Conductive Cu doped TiO₂ nanotubes for enhanced photoelectrochemical methanol oxidation and concomitant hydrogen generation

Shiva Mohajernia,^[a] Seyedsina Hejazi,^[a] Pavlina Andryskova,^[b] Giorgio Zoppellaro,^[b] Ondrej Tomanec,^[b] Radek Zboril^[b] and Patrik Schmuki^{*[b],[b],[c]}

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- [a] Sh. Mohajernia, S. Hejazi, P. Schmuki
Department of Materials Science Engineering
University of Erlangen-Nuremberg
Martensstrasse 7, D-91058, Erlangen,
Germany
Tel: +49-9131-852-7575, Fax: +49-9131-852-7582
E-mail: schmuki@ww.uni-erlangen.de
- [b] P. Andryskova, G. Zoppellaro, O. Tomanec,
Prof. R. Zboril, Prof. P. Schmuki
Department of Chemistry
King Abdulaziz University
Jeddah, Saudi Arabia
- [c] Prof. P. Schmuki
Department of Chemistry

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Abstract: Cu-doping in titania is usually detrimental to the material's photoconductivity which prevents the use of this combination in photoanodes. In this work, we produce TiO₂ nanotube arrays intrinsically doped with copper and establish sufficient conductivity to use them as efficient photoanodes for methanol oxidation in a photoelectrochemical hydrogen generation setting. Firstly, Cu doped TiO₂ nanotubes were produced by anodizing a Ti-Cu binary alloy. By subsequent thermal reduction of the structure in an Ar/H₂ environment, conductive copper doped TiO₂ nanotubes (TiCuTN-Ar/H₂) can be achieved with an approximately 10³ times higher conductivity than the non-reduced material. When these reduced Cu doped TiO₂ nanotubes are used as photoanode, copper species embedded in the TiO₂ wall catalyze the methanol oxidation reaction. As a result of the combined effect of conductivity and catalytic effect of Cu, such a reduced Cu:TiO₂ nanotubes can generate a photocurrent of 0.76 mA.cm⁻² at 1 V vs. RHE, under AM1.5 (100 mW/Cm²) irradiation – in a 50:50 MeOH/water solution – this is 33 times higher than for pristine Cu:TiO₂ nanotubes.

Introduction

Ever since Fujishima and Honda reported on the photoelectrolysis of water into H₂ and O₂ using a rutile titanium dioxide single crystal, TiO₂ has been widely explored for applications in photoelectrochemical (PEC) water splitting [1–3].

This is due to the semiconductive properties of the material, its natural abundance, chemical stability in liquid solutions, non-toxicity, high resistance to photocorrosion, and low production costs. Instead of using purely aqueous electrolytes for photoelectrochemical H₂ evolution, alcohol containing solutions are beneficial on TiO₂ photo-anodes for capturing the photogenerated holes, which increases the reaction rate and thus the overall photocurrent. Organic compounds, namely methanol and ethanol, may in this scheme not only be hole capture agents, but may additionally improve the oxidation rate by an effect known as current-doubling [4–6]. Due to the enhanced oxidation reaction of the photoanode, the overall photoelectrochemical current also enhances the electrocatalytic H₂ evolution on the cathode. In a conventional PEC device, the reduction and oxidation reactions occur at the surface of photoelectrodes. Therefore, a larger specific surface area of the photoanode represents a great advantage [1–3].

An efficient route to obtain highly defined nanoscale photoanodes is the anodic growth of self-organized TiO₂ nanotube layers on Ti. Length, diameter, and crystallinity of such layers can be adjusted by the selection of the anodization parameters and the thermal post-treatment. These TiO₂ nanotubular layers grow vertically aligned on the Ti substrate (i.e., represent directly back contacted electrodes) [3,7,8].

However, the efficiency of using pure TiO₂ as a water splitting photoanode – even in a nanotube form – is still low due to the fact that only a sluggish charge transfer kinetics to H₂O is

obtained [9,10]. As mentioned, one way to enhance the overall reaction rate of the photocurrent is to use hole-capture agents that facilitate the oxidation reaction, such as various alcohols, namely methanol. A further enhancement of the reaction can be the use of additional co-catalysts for catalyzing methanol photoelectrochemical and electrochemical oxidation – typically these are noble metal based catalysts [11–16]. An inexpensive alternative may be copper that has been reported as an efficient electrode for methanol electro-oxidation. The improved reaction rate for this electrode is ascribed to the electro formation of copper (II)/(III) ion intermediate that catalyzes methanol oxidation [17–19]. It is therefore conceivable to design a copper doped titania structure to create an efficient photoanode for methanol oxidation. However, copper doped titania has never been reported for photoelectrochemical methanol oxidation. The key obstacle is that copper doping (Cu^{2+} and Cu^+) drastically reduces the conductivity and photo-conductivity of a TiO_2 scaffold [20] and thus prevents the practical use of Cu doped-titania as electrodes or photoelectrodes.

In previous work, we showed that optimized annealing of TiO_2 nanotubes in Ar/H_2 can not only drastically improve the conductivity of TiO_2 nanotubular structures but also preserve the semiconductor properties of TiO_2 , thus providing efficient photoelectrodes [21,22].

Within the present work, we explore the feasibility to overcome the conductivity restrictions of copper doped titania nanotube electrodes by an appropriate Ar/H_2 treatment and thus enable the use of this configuration in photoanodes for methanol oxidation. For this, we anodize a Ti-Cu binary alloy to form Cu-modified TiO_2 nanotubes. After a thermal reduction treatment in Ar/H_2 we find a drastically enhanced conductivity that indeed allows its use as a photoanode. This photoanode provides a significantly enhanced photoelectrochemical methanol oxidation rate (and therefore an enhanced hydrogen evolution rate at the photocathode).

Results and Discussion

Figure 1a-b show SEM images of highly-ordered anodic TiO_2 nanotubes which are grown from a Ti-Cu substrate in an $\text{EG}-\text{NH}_4\text{F}$ based electrolyte (see experimental section) before (TiCuTN) and after a reduction treatment in Ar/H_2 atmosphere at 550°C ($\text{TiCuTN-Ar}/\text{H}_2$), respectively. The nanotubes have an outer diameter of ≈ 150 nm and length of $3\ \mu\text{m}$. A comparison of Figure 1a and b shows that the reduction treatment does not have any significant influence on the morphology of the nanotubes. The structures in Figure 1a-b were characterized by HRTEM and SAED patterns in view of their structure (see Figure 1 c-f). The HRTEM lattice fringes reveal the formation of anatase with a lattice spacing characteristic of the (101) plane which is $0.35\ \text{\AA}$ (see Figure 1 c-d). The HRTEM images and the SAED patterns in Figure 1 e-f show that there is no evidence of crystalline copper oxide present in the structures both before and after the reduction treatment. However, from the HRTEM EDS maps of Ti and Cu it is evident that copper is well distributed within the structure (see Figure 1g). Important to note is that nanotubes grown in organic electrolytes consist of a two layer structure, with an inner carbon-rich shell and an outer shell that is clearly visible for the nanotubes before and after the reduction treatment (see inset of Figure 1c-d). To further

investigate the distribution of copper over the nanotubes length we carried out glow discharge optical emission spectroscopy (GDOES) on the TiCuTN . Figure 1h shows the qualitative GDOES depth profile. The resulting profile of the composition shows that copper is homogeneously distributed throughout the tubes.

The EPR spectra of TiO_2 nanotube (TiTN) and TiCuTN before and after Ar/H_2 treatment is reported in Figure 2a. The observed EPR resonances for TiCuTN samples reveal a clear signature associated to the Cu(II) cation (d^9 , $S = \frac{1}{2}$) that is subjected to a tetragonal field, in which $g_{\parallel} > g_{\perp} > g_e$ (2.0023). The $\text{TiCuTN-Ar}/\text{H}_2$ reveals the significant presence of Ti^{3+} cations ($g = 1.997$) in the TiO_2 lattice, together with doped Cu^{2+} . Gray et al. showed similar spectra in which highly dispersed doped Cu^{2+} sites were formed on TiO_2 [23]. In order to study the possible electronic correlation between Ti^{3+} and Cu^{2+} signals in the $\text{TiCuTN-Ar}/\text{H}_2$ in more detail, saturation experiments were performed at 123 K upon monitoring the sharp $g \sim 1.996$ component as well as the entire EPR resonance line (see Figure 2b). To analyse the saturation trends, the data were fitted using the Portis and Castner's theory [24,25]. The fitting analysis (solid lines in Figure 2b) of the experimental saturation data (circles and triangles in Figure 2b) indicates that the spin/spin and spin-lattice relaxation of the two systems (Ti^{3+} and Cu^{2+}) are not correlated to each other through exchange interaction. Therefore, EPR results suggest that Cu^{2+} has been doped in TiCuTN samples and that the Ar/H_2 treatment forms Ti^{3+} species in TiO_2 lattice, while the Cu^{2+} signal remains almost unchanged (a possible presence of Cu^+ cations (d^{10}) cannot be excluded, because it is undetectable by EPR).

Figure 2 c-d show the high resolution XPS $\text{Cu}2p$ spectra for TiCuTN and $\text{TiCuTN-Ar}/\text{H}_2$, respectively. $\text{Cu}2p$ in both spectra has significantly split spin-orbit components. The $\text{Cu}2p$ in the air annealed sample shows strong satellite features which is a typical characteristic of Cu^{2+} in the structure and it can be deconvoluted into two peaks. The presence of two main peaks at 934.4 eV and 954.3 eV is ascribed to the $\text{CuO } 2p_{3/2}$ and $2p_{1/2}$ (see Figure 2c). Figure 2d shows the high resolution spectra of $\text{Cu}2p$ for the reduced TiCu nanotubes. From the deconvolution of the $\text{Cu}2p$ peak it is apparent that after reduction treatment the Cu^{2+} is mainly converted to Cu^+ . The main peaks at 932.7 eV and 952.7 eV match $\text{Cu}_2\text{O } 2p_{3/2}$ and $2p_{1/2}$ while the peaks at 934.6 eV and 954.4 eV correspond to the $\text{CuO } 2p_{3/2}$ and $2p_{1/2}$, respectively. It is worth mentioning that distinguishing Cu^0 and Cu^+ is difficult by XPS, as they have very similar binding energies. However, as previously mentioned in the EPR section, Cu^+ is not detectable in EPR and there is no evidence of Cu^0 in the EPR spectra for the TiCuTN . Therefore, combining the result from XPS and EPR for the reduced TiCuTN s we can prove the formation of Cu^+ rather than Cu^0 .

In order to evaluate the effect of reduction treatment on the crystallinity of the samples XRD was performed on TiTN , $\text{TiTN-Ar}/\text{H}_2$, TiCuTN and $\text{TiCuTN-Ar}/\text{H}_2$. The results show that there is no significant difference in the XRD patterns of the samples; all peaks can be assigned to TiO_2 (101) anatase (see Figure 2e). This is well in line with literature reports on a wide range of hydrogenation conditions [22]. Moreover, there is no evidence of copper oxide peaks, which further supports the SEM and HRTEM results regarding the fact that copper is doped in the structure.

To investigate the electrochemical behavior of the samples, electrochemical impedance spectroscopy (EIS) measurements were performed. The results are shown in Figure 3 a-b. In the phase angle plot (a), one can see two distinct peaks that correspond to two time constants. These may be ascribed to two different electron transfer steps: one within the semiconductor and the other at the semiconductor/electrolyte interface. In other words, the first time constant at high frequencies can be associated with the space charge region, and the second one at low frequencies can be ascribed to the charge transfer at the solid-liquid interface (Helmholtz double layer). This enables the determination of two capacitive contributions involved in the measured impedance spectra [26–28]. For the reduced structures, the peak at higher frequency shifts to lower frequencies, this can originate from the incorporation of Ti^{3+} species in the reduced sample [29,30]. The increase in the Ti^{3+} concentration decreases the resistivity [29,30] and thus shifts the time constant of space charge transfer towards a higher value (Figure 3b). The results in the Bode diagram (modulus vs. frequency) indicate that un-reduced tubes show a significantly higher resistance than the Ar/H_2 treated samples. Clearly, the TiCuTN shows the highest resistance, this is likely due to the fact that copper ions act as electron traps in TiO_2 nanotubes [31]. However, the impedance spectra of the $\text{TiCuTN-Ar}/\text{H}_2$ show that after the Ar/H_2 treatment the conductivity of the layer increases significantly and become similar to the $\text{TiTN-Ar}/\text{H}_2$.

In addition, solid-state conductivity measurements of the TiTN , $\text{TiTN-Ar}/\text{H}_2$, TiCuTN and $\text{TiCuTN-Ar}/\text{H}_2$ are shown in Figure 3c. It is apparent that the presence of copper decreases the conductivity of TiO_2 significantly. However, after the reduction treatment in an Ar/H_2 environment, the conductivity of the tubes significantly increases (more than 10^3 times) and the $\text{TiCuTN-Ar}/\text{H}_2$ shows approximately the same conductivity as the non-copper doped $\text{TiTN-Ar}/\text{H}_2$. The results from solid state conductivity and EIS measurements thus confirm the strongly detrimental effect of copper doping on the conductivity of TiO_2 nanotubes but most importantly this drop can be overcome by the reduction treatment in an Ar/H_2 environment. (Essentially the high conductivity of Ar/H_2 treated tubes can be established also for Cu-dopedTiO_2). In order to examine the performance of these treated tubes as photoelectrodes we first acquired photocurrent spectra in Na_2SO_4 solution at 500mV vs. Ag/AgCl . Incident photon to electron conversion efficiency (IPCE) for the TiTN , $\text{TiTN-Ar}/\text{H}_2$, TiCuTN and $\text{TiCuTN-Ar}/\text{H}_2$ photoanodes data are shown in Figure 3d. The results show that all the photoanodes show a significant photoactivity in the UV region. The $\text{TiCuTN-Ar}/\text{H}_2$ has the highest IPCE value reaching 30 % at 330 nm, which is in line with conductivity results showing lowest resistivity for the Ar/H_2 treated copper doped TiO_2 nanotubes. In addition, the lowest IPCE was obtained for the low-conductive TiCu sample (TiCuTN). It can thus be deduced that the improvement in IPCE behavior for the Ar/H_2 treated tubes is to a large extent due to the enhancement in conductivity. Notably, no visible light absorption can be observed in the IPCE spectra.

To further characterize the photoelectrochemical characteristics, intensity modulated photocurrent spectra (IMPS) were measured to determine transport times of photo generated electrons. The extracted transport times for TiTN , $\text{TiTN-Ar}/\text{H}_2$, TiCuTN and $\text{TiCuTN-Ar}/\text{H}_2$ are shown in Figure 3e. Clearly a significantly faster electron transport is observed for the reduced nanotubes. The TiCu sample annealed in Ar/H_2 shows the shortest transport

times. Also the results indicate that the same power-law dependence on the incident light intensity holds for all the tubes. Therefore, IMPS results confirm that the observed trend in the photocurrent and conductivity measurements are reflected in the transport time of the photo generated charges.

To evaluate the performance as a photoanode in methanol solution, photocurrent-voltage curves of the different samples were acquired under AM 1.5 light irradiation. The results in Figure 3f indicate that copper doped TiO_2 nanotubes show the lowest generated photocurrent, however, after reduction treatment the photocurrent improved drastically to 33 times higher than the TiCu nanotubes and 5 times higher than the plain TiO_2 nanotubes. This can be ascribed to the established high conductivity of the electrode that allows to exploit surface exposed copper species as catalytic centers for methanol oxidation. To correlate this, we recorded CV curves similar to Heli et al.'s report on poly-crystalline copper electrodes [19] but in our case for Cu-doped TiO_2 photoelectrodes Figure 3g [17,19]. Cyclic voltammetry (CV) results of the copper doped TiO_2 nanotubes in electrolytes without methanol with oxidation peaks at -400, -140, 580 mV vs. Ag/AgCl which corresponds to Cu/Cu^+ (I_a), $\text{Cu}^+/\text{Cu}^{2+}$ (II_a) and $\text{Cu}^{2+}/\text{Cu}^{3+}$ (III_a) respectively are coincident with the peaks reported by Heli et. al but of a 1000 times lower current range than obtained on pure copper electrode. Heli et. al suggested that Cu^{3+} as intermediate can catalyze the methanol oxidation [19]. They showed that by increasing methanol concentration an irreversible methanol oxidation peaks develops at around 600 mV vs. Ag/AgCl . Thus, it is probable that the electro-generated Cu^{3+} species is the active moiety, which efficiently enhanced the oxidation of methanol. Figure 3h shows the CV results of TiTN and $\text{TiCuTN-Ar}/\text{H}_2$ electrolyte containing methanol. The result shows that for the reduced copper doped TiO_2 nanotube one can clearly see a methanol oxidation peak around 0.5 V vs. Ag/AgCl . Important is that if the CV measurements are carried out under dark conditions, the electrocatalytic methanol oxidation peak is in the range of μA , whereas in the presence of light the obtained photocurrent is in mA range. This means that in the photoelectrochemical experiments it is plausible to ascribe the enhanced catalytic oxidation of methanol to photo activated $\text{Cu}^{2+}/\text{Cu}^{3+}$ species, concomitant with enhanced H_2 evolution at the cathode.

Conclusions

In summary, we report the fabrication of a conductive vertically aligned copper doped TiO_2 nanotube layers by anodic oxidation of Ti-Cu binary alloys. The plain copper doped TiO_2 nanotubes have a very low conductivity making their use as an electrode virtually impossible. However by a reducing treatment in an Ar/H_2 atmosphere at 550^o C, we overcome this conductivity limitation. A main feature of the copper doping is that it can act as a catalyst for methanol oxidation. This can be exploited in photoelectrochemical applications, where conductive Cu doped tubes can be efficient photoanodes, for example, coupled with a suitable cathode where concomitant H_2 is generated. We believe that this method can be used for other dopants in TiO_2 nanostructures, which a priori have a negative effect on the conductivity of the structure but can be "out doped" by a suitable reductive treatment.

Experimental Section

A Ti-Cu alloy with a copper concentration of 1.5 at% was prepared by controlled argon atmosphere arc melting. The as-prepared samples were cut and ground up to 800 grit with silicon carbide paper. After grinding, the sample was cleaned by sonicating in acetone, ethanol and deionized (DI) water, respectively, followed by drying in a nitrogen stream. The tubes were grown in an electrolyte consisting of 0.1 M ammonium fluoride (NH₄F), and 5 wt% deionized H₂O in ethylene glycol (99 vol %) for 10 min. Two electrode configurations were used with the Ti-Cu substrate as the working electrode, and a platinum plate serving as the counter electrode. After anodization, the samples were dipped into ethanol for 30 minutes and then dried in a N₂ stream.

Crystallization of the as-anodized amorphous tube layers was carried out by annealing in a Rapid Thermal Annealer (Jipelec JetFirst 100) at 450°C for 1 hour in air with a heating/cooling rate of 5°C min⁻¹, and the reduced layers were obtained by annealing in Ar/10% H₂ at an optimized temperature of 550 °C [21,22].

The samples' morphology was investigated using a scanning electron microscope (SEM) Hitachi FE-SEM 4800, and a high resolution transmission electron microscope (HRTEM, FEI TITAN G2 60-300) was used to characterize the morphology of the samples. The composition and the chemical states were characterized using X-ray photoelectron spectroscopy (XPS, PHI 5600, US), and peak positions were calibrated on the Ti2p peak at 458.5 eV. Solid-state conductivity measurements were carried out in an adapted scanning electron microscope (SEM, TESCAN LYRA3 XMU) by 2-point measurements using a semiconductor characterization system (Keithley 4200-SCS). Tungsten tips were used as electrical contacts between tube tops and the substrate. Resistivity values were then obtained from the I-V curves (5 mV/s sweep rate). EPR spectra were recorded on JEOL JES-X-320 operating at X-band frequency (~9.1 GHz), equipped with a variable temperature control ES 13060DVT5 apparatus, and were performed on powder samples at 123 K.

Elemental depth profile analysis was performed using a GD Profiler 2 from HORIBA Scientific. Plasma conditions were optimized using 650 Pa for the plasma gas and a standard RF (13.56 MHz) power of 27 W. In order to reduce the sputtering rate, the RF source was pulsed at 3 kHz with a 0.25 duty cycle, giving an average power of 6.75 W. A 4 mm diameter anode was used. For the plasma discharge, argon gas was used.

Electrochemical impedance measurements were carried out in 0.1 M Na₂SO₄ and cyclic voltammetry was carried out in 0.1 M NaOH with and without 10% methanol, in a classical three-electrode set-up. For this, the TiCu nanotube layers were used as working electrode; a platinum plate served as a counter electrode, and an Ag/AgCl (3 M KCl) electrode served as a reference electrode. The electrochemical measurements were carried out with an Autolab PGSTAT 30 Potentiostat/Galvanostat (Ecochemie, The Netherlands).

Photoelectrochemical characterization was carried out with a setup consisting of a 150 W Xe arc lamp (LOT-Oriel Instruments) as the irradiation source and a Cornerstone motorized 1/8 m monochromator. Photocurrent spectra were acquired in 0.1 M Na₂SO₄ containing 10% methanol at a potential of 500 mV (vs. Ag/AgCl). Photocurrent spectra were measured in a three-electrode configuration, consisting of 1 cm² TiO₂ nanotubes as photoanode area, platinum wire as a counter electrode and an Ag/AgCl (3 M KCl) electrode as a reference with a JAISSE IMP 83 PCT-BC Potentiostat-Galvanostat. The electrochemical cell was adjusted horizontally in front of the light source. The incident photon-to-current efficiency (IPCE) for each wavelength was calculated according to (Eq. (1) and (2)):

$$IPCE(\%) = \frac{I_{ph} \times h\nu}{P \times q} \times 100 \quad (1)$$

$$I_{ph} = I_{on} - I_{off} \quad (2)$$

where I_{on} is the steady-state current after light illumination in each wavelength, I_{off} is steady-state current after light illumination at each wavelength, I_{ph} is photocurrent density, P is the power density of the light, $h\nu$ (≈ 1240) photon energy of the incident light, q charge of the electron.

Photoelectrochemical water splitting experiments were performed under AM 1.5 solar simulator illumination (100 mW cm⁻²), in 0.1 Na₂SO₄ containing 10% methanol aqueous solution. A three-electrode configuration was used in the measurement, with the nanotubes as a working electrode (photoanode), Ag/AgCl as a reference electrode, and a platinum foil as a counter electrode. Photocurrent versus voltage curves were acquired by scanning the potential from 0.5 to 2 V with a scan rate of 1 mV.s⁻¹ using a Jaissle IMP 88 PC potentiostat.

Intensity modulated photocurrent spectroscopy (IMPS) measurements were carried out using a Zahner IM6 (Zahner Elektrik, Kronach, Germany) with a UV modulated light ($\lambda = 369$ nm).

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Keywords: TiCu Alloy • anodic TiCu nanotube • conductivity • photoelectrochemical methanol oxidation • Photoanode

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Figure 1. SEM images of a) Cu-doped TiO_2 nanotubes, b) conductive Cu-doped TiO_2 nanotubes, HRTEM images of c) Cu-doped TiO_2 nanotubes, d) conductive Cu-doped TiO_2 nanotubes, SAED patterns of e) Cu-doped TiO_2 nanotubes, f) conductive Cu-doped TiO_2 nanotubes, g) EDX map of O, Ti and Cu and h) GDOES depth profile of the Cu-doped TiO_2 nanotubes (for representation purpose Cu magnified 7 times).

Figure 2. EPR spectra recorded at 123 K of pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples, b) fitting analysis and experimental saturation data of the Ti^{3+} and Cu^{2+} in reduced TiCu nanotube, high resolution XPS spectra and peak fitting of the c) TiCu nanotube and d) reduced TiCu nanotube, e) XRD pattern of pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples.

Figure 3 a,b) EIS results (Bode plots) of pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples c) resistivity of pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples, d) incident photon to current conversion efficiency (IPCE) of pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples, e) comparison of the transport time constant for pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples as a function of the incident photon flux for monochromatic 369 illuminations, f) photocurrent spectra of the pristine TiO_2 and TiCu nanotubes and the Ar/H_2 treated samples under AM1.5 illumination, g) CV results of the conductive TiCu nanotubes in 0.1 M NaOH without methanol and h) CV results of the conductive TiCu nanotubes and TiO_2 nanotubes in 0.1 M NaOH with methanol.