

Electronic Supplementary Information (ESI)

One-pot photoassisted synthesis, *in situ* photocatalytic testing for hydrogen generation and the mechanism of binary nitrogen and copper promoted titanium dioxide

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Experimental

Synthesis of N-TiO₂ precursor. 0.75 ml of 0.33 M solution of ammonium nitrate in DI water was added dropwise to solution of 2.870 g Ti isopropoxide and 0.300 g ethylenediamine in 25 ml absolute ethanol under intensive stirring at 75 °C, until formation of a gel. Without adding ammonium nitrate, the gel did not form. The resultant gel was dried in vacuum at room temperature until constant weight. Dried gel was further calcined in tubular furnace (ThermCraft model L-17313) in the flow of air (1 standard cubic foot per hour, scfh) which had passed through a 20 % solution of ammonia in water, in order to deliver oxygen and ammonia vapours to the sample during calcination. The temperature ramp during the calcination was achieved using the Proportional Integral Derivative (PID) temperature controller (SYL-2342P, Auber Instruments) connected to the calcination furnace. The temperature ramp has been as follows: the temperature was linearly increased from 25 °C to 450 °C for 3 h., then it was held constant at 450 °C for 3 h., linearly increased to 500 °C for 3 h., and held at 500 °C for 3 h. Finally, the

sample was allowed to spontaneously cool to room temperature in the flow of the gas as described above.

Testing an in-line sensor in periodic analysis of photocatalytically generated hydrogen.

Photocatalytic vessel made of Pyrex with an outgassed suspension has been purged with the UHP argon (99.999 %) and closed. A 450 W medium pressure mercury lamp from Ace Glass was used as a light source. Photocatalytic vessel and a mercury lamp were immersed into a water circulation thermostat from Neslab Inc. filled with a mixture of water and ethylene glycol and maintained at 30 °C. The mercury light source was turned ON for the given period of time to illuminate photocatalytic suspension in the vessel filled with argon. After that, the vessel was shielded from illumination, and purging and collection of hydrogen using the UHP argon as carrier gas was conducted. We have used mass flow controllers (MFCs) from Omega Engineering: model FMA5506-AR for argon (0-50 sccm) and model FMA5502-O2CLEAN for oxygen (0-10 sccm). Specifically, the photocatalytic vessel after illumination was purged with the UHP argon at a constant flow rate of 40 sccm, this stream was in-line mixed with the stream of the UHP oxygen at 10 sccm flow rate, and the resultant gas mixture was delivered to the in-line sensor for quantitative determination of hydrogen. The concentration of evolving hydrogen was measured with an inline electrochemical hydrogen sensor (model 4101-07, from Sierra Monitor Inc.) that provides readings in part per million by volume (ppmv). The analog signal from hydrogen sensor was acquired using the LabView program written in-house. This sensor has been calibrated against commercially obtained mixtures of hydrogen in the UHP argon at 40 sccm flow rate that were in-line mixed with the stream of the UHP oxygen at 10 sccm. Prior to the photocatalytic tests, the suspension of P25 TiO₂ in DI water was outgassed to remove dissolved oxygen, and illuminated for 20 min. starting from a “zero time”, without collecting hydrogen. It has been shown in the reference experiments that when this initial “preparation step” was avoided, the lower reaction rates were obtained. After the “preparation step”, repeated accumulations and collections of the photocatalytically generated hydrogen have been started. The time of each illumination with the simultaneous hydrogen accumulation was 20 min., and three accumulations with the subsequent collections and analysis were made. Each subsequent collection of the photocatalytically produced hydrogen was started by removing optical shield

protecting photocatalytic vessel from the light source, *after* the signal of the sensor obtained in the previous collection of hydrogen had returned to the baseline.

An in-situ photosynthesis of model photocatalytic colloid Cu(0)/TiO₂. First, colloidal solution of P25 TiO₂ in water was prepared by magnetic stirring 1.0 g P25 TiO₂ with 100 ml DI water at room temperature and centrifugation at 3400 rpm (1318 rcf) for 1 hr. using VanGuard V6500 centrifuge from Hamilton Bell. Then, a clear supernatant was collected and centrifuged for an additional 1 hr. to obtain an optically transparent solution. The obtained colloidal solution of TiO₂ was diluted with DI water to achieve optical absorbance $A=1$ at $\lambda=366$ nm. The $\lambda=366$ nm corresponds to the wavelength of a major emission line of Hg lamp as our photocatalytic light source (see Figure S4). To mimic chemical composition of the liquid phase in the “one-pot” synthesis and *in-situ* testing of Cu(0)-N-TiO₂ photocatalyst, 3.0 mL of obtained colloidal solution of P25 TiO₂ in water was mixed with 0.3 ml glycerol in the 3.5 cc quartz cuvette, and 0.1 mL of 0.033 M Cu(NO₃)₂ precursor solution in water was added. Finally, this colloidal solution in the cuvette was purged with argon for 5 min., the cuvette was sealed to prevent exposure of its content to air, and illuminated with a 450 Watt medium pressure mercury lamp from Ace Glass at the time increments of 1 min. to degenerate desired Cu(0)/TiO₂ model photocatalytic colloid.

An in-situ UV-Vis spectroscopy of model photocatalytic colloid. The *in-situ* UV-Vis spectra of model photocatalytic colloid Cu(0)/TiO₂ were obtained using Cary 50 spectrophotometer. Colloidal solution of TiO₂ in 10 wt. % solution of glycerol in water with dissolved Cu(NO₃)₂ precursor was exposed to the light of a medium pressure Hg lamp as described above, and an *in-situ* UV-Vis absorbance spectrum was immediately collected for 20 sec. The sequence of an exposure to a Hg lamp and collection of the *in-situ* UV-Vis spectrum was repeated several times.

Results and discussion

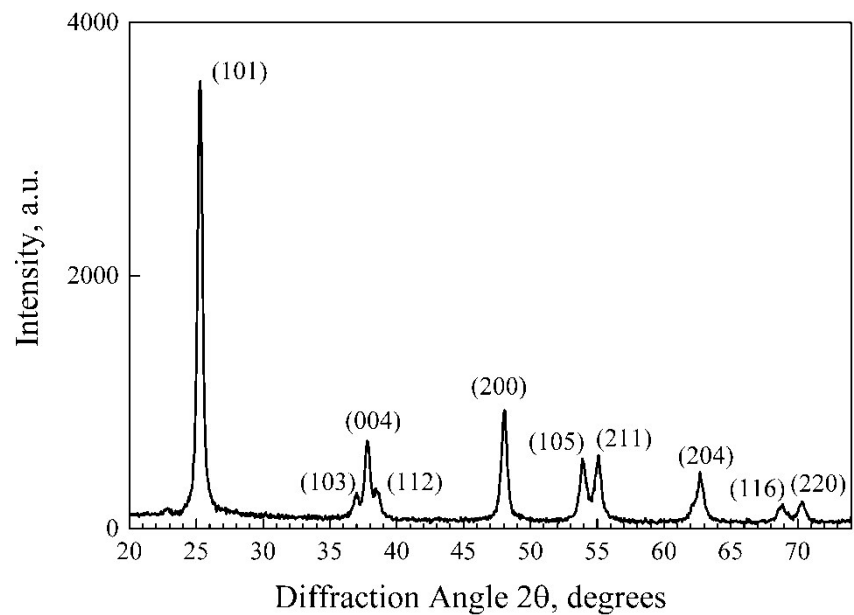


Figure S1. XRD pattern of N-TiO₂.

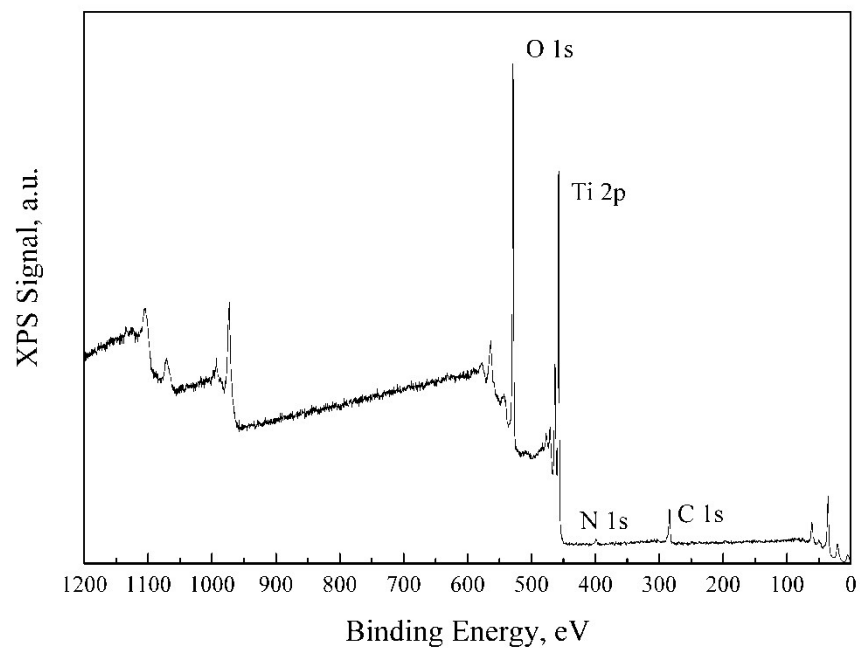


Figure S2. The XPS survey spectrum of N-TiO₂.

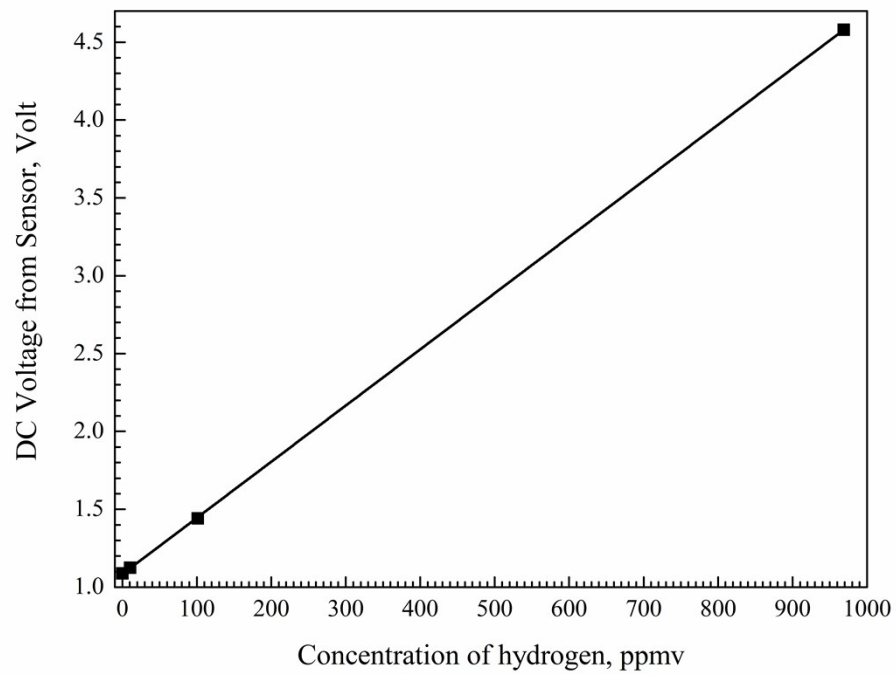


Figure S3. Calibration of electrochemical hydrogen sensor.

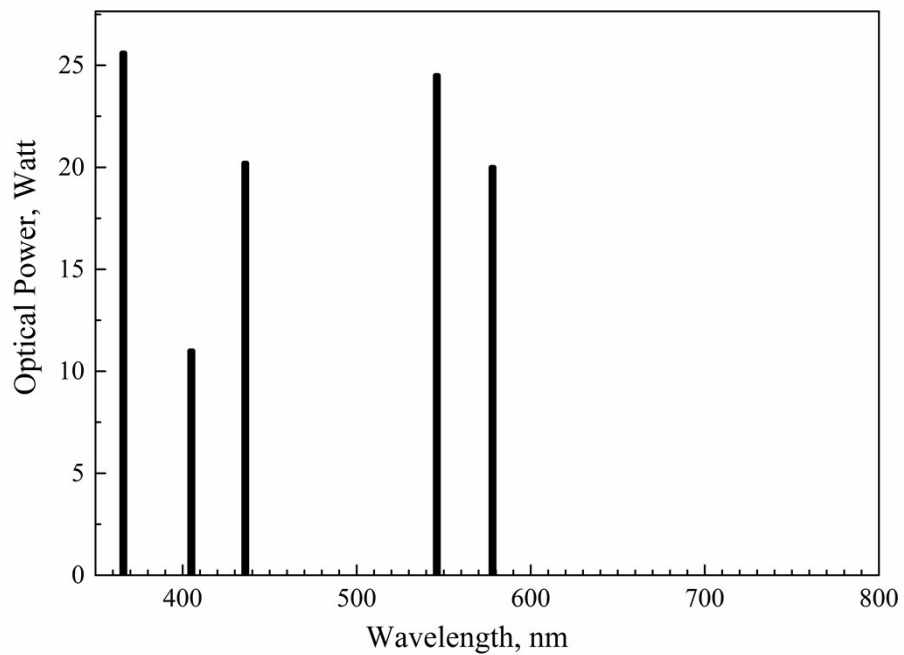


Figure S4. Optical spectrum of the light used in photocatalytic experiments.

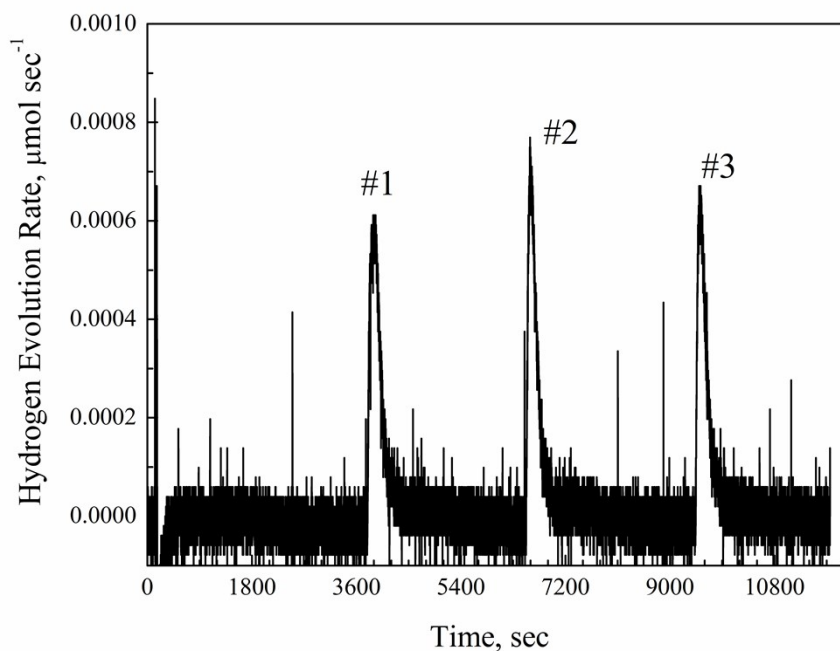


Figure S5. Hydrogen evolution rate with P25 TiO₂ measured by hydrogen sensor.

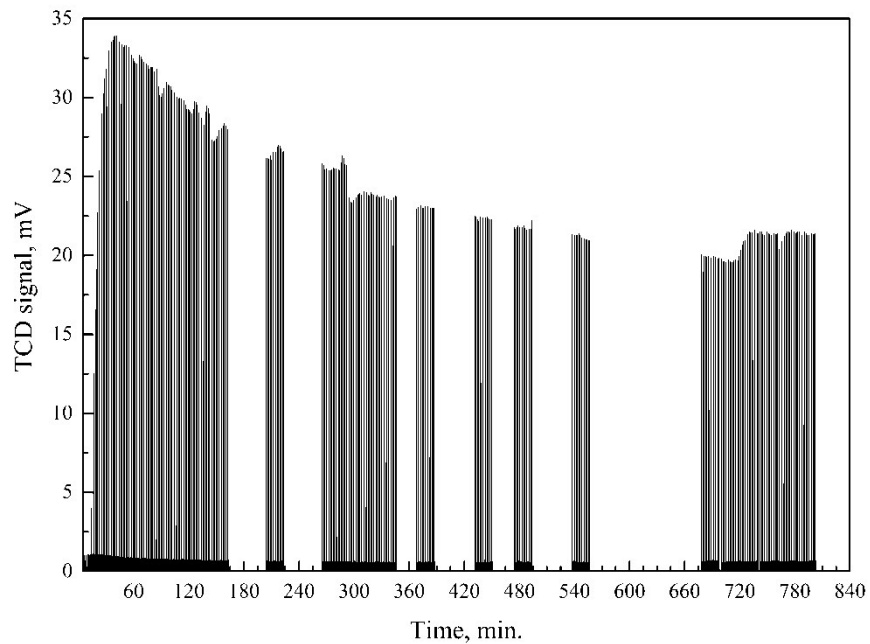


Figure S6. Hydrogen evolution with “one-pot” prepared Cu(0)-N-TiO₂ photocatalyst.

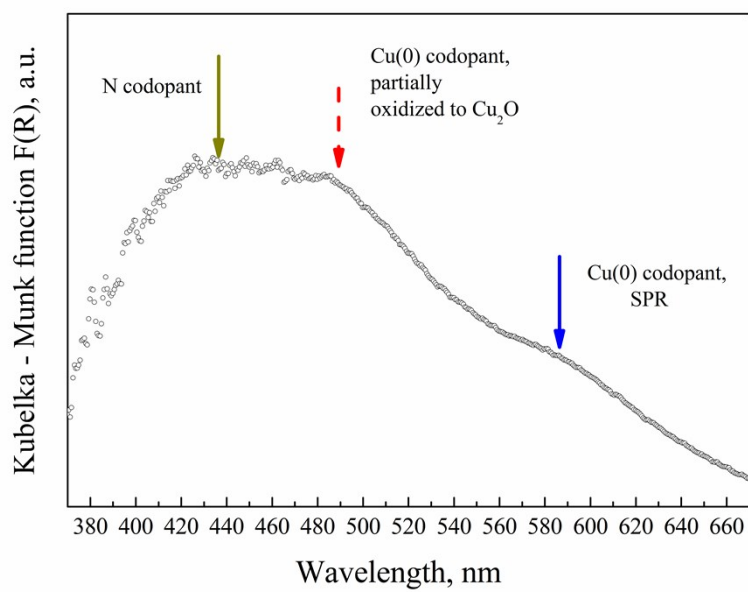


Figure S7. The UV-Visible DRS spectrum of “one-pot” prepared Cu(0)-N-TiO₂ photocatalyst as measured in air.