

Supplementary Material

# Photocatalytic CO<sub>2</sub> Conversion Using Anodic TiO<sub>2</sub> Nanotube-Cu<sub>x</sub>O Composites

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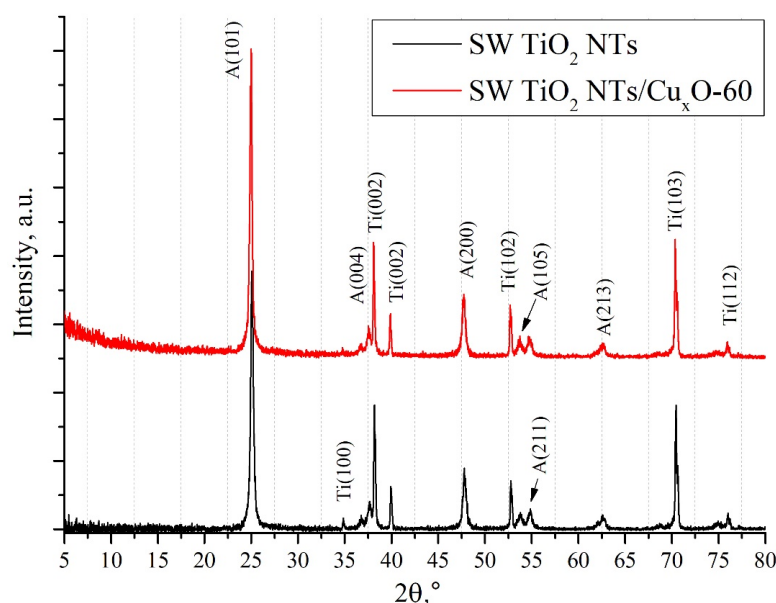
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The obtained SW TiO<sub>2</sub> NTs and SW TiO<sub>2</sub> NTs/Cu<sub>x</sub>O-60 samples were investigated by X-ray diffraction analysis (Figure 1). X-ray diffractometer Rigaku MiniFlex XRD was used. We show as example the SW-60S-TiO<sub>2</sub> sample because of the largest amount of copper oxide on its surface. It can be seen that the copper oxide phase was not recorded by XRD, because of the amount of the Cu<sub>x</sub>O is too small to be registered by this method.



**Figure S1.** XRD spectra of the SW TiO<sub>2</sub> NTs and SW TiO<sub>2</sub> NTs/Cu<sub>x</sub>O-60 samples.

The variations of the specific surface area of TiO<sub>2</sub> NTs arrays after deposition of copper oxide in this work were neglected due to following arguments.

Deposition of copper oxide nanoparticles takes place on the top of TiO<sub>2</sub> NTs arrays only. Therefore an amount of deposited nanoparticles is limited by an available surface area ( $S_{top}$ ) of TiO<sub>2</sub> NTs arrays without pores. According to SEM data: amount of pores per 1 cm<sup>2</sup> of geometrical area of the sample is about  $7 \cdot 10^9$  ( $n_p$ ), mean inner diameter of pore ( $D_p$ ) is equal to 78 nm ( $78 \cdot 10^{-7}$  cm).

$$S_{top} = 1 - \pi \left( \frac{D_p}{2} \right)^2 \cdot n_p \quad (1)$$

The  $S_a$  value is equal to about  $7 \cdot 10^{-5} \text{ m}^2/\text{cm}^2$ .

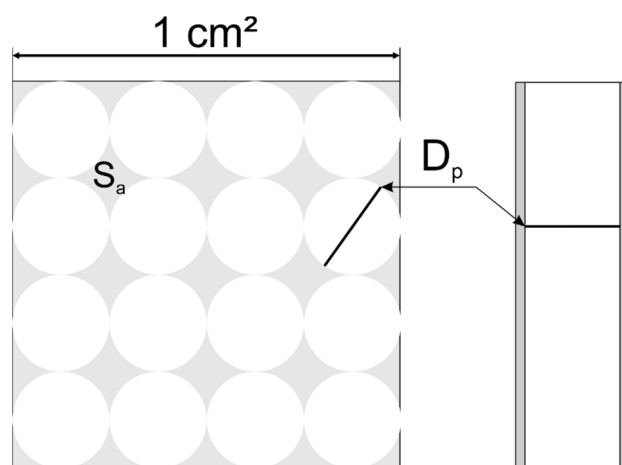
Possible penetration of copper oxide nanoparticles in 100 nm (H-cylinder height) depth in the pores leads to enhancement of available surface area ( $S_{pore}$ ) by  $3.1 \cdot 10^{-4} \text{ m}^2/\text{cm}^2$ .

$$S_{pore} = 2\pi \left( \frac{D_p}{2} \right) H \quad (2)$$

$$S_{total} = S_{top} + S_{pore} \quad (3)$$

At total available surface area  $3.8 \cdot 10^{-4} \text{ m}^2/\text{cm}^2$  maximum amount of  $1.2 \cdot 10^{12}$  semi-spherical nanoparticles of 20 nm size can be deposited. Effective surface area of such amount of nanoparticles can be estimated as  $0.76 \cdot 10^{-3} \text{ m}^2/\text{cm}^2$ . Specific surface area of pure  $\text{TiO}_2$  NTs arrays with 78 nm pore diameter and length  $\sim 4.4 \text{ mm}$  is  $7.7 \cdot 10^{-3} \text{ m}^2/\text{cm}^2$  according geometry model presented in supplementary material earlier [10.1088/1361-6528/ac317e].

Calculated  $S_{total}$  value is about 10% of specific surface area of pure  $\text{TiO}_2$  NTs arrays. The increase of specific surface area to 10% occurs only in the described ideal case, but in the real system this value will be lower. For example, nanoparticles do not cover all available surface of  $\text{TiO}_2$  and the place of the contact of  $\text{TiO}_2$  and  $\text{Cu}_x\text{O}$  is not available for reagents. In this case we expect less than 5 % enhancement of specific surface area. Therefore, we neglect variation of surface area because it is not determining factor for efficiency and selectivity of the catalysts. A simplified geometric scheme of the nanotube array is shown in the Figure 2 below.



**Figure S2.** Geometric scheme of the nanotube array.

Kinetics of acetaldehyde formation are presented below for each sample (Figure 3). As one can see the trend of kinetic remains unchanged after  $\text{CO}_2$  supply into reactor, i.e.,  $\text{CO}_2$  to acetaldehyde conversion does not take place. Output of other products can not be determined quantitatively. However the times of experimentally observed peaks coincide with calibration data. This allows to detect the output these products qualitatively.

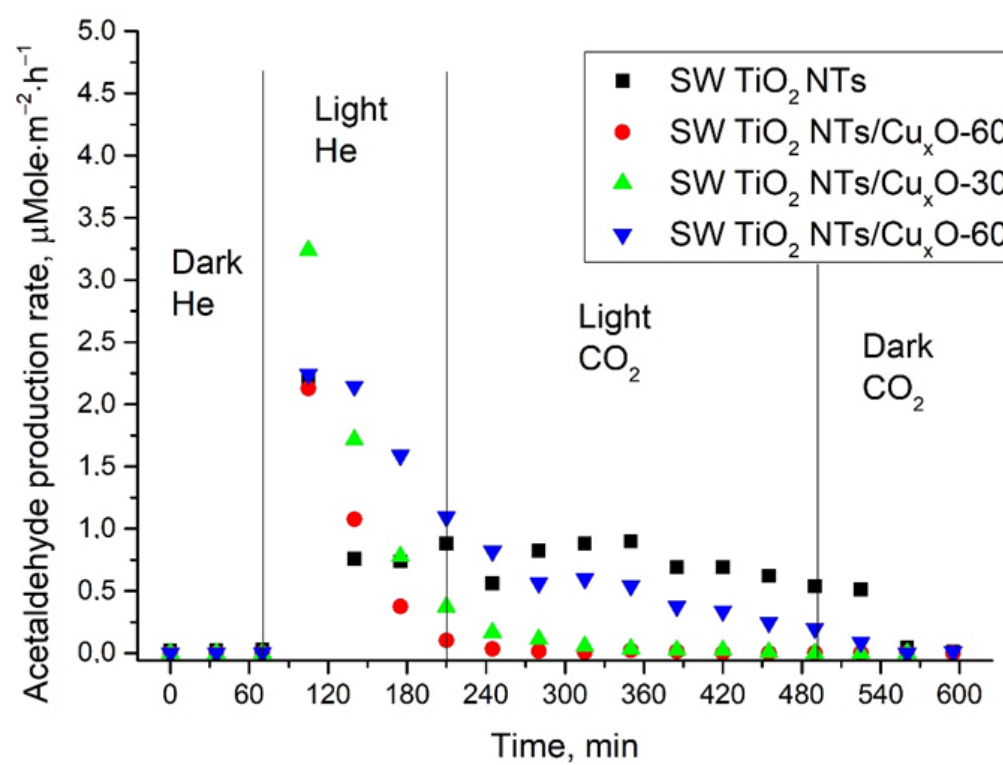


Figure S3. Kinetics of acetaldehyde formation.