

## Supporting Information

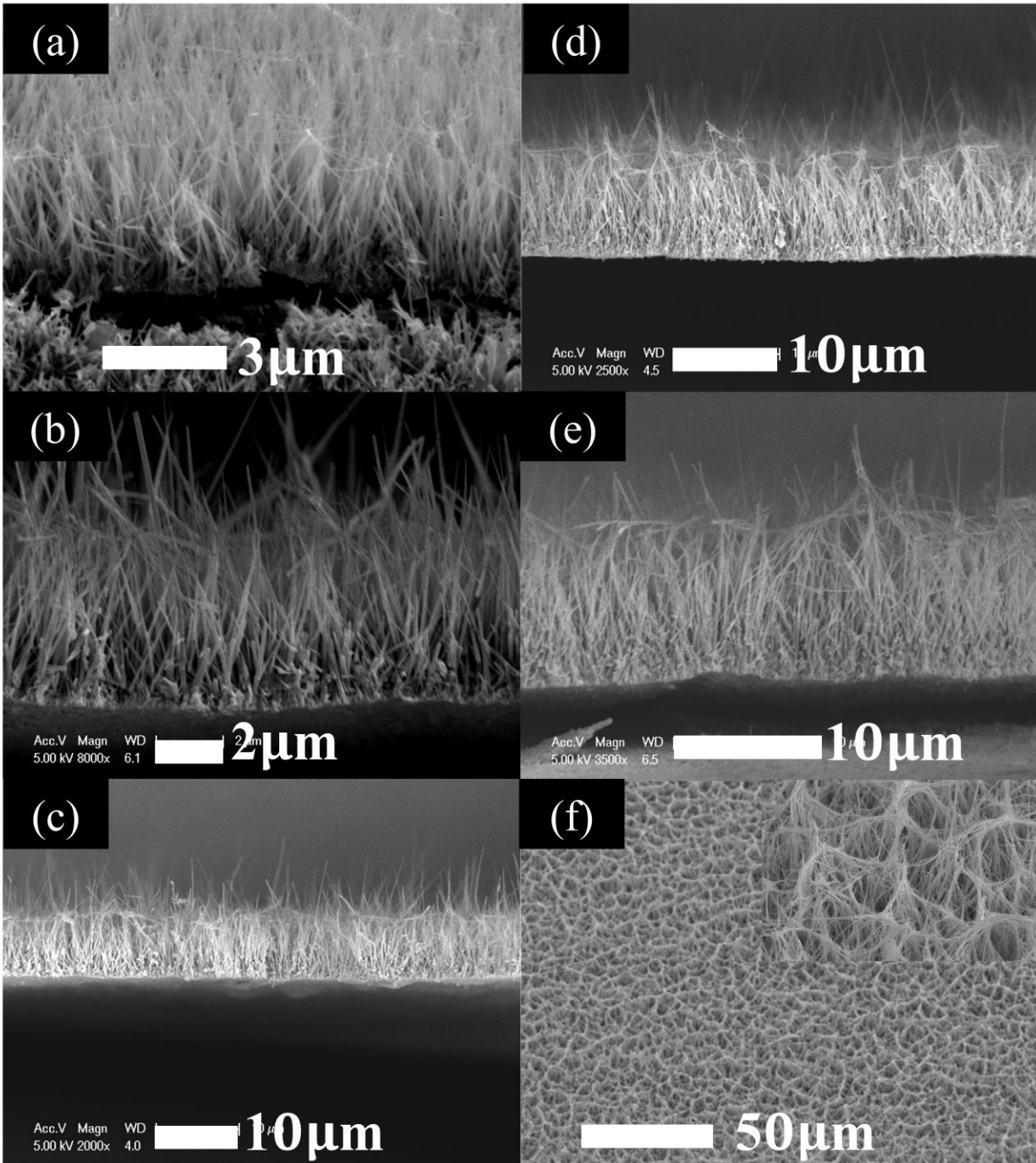
# A facile strategy to fabricate high-quality single crystalline brookite TiO<sub>2</sub> nanoarrays and their photoelectrochemical properties

*Mingi Choi, Kijung Yong\**

Surface Chemistry Laboratory of Electronic Materials (SCHEMA), Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 790-784, Korea

\*E-mail: [kyong@postech.ac.kr](mailto:kyong@postech.ac.kr). Tel: +82-279-2278. Fax: +82-279-8619

Web address: <http://schema.postech.ac.kr>

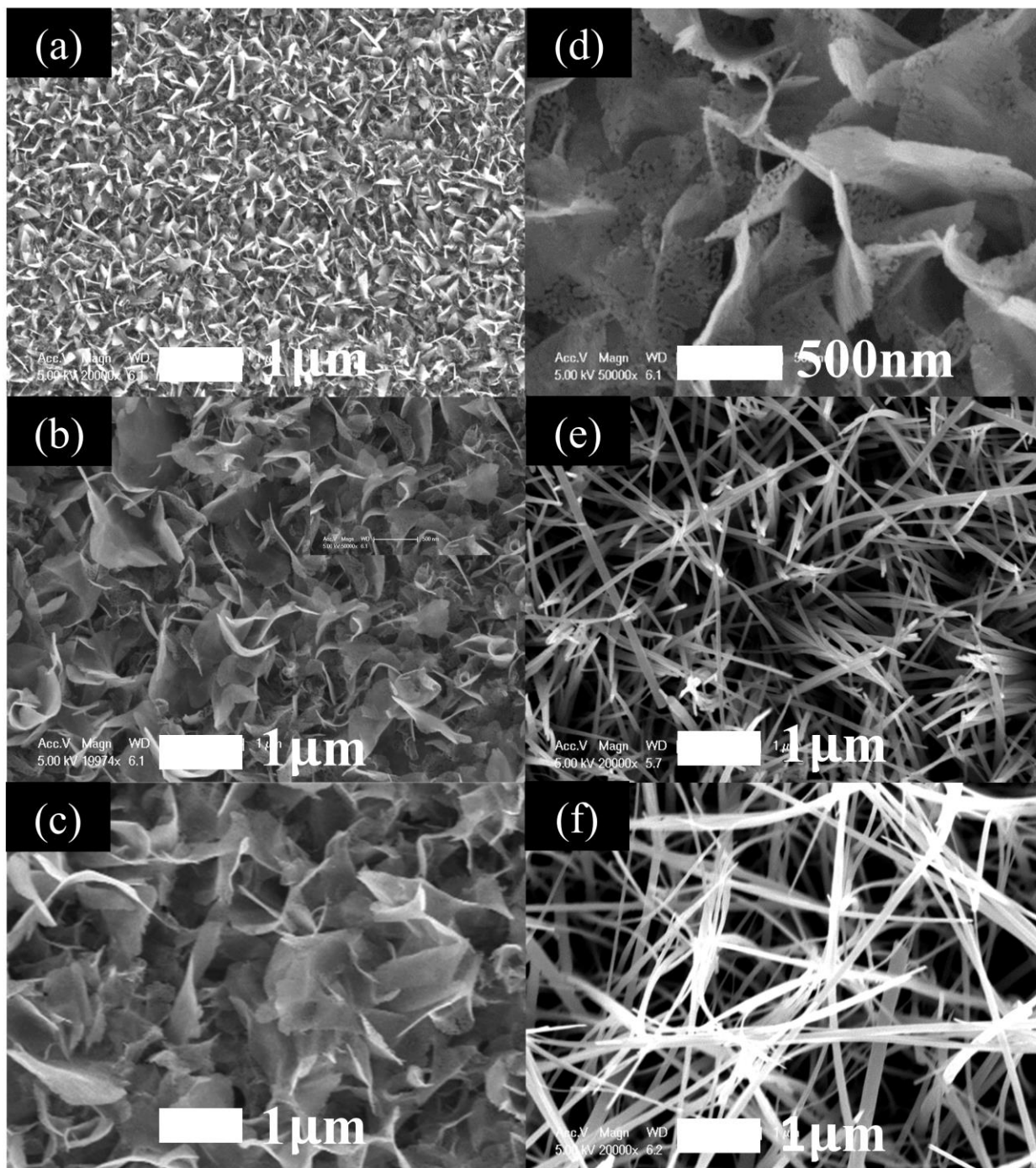


**Figure S1. SEM images of TiO<sub>2</sub> structures depending on the reaction time.** Cross-sectional view SEM images of TiO<sub>2</sub> wire structures with 0.5 M NaOH at 220 °C after (a) 4h, (b) 8h, (c) 12h, (d) 16h, and (e) 24h reaction. (f) Top view SEM image of TiO<sub>2</sub> wire structure after 24h reaction.

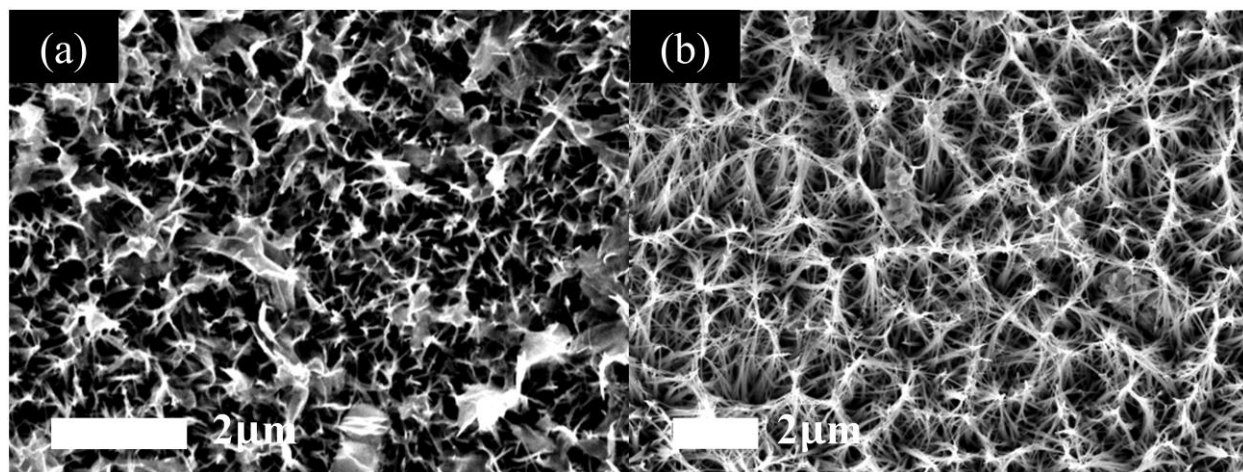
Table S1. The lengths of nanowire structures after hydrothermal reaction with 0.5M NaOH at 220 °C.

Reaction Time (hours)	4	8	12	16	24
Length ( $\mu\text{m}$ )	2.8~3.2	5~5.4	7~7.5	8.5~9	10~11

To find out the effect of the reaction temperature, we fabricated TiO<sub>2</sub> with various temperatures from 130 °C to 260 °C with constant 0.5 M NaOH concentration and 6h reaction time (Figure S2). The sheet structures were fabricated at 130~200 °C samples, showing increased sizes with increasing temperatures. On the other hand, the wire structures were obtained at 220 °C and 260 °C due to fast reaction rate at high temperatures. The sheet structures were fabricated at low temperatures because of the slow rate of reaction. If we change the concentration of NaOH which is another reaction parameter determining the reaction rate, the wire structures could be synthesized at low temperature. As can be seen from the Figure S3, the wire structures were fabricated at low temperature (200 °C) with high concentration of NaOH (1 M). In spite of low temperature, the fast rate reaction occurred due to high concentration of NaOH.



**Figure S2. SEM images of TiO<sub>2</sub> structures depending on the reaction temperatures. Top view SEM images of TiO<sub>2</sub> structure with 0.5M NaOH after 6h reaction at (a) 130 °C, (b) 180 °C, (c) 200 °C, (e) 220 °C and, (f) 260 °C. (d) High resolution SEM image of sheet structures which were composed of agglomerated particles (reaction temperature of 200 °C).**



**Figure S3. SEM images of wire structures.** Top view SEM images of  $\text{TiO}_2$  wire structures with 1 M NaOH at 200 °C after (a) 3 h, (b) 6 h reaction.

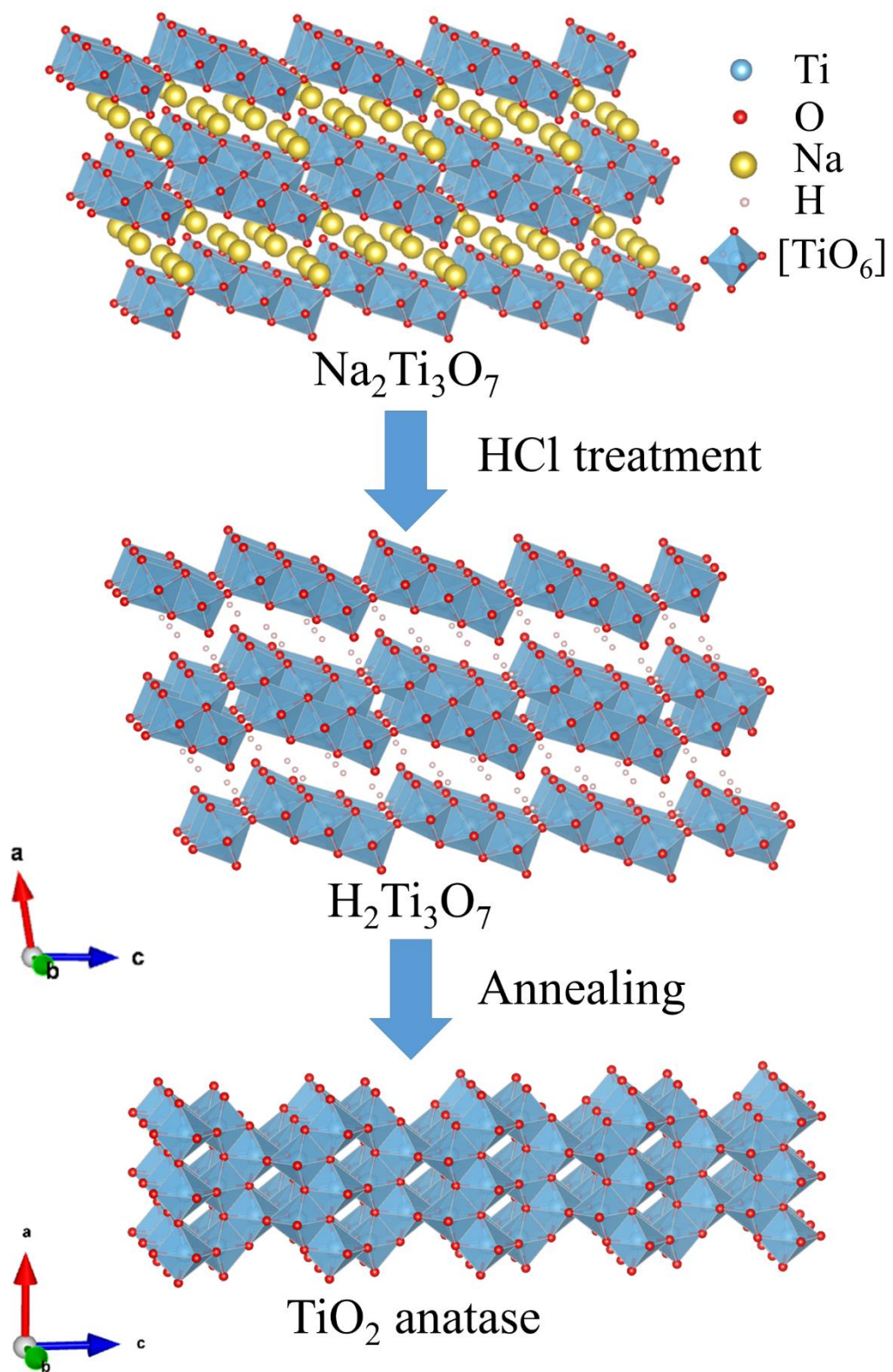


Figure S4. Scheme of sodium titanate converted into anatase.

Bandgap energy of the semiconductor nanostructure could be estimated by using UV-visible diffuse reflectance spectrum (DRS) with its representation as a Kubelka–Munk function  $F(RD)$ , where the RD is the diffuse reflection coefficient.

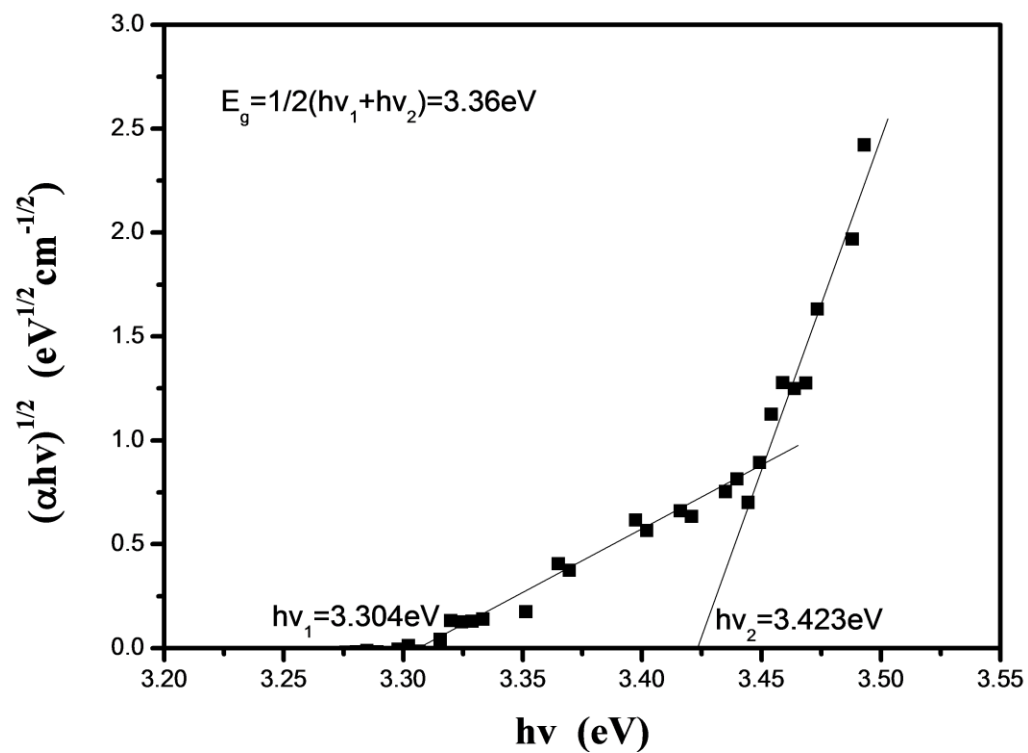
For an indirect semiconductor such as TiO<sub>2</sub>, the expected variation of  $\alpha$  with the photon energy,  $h\nu$ , can be expressed as follows:

$$\alpha(h\nu) = \frac{B}{h\nu} (h\nu - E_g)^2 \quad (1)$$

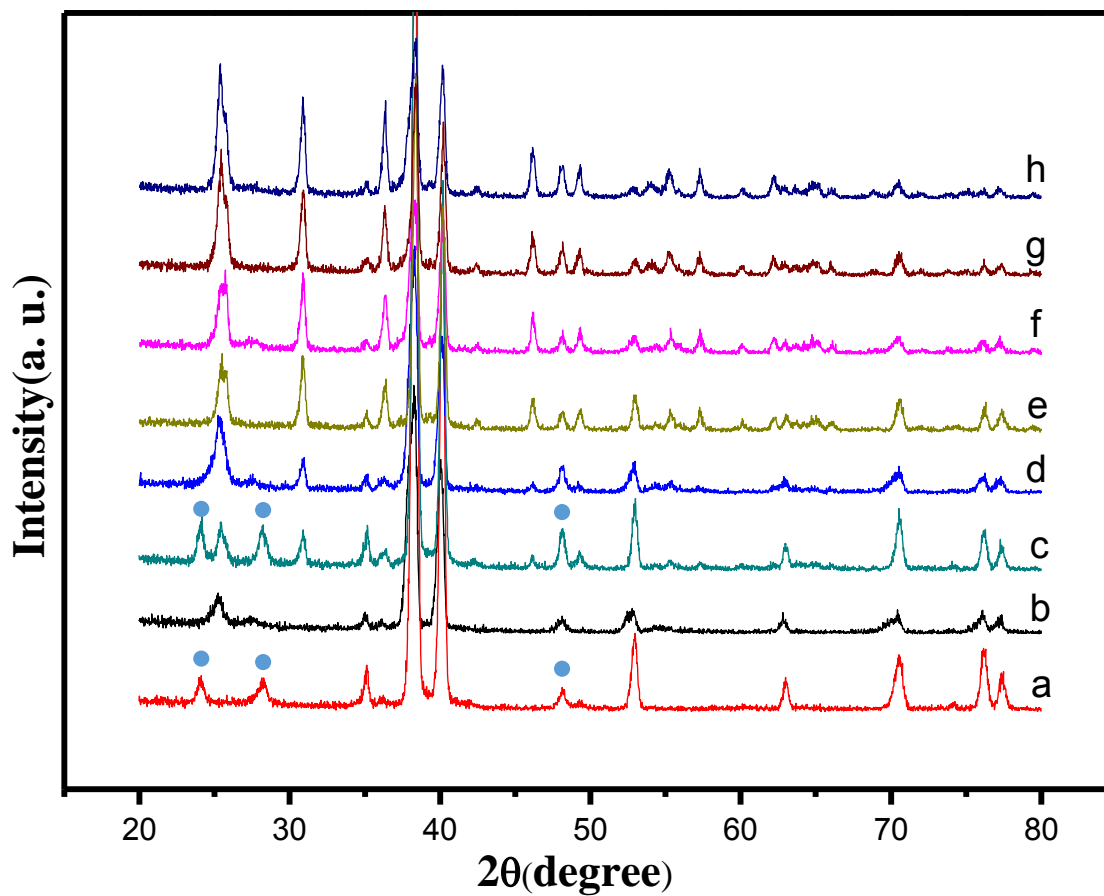
where B is the absorption constant for the indirect transition, h is Planck's constant,  $\nu$  is the light frequency, and  $E_g$  is the optical bandgap energy.<sup>29</sup> The plot of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  from experimental Kubelka–Munk spectrum and its fitting with relation (1) is presented in Figure S5. The fitting yields two tangent lines and two intercepts on the energy axis. Thus, the bandgap energy can be calculated as follow:<sup>1,2</sup>

$$E_g = \frac{1}{2}(h\nu_1 + h\nu_2) \quad (2)$$





**Figure S5.** The plot of  $(\alpha h\nu)^{1/2}$  versus the incident photon energy ( $h\nu$ ) from experimental absorption spectrum of brookite sample, obtained from the UV-visible DRS using a Kubelka–Munk function. The fitting yields two tangent lines and two intercepts on the energy axis.



**Figure S6. XRD pattern of brookite depend on reaction time.** TiO<sub>2</sub> nanostructures after hydrothermal reaction at 220 °C with 0.1 M NaOH for (a) 3 h, (c) 6 h, (e) 12 h, and (g) 24 h. The samples with HCl and heat treatment after the hydrothermal reactions for (b) 3 h, (d) 6 h, (f) 12 h, and (h) 24 h.

## Refereces

- (1) Pankove, J. I. *Optical processes in semiconductors*; Courier Dover Publications, 2012.
- (2) Tsvetkov, N. A.; Larina, L. L.; Shevaleevskiy, O.; Al- Ammar, E. A.; Ahn, B. T. *Prog. Photovoltaics Res. Appl.* **2012**, *20*, 904–911.