<u>Supplemental Information</u>

Crystal structures of the films determined by the XRD analysis are shown in Fig. S1(a). The sample prepared at atmospheric pressure and 40 °C showed characteristic peaks of the Ti substrate only. As the temperature increased to 70 °C, a diffraction peak corresponded to (101) crystal orientation of anatase TiO_2 (JCPDS #89-4921) was observed, which confirmed the presence of crystalline TiO_2. Also, the samples prepared at elevated pressure all showed the presence of anatase TiO_2. In order to clarify the hydrobaric effect, average grain sizes of the TiO_2 prepared at 70 °C were estimated using full width at half maximum of the (101) peak and the Scherrer equation. As shown in Fig. S2, the grain coarsening effect was observed with an increase in the applied pressure. The results suggested the hydrobaric effect had a positive effect on crystallinity of the TiO_2 prepared by cathodic deposition in an aqueous solution.

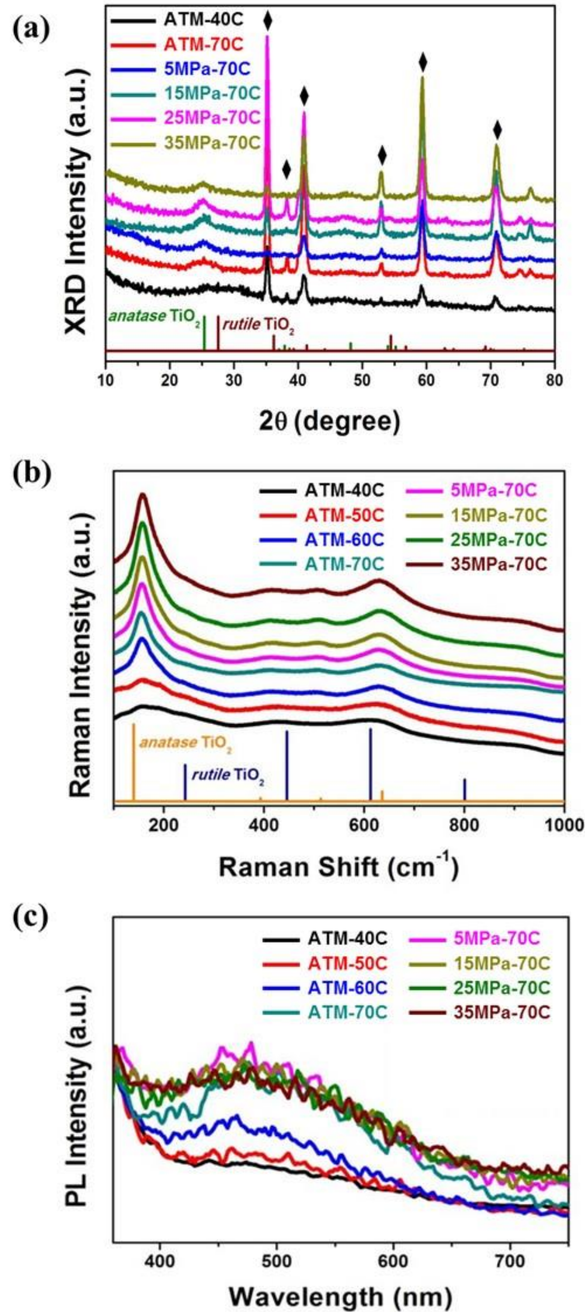

Figure S1 (a) XRD patterns (b) Raman spectra, and (c) PL spectra of the TiO_2 films deposited under different conditions. The standard patterns of anatase (JCPDS #89-4921) and rutile TiO2 (JCPDS #89-4920) were also included in the XRD patterns for comparison. The rhombus marks (♦) represented the diffractions from the Ti substrate.

Raman scattering spectra was used to further analyze crystal structure of the TiO_2

films. There are several Raman vibration modes for bulk anatase TiO_2, including Eg,ν6, B1g, A1g or B1g, and Eg,ν1 modes located at 140, 393, 513 and 613 cm^{-1}, respectively, and the vibration mode at 141 cm-1 is assigned to the O-Ti-O bending vibration [S1]. As shown in Fig. S1(b), all of the TiO_2 films exhibited typical anatase TiO_2 vibration modes except for the ATM-40C and the ATM-50C. Raman signals related to the rutile phase were not observed. All of the TiO_2 films showed a certain blueshift in the vibration frequency when comparing to bulk anatase TiO_2, which is suggested to be due to the nanoscale crystal size of the TiO_2 thin films [S2]. Besides, Raman peak intensity ratio of the samples corresponded well to the reference anatase TiO_2.

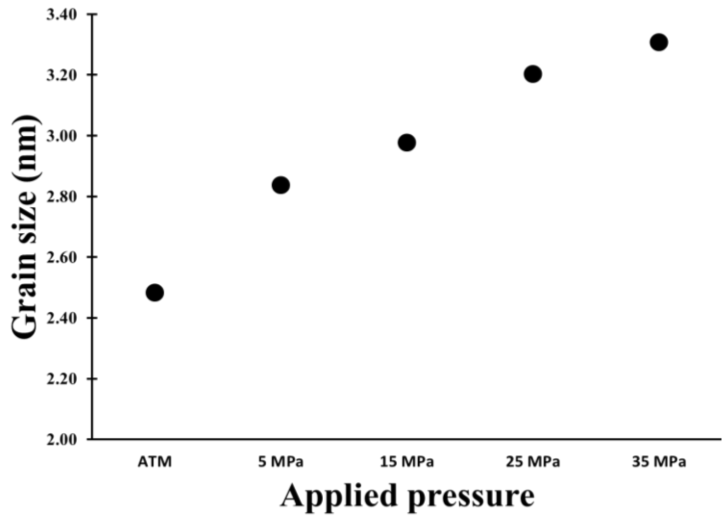

Figure S2 Estimated average grain size of the TiO_2 deposited at 70 ˚C.

PL spectra of the as-synthesized anatase TiO_2 films excited by a He-Cd laser with a wavelength of 325 nm are presented in Fig. S1(c). Broad emission peaks were recorded in a range from about 400 to 550 nm, which are generally regarded as overlap of the excitonic emission and the oxygen vacancy related emission of anatase TiO_2 [S3]. This broad emission peak became pronounced while increasing the reaction temperature from 40 to 70 °C, and then remained at almost the same emission intensity with the introduction of high pressure from 5 to 35 MPa.

Reference

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