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# Effect of $TiO_2$ Nanotube Structure on Photocatalytic Production of Methane

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Photocatalytic hydrogenation of $CO_2$ is a potential approach for creating useful solar fuels. $TiO_2$ based materials are effective photocatalysts although they work only under UV irradiation. Tubes provide potential advantages over powders owing to their higher surface areas, since heterogeneous reactions occur on the surface of the catalyst. Even though a great number of works [1] have been accomplished related to$TiO_2$ nanotubes, few studies have been performed on their use for photocatalytic reduction of $CO_2$. In the current work, we are comparing the structure and catalytic efficiency of the titania nantubes for the same reaction based on different annealing temperatures and phase compositions.

Aligned $TiO_2$ nanotubes were synthesized by anodization of polished and cleaned Ti foils in fluoride mediated ethylene glycol solvent, using a Pt foil as cathode. The as synthesized tubes were cleaned in distilled water and annealed in ambient atmosphere at different temperatures to produce tubes composed of different percentages of anatase and/or rutile. The tubes were characterized by XRD, SEM and TEM techniques. Photocatalytic hydrogenation of $CO_2$ with $H_2$ to produce methane was performed in photoreactor with UV lamp ($\lambda$= 254 nm). Product gas analysis was carried out with a Varian gas chromatography system. Here we present and compare 4 samples; amorphous tubes (TT-A), anatase tubes (TT-AN), tubes which have mixed phases (TT-ANR) and P-25, a commercially available reference photocatalyst.

An SEM image recorded in an FEI XL 30 of the as synthesized tubes is shown in Fig 1 and shows the tubes are well aligned unidirectional (about 120 nm in diameter and 20 μm in length). XRD results in Fig 2 of as synthesized and tubes annealed at 460 and 600 $^0$C are compared with that of P-25 and the quantification is summarized in TABLE 1. TT-A is an amorphous structure. TT-AN is anatase while TT-ANR is a mixture of rutile and anatase. Table 1 shows that methane production is highest from TT-AN and almost 600 times greater than P-25, with respect to surface area of both the catalysts. The production declines about a factor of 5 for TT-ANR, when tubes are 39% rutile. The TEM images of the TT-AN samples are shown in Fig 3a and Fig 3b. The lattice spacing is about 0.351 nm, which corresponds to the (101) plane of the anatase structure confirming that annealing resulted in crystallization of anatase in the tubes. The lattice fringes are almost continuous throughout the tubes, which show a good crystallinity as a result of the heat treatment. Wall thickness of the tube is about 12 nm. We have found that the wall thickness and tube diameter depend on the voltage variation during the synthesis process, and its effect on anatase to rutile conversion, which are not discussed here. In our future studies, we will study the effect of wall thickness on anatase to rutile conversion in more details. We will also correlate the structure and composition of the nanotubes with photocatalytic production of methane [2, 3].

References

[1] C.A. Grimes et al., *$TiO_2$ Nanotube Arrays: Synthesis, Properties, and Applications*, Springer,

2009
[2] J. Zhang et al, *Angew Chemie International Edition*, 47 (2008) 1766.
[3] The support from the National Science Foundation (NSF-CBET-0553445) and the use of TEM at the John M. Cowley Center for High Resolution Microscopy at Arizona State University are gratefully acknowledged.

TABLE 1. Sample nomenclature, annealing temperature and photocatalytic activity

| Sample | Annealing Temperature ($^{o}$ C) | Phase | Photocatalytic Production ($CH_4$) (μmol/m$^2$/hr) |
|---|---|---|---|
| TT-A | - | amorphous | - |
| TT-AN | 460 | Anatase | 0.009081398 |
| TT-ANR | 600 | 61% anatase, 39% rutile | 0.001903197 |
| P-25 | - | 75% anatase, 25% rutile | 1.55852E-05 |

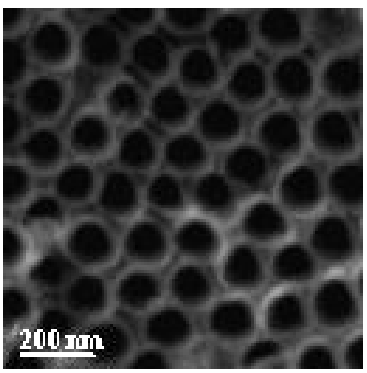


FIG. 1. SEM image of as prepared $TiO_2$ nanotubes

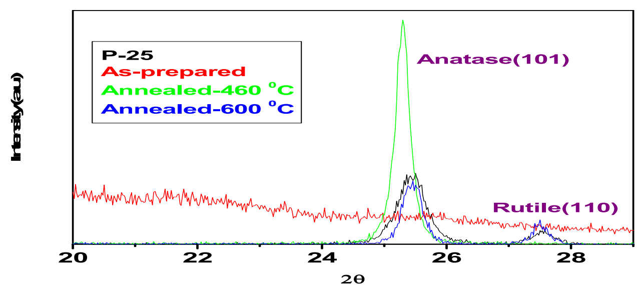


FIG. 2. XRD of as prepared sample, samples annealed at different temperatures and P-25.

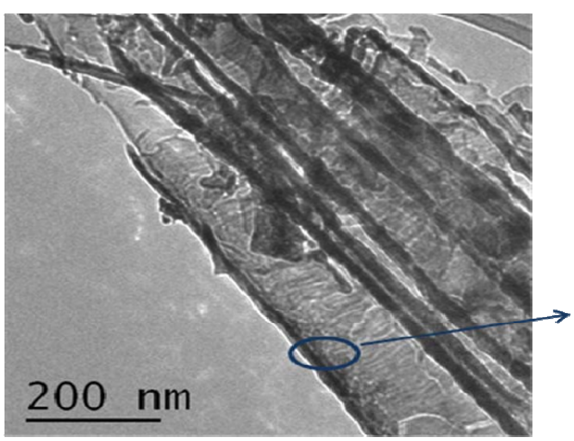


FIG. 3a. TEM image of tubes annealed at 460 $^{0}$C in air.

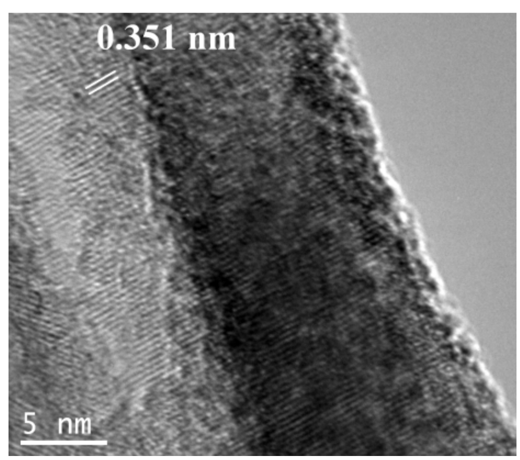


FIG. 3b. High resolution image of the same tube from 3a.

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