan rate of 50 mV/s.
- Fig. 2 EIS plots of various TNTs measured at 0.2 V with 10 mV amplitude sinusoidal perturbation in 1mol/L CuSO<sub>4</sub> solution.
- Fig. 3 Ti2p XPS spectra of the TNTs reductive doped at different potentials.
- Fig. 4 XRD patterns of TNTs and CuO/reductive doped TNTs electrodes.
- Fig. 5 Top and cross-section views of the CuO/TNTs (a, b) without reductive doping and (c, d) reductive doped at -1.5 V.
- Fig. 6 TEM and HRTEM analysis of CuO/TNTs (a,b) with reductive doping and (c) without reductive doping.
- Fig. 7 Schematic illustration of Cu electrodeposition on (a) undoped TNTs and (b) self-doped TNTs.
- Fig. 8 The Linear Sweep Voltammetry of CuO/TNTs electrode in N<sub>2</sub>-saturated and CO<sub>2</sub>-saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution with the scan rate of 50 mV/s under light on/off.
- Fig. 9 Transient photocurrent response of CuO/TNTs at -0.5 V under visible light, (a) TNTs is reductive doped at different potentials for 60 sec, (b) TNTs is reductive doped at -1.5 V for different time.
- Fig. 10 Methanol yield by using different CuO/TNTs electrodes.
- Fig. 11 Methanol and formaldehyde concentrations at different reductive potentials within 5h.
- Fig. 12 Mechanism of photoelectrocatalytic reduction of CO<sub>2</sub> on CuO/TNTs.





Fig. 3























### Highlights

- CuO/TNTs composite electrode with an embedded structure was successfully fabricated via using self-doped TNTs.
- The activated surface of TNTs by reductive doping benefits the deposition of Cu nanoparticles.
- High activity and stability for CO<sub>2</sub> reduction are achieved with the CuO/self-doped TNTs electrode.
- The yields of methanol produced by CuO/self-doped TNTs electrode increased significantly.