Supplementary Information

Effect of Doping Level of Colored TiO_2 Nanotube Arrays Fabricated by Electrochemical Self-doping on Electrochemical Properties

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~~XRD pattern of the blue Ti~~O_2 nanotube array fabricated with various electrochemical

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self-doping times

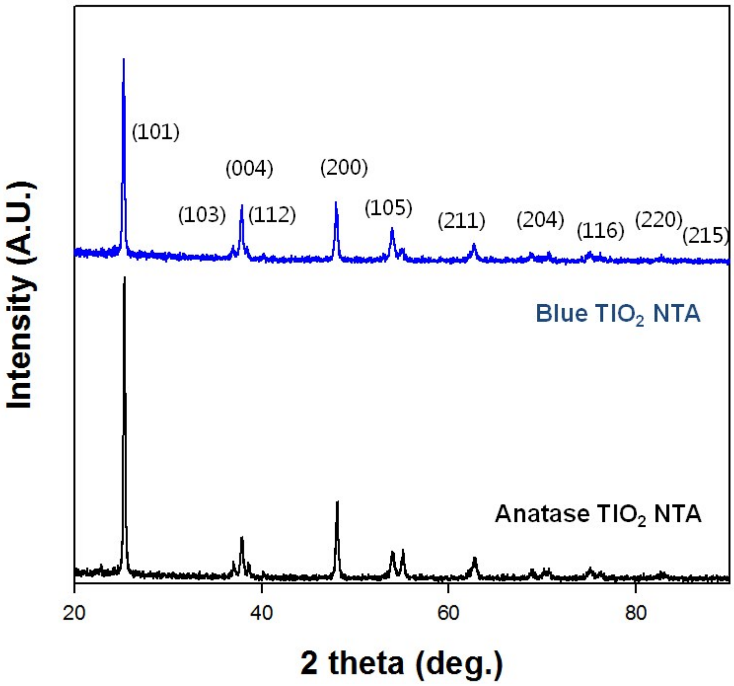


Fig. S1. XRD patterns of the blue TiO_2 NTA and anatase TiO_2 NTA: The electrochemical self-doping was conducted with a constant current ($i = 17$ mA/cm^2) for 360 s in 0.1 M of KH_2PO_4 with NaOH (pH = 7.2)

Fig. S1 shows the XRD patterns of the blue TiO_2 NTA and anatase TiO_2 NTA. As shown in Fig. S1, the peaks in the XRD patterns for the blue TiO_2 NTA were well matched with that of the anatase TiO_2 NTA. It indicates that the electrochemical self-doping did not significantly affect the structural property of TiO_2 NTA. However, the (101) peak intensity in the XRD pattern of the blue TiO_2 NTA was slightly decreased compared with that of the anatase TiO_2 NTA. It can be explained in that the electrochemical self-doping caused a decrease in the grain size. Note that the grain size of the blue TiO_2 NTA, which was estimated by the (101) peak using the Scherrer equation[1], was approximately 32 nm. The size was slightly smaller than that of anatase TiO_2 NTA (~33 nm).

Mott-Schottky Plot of the blue and black TiO_2 nanotube array

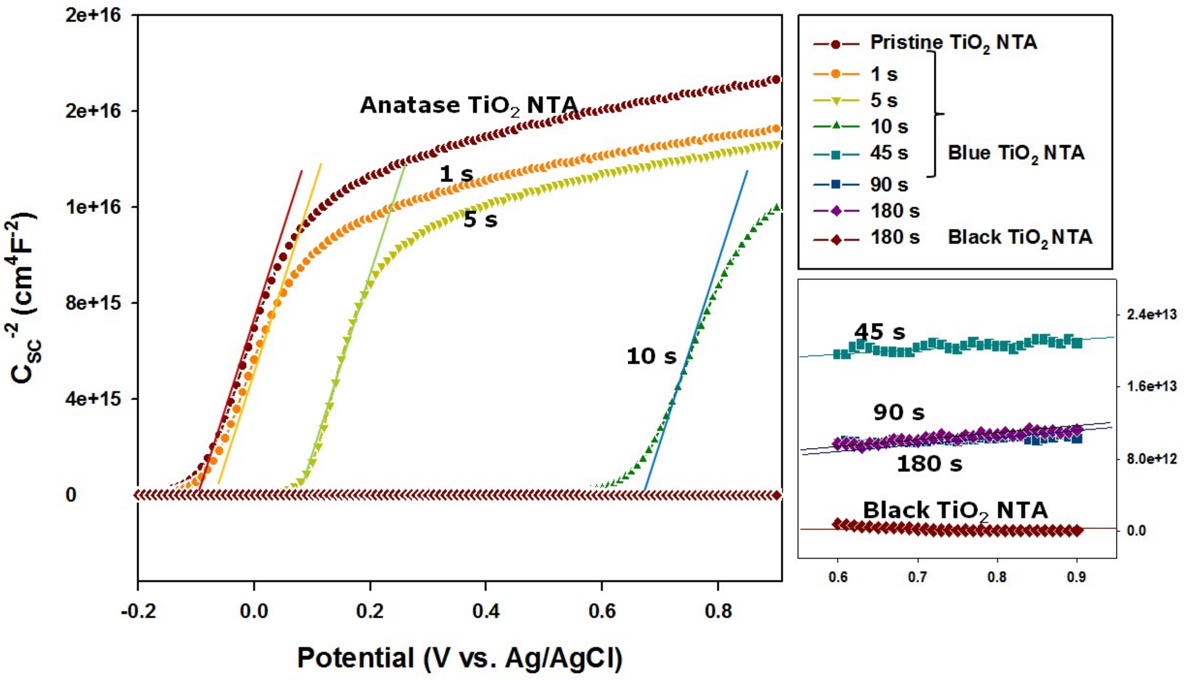


Fig. S2. Mott-Schottky plot of the blue TiO_2 nanotube array (NTA) fabricated with various electrochemical self-doping times (1,5, 10, 45, 90, and 180 s) compared with that of the anatase and black TiO_2 NTA ($[KH_2PO_4]_0$ = 0.1 M with NaOH (pH = 7.2), AC potential = 10 mV, frequency = 100 Hz): The electrochemical self-doping was done with a constant current (i = 1.7 mA/cm^2) in 0.1 M of KH_2PO_4 with NaOH (pH = 7.2). The inset shows the enlarged Mott-Schottky plot in a potential range of 0.6 – 0.9 V.

Fig. S2 presents the Mott-Schottky plot of the blue TiO_2 NTAs fabricated with various electrochemical self-doping times compared with the anatase and black TiO_2 NTA examining the effect of electrochemical self-doping on the doping level of TiO_2 NTA. The doping level of the blue TiO_2 NTAs was controlled by the electrochemical self-doping time. And the surface area (A) of TiO_2 NTAs was calculated by following equations[2]

$$A = A_p\left(\frac{4\pi L(D+W)}{\sqrt{3}(D+2W)^2}+1\right) \tag{S.1}$$

where *D, W* and *Ap* are the inner diameter, wall thickness and the planar apparent area of TiO_2 NTAs, respectively. In this study, the *D and W* were approximately 80 and 10 nm; the *Ap* was 2.54 cm^2 (d =1.8 cm).

As can be seen in Fig. S2, the electrochemical self-doping led to a change in the flat band potential and doping level which can be estimated by the x-intercept and inverse slope of the linear region in the Mott-Shottky plot[3], respectively.

As the electrochemical self-doping time was increased from 1 to 10 s, the flat band potential of the blue TiO_2 NTAs was positively shifted without a detectable increase in the doping level compared with that of the anatase TiO_2 NTA. Additionally, for an electrochemical self-doping time over 45 s (inset of Fig. S2), it was observed that the doping level of the blue TiO_2 NTAs was significantly increased and eventually converged to a certain doping level. A further increase in the doping level of the blue TiO_2 NTA was not observed (data not shown). However, the converged doping level of the blue TiO_2 NTA was slightly smaller than that of the black TiO_2 NTA (inset of Fig. S2). Note that the slope in the Mott-Schottky of the black TiO_2 NTA was nearly flat in spite of the slight instability. These results imply that the black TiO_2 NTA is unable to be prepared with the fabrication method for the blue TiO_2 NTA, and electrochemical self-doping is a critical factor for the increased doping level of TiO_2 NTA.

Cyclic voltammograms of the blue and black TiO_2 nanotube array

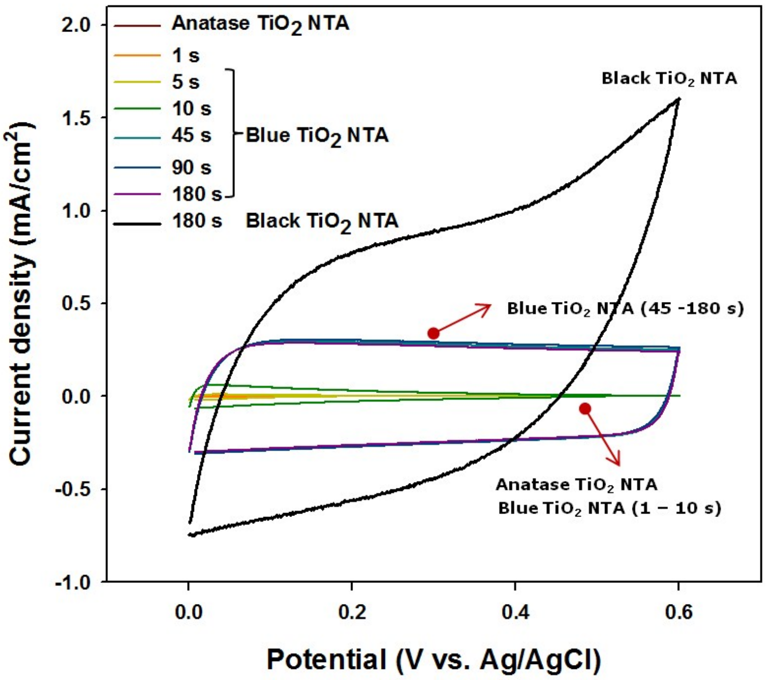


Fig. S3. Cyclic voltammograms of the blue TiO_2 nanotube array (NTA) fabricated with various electrochemical self-doping times (1, 5, 10, 45, 90 and 180 s) compared with that of the anatase and black TiO_2 NTA (scan rate = 50 mV/s, $[KH_2PO_4]_0$ = 0.1 M with NaOH (pH = 7.2))

Fig. S3 shows cyclic voltammograms (CVs) of the blue TiO_2 NTAs fabricated with various electrochemical self-doping times. As shown in Fig. S3, the blue TiO_2 NTAs exhibited a distinct shape for the CV curves according to the different electrochemical self-doping times. The shape of the CV curves for the blue TiO_2 NTAs, which were fabricated with 45, 90 and 180 s of electrochemical self-doping time, was nearly rectangular implying the electrical double layer capacitive property, whereas those of the blue TiO_2 NTAs fabricated with short electrochemical self-doping times (1, 5 and 10 s) did not, and they were similar with the CV of the anatase TiO_2 NTA. In addition, the black TiO_2 NTA exhibited a higher plateau current than that of the blue TiO_2 NTAs indicating the larger areal capacitance of the black TiO_2 NTA. The tendency of the capacitive properties of TiO_2 NTAs is well consistent with that of the doping level in Fig. S2. It indicates that the capacitive properties of the blue and black TiO_2 NTAs was significantly correlated with the doping level.

Nyqusit plot of the blue TiO_2 nanotube array

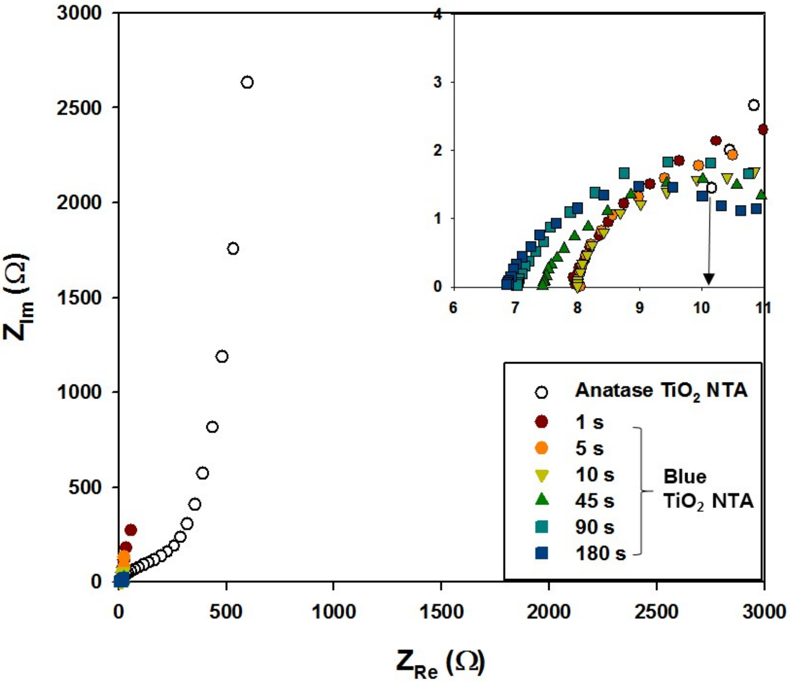
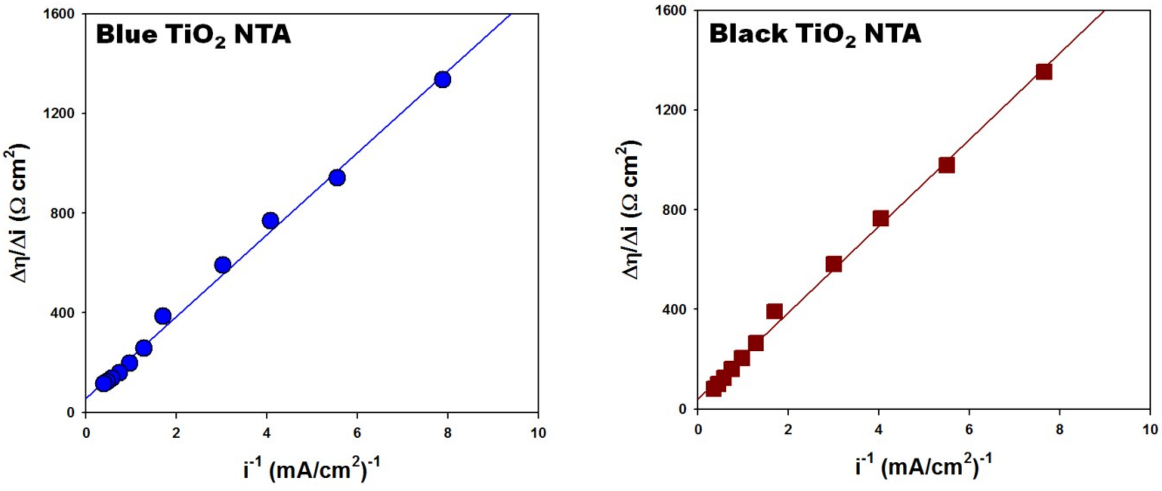


Fig. S4. Nyquist plot of the blue TiO_2 nanotube array (NTA) fabricated with various electrochemical self-doping times (1, 5, 10, 45, 90 and 180 s) compared with that of anatase TiO_2 NTA ($[KH_2PO_4]_0$ = 0.1 M with NaOH (pH = 7.2), AC potential = 10 mV, DC potential = open circuit potential): The electrochemical self-doping was conducted with a constant current (i = 1.7 mA/cm^2) in 0.1 M of KH_2PO_4 with NaOH (pH = 7.2). The inset shows the enlarged Mott-Schottky plot in the potential range of 0.6 – 0.9 V, and the arrow indicates the initial point of the anatase TiO_2 NTA in the Nyquist plot.

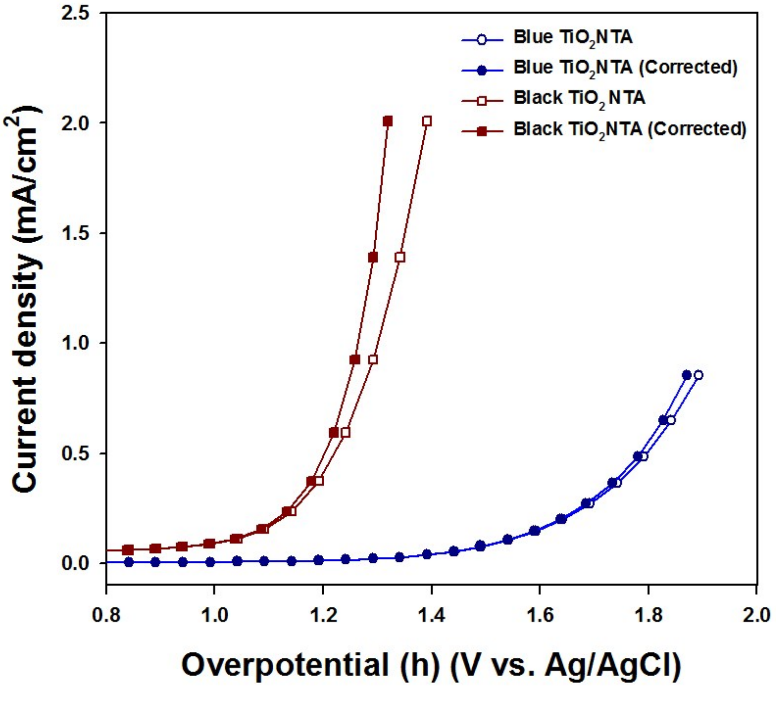
Fig. S4 shows a Nyquist plot of the blue TiO_2 NTA fabricated with various electrochemical self-doping times compared with that of the anatase TiO_2 NTA. As shown in Fig. S4, the blue TiO_2 NTA exhibited a vertical line in the low frequency region in the Nyquist plot compared to the anatase TiO_2 NTA. It indicates that the electrochemical self-doping triggers the good capacitive property[4] of the blue TiO_2 NTAs despite the short self-doping time. Furthermore, the intrinsic resistance of the blue TiO_2 NTAs (the inset of Fig. S4), which can be evaluated by the initial point of the Nyquist plot, was gradually reduced from 10 Ω (anatase TiO_2 NTA) to 7 Ω (blue TiO_2 NTA fabricated with 180 s of electrochemical self-doping) with the increase in the electrochemical self-doping time.

From these results in Figs. S2 – S4, it can be concluded that the doping level of TiO_2 NTA has a fundamental role in the enhancement of metallic characteristic of TiO_2 NTA leading to the good electrochemical properties of electrochemically doped TiO_2 NTAs.

The correction of uncompensated resistance in the oxygen evolution reaction (OER) for Tafel analysis



(a)



(b)

Fig. S5. (a) Area-specific uncompensated resistance (Ω cm^2) as a function of the inverse current density for the oxygen evolution reaction (OER) on the blue and black TiO_2 NTAs and (b) the current-overpotential curves with and without correcting for the uncompensated resistance measured by the staircase linear sweep voltammetry of the blue and black TiO_2 NTAs in 1 M of KH_2PO_4 with NaOH (pH = 7.2)

Fig. S5a shows the area-specific uncompensated resistance (Ω cm^2) as a function of the inverse current density for the oxygen evolution reaction (OER) on the blue and black TiO_2 NTAs. The uncompensated resistance in the OER was evaluated by Eqs. (3) and (4) in the manuscript [5,6]. In this study, the areal specific uncompensated resistances for the OER, which were obtained from the y-intercept in Fig. S5a according to Eq. (3), were 23.9 and 13.8 Ω cm^2 for the blue and black TiO_2 NTAs, respectively. With the correction of the uncompensated resistance (Eq. (4)), the anodic polarized current-potential curves were shifted to the negative range of the potential (Fig. S5b).

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