**Supporting Information**

**The synergetic effect of cobalt content on enhancing the photoelectrochemical hydrogen production performance of in-*situ*-doped TiO2 photocatalysts**

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**Abstract**

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**1. Experimental**

**1.1. Materials**

Cobalt nitrate hexahydrate (Co (NO3)2.6H2O), titanium n-propoxide (98%), hydrofluoric acid (HF 40%), potassium hydroxide (KOH), and formamide (FA: H2N-CHO) were obtained from Sigma-Aldrich. Also, 2.2 mm thick Fluorine-doped Tin Oxide (FTO) glass (sheet resistance = 7 Ω/cm2) was obtained from Solaronix. All the other chemicals were of pure grade and employed as obtained without any extra purifications, and the distilled water was employed for the preparation of the aqueous solutions.

**1.2. Preparation of TiO2-XCo nanoparticles**

The suggested TiO2-XCo nanoparticles (NPs) were prepared using a simple sequence of sol-gel method and topotactic transformations [11]. Initially, 3 mL of HF were dropwise added to 4.84 mL of titanium n-propoxide with continuous stirring at 0 °C using an ice-bath. Then, x g of cobalt nitrate was dissolved in 5.2 mL of FA/DW aqueous solution (86%, v/v), then, these solutions were dropwise added to the former solution and magnetically stirred for 2 h. Finally, the samples were subjected to drying in air at 100 °C and calcination at 400 °C for 4 h; these samples were denoted as “*TiO2-XCo*”, where X= 0.125, 0.25, 0.325, 0.625 g of cobalt nitrate. The cobalt-free TiO2 nanoparticles were prepared according to the same method by addition of 5.2 ml of the mixture of FA/DW without the addition of cobalt nitrate, this sample was denoted as “*Pure TiO2*”.

**1.3. Physicochemical characterizations**

The crystalline nature of the as-fabricated samples was examined by powder X-ray diffraction (PXRD) patterns which measured by PANalytical X’Pert PRO X-ray diffractometer with Cu Kα radiation, where λ = 0.15418 nm, the 2θ range was from 5˚ to 80˚, the step size was 0.04˚, and the scan-step time was 0.5 s. The Raman spectra were detected using a Raman microscope (ProRaman-L Analyzer), where the wavelength of the employed excitation laser beam was 532 nm. Besides, the Fourier transform infrared (FTIR) spectra were measured on Thermo-Scientific Nicolet 380 in the range from 400 to 4000 cm-1. In addition to this, the micro-morphologies of the as-fabricated samples were explored by Zeiss SEM Ultra 60 field-emission scanning electron microscope (FESEM) operated with an accelerating voltage of 5 kV. Also, the nano-morphologies of the as-fabricated samples were explored by JOEL JEM-2100 high-resolution transmission electron microscope (HR-TEM) operated with an accelerating voltage of 200 kV. Additionally, the optical characteristics of the powders were explored by measurement of the UV–Vis absorbance spectra by Shimadzu UV-2600i UV–Vis-NIR spectrophotometer. Finally, the photoluminescence spectra (PL) of the fabricated samples were measured by a ThermoScientfic LUMINA fluorescence spectrometer.

**1.4. PEC characterizations**

The PEC performance of the fabricated samples was explored through three-electrode configurations in a typical PEC cell, where the as-synthesized TiO2-XCo/FTO was used as the working electrode, Ag/AgCl electrode utilized as the reference electrode, and a sheet of platinum was employed as the counter electrode; all the electrodes are immersed in KOH (1 M). The photocurrents were recorded using Bio-Logic SP 200 potentiostat, where the scan rate was set to be 0.05 V/s and the applied bias range was -1:1 V vs. Ag/AgCl supplied to the anode. Typically, 300 W Ozone-free Xenon lamp settled with AM 1.5G filter was used as a sunlight simulator; light intensity =100 mW/cm2. Also, the electrochemical impedance spectra (EIS) were recorded.