

Supplementary materials

Article

Influence of $\text{HB}_2\text{Nb}_3\text{O}_{10}$ -Based Nanosheet Photocatalysts (B = Ca, Sr) Preparation Method on Hydrogen Production Efficiency

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Figure S1

TG curves of the protonated forms and reassembled nanosheets of HCN_3 (a) and HSN_3 (b) niobates

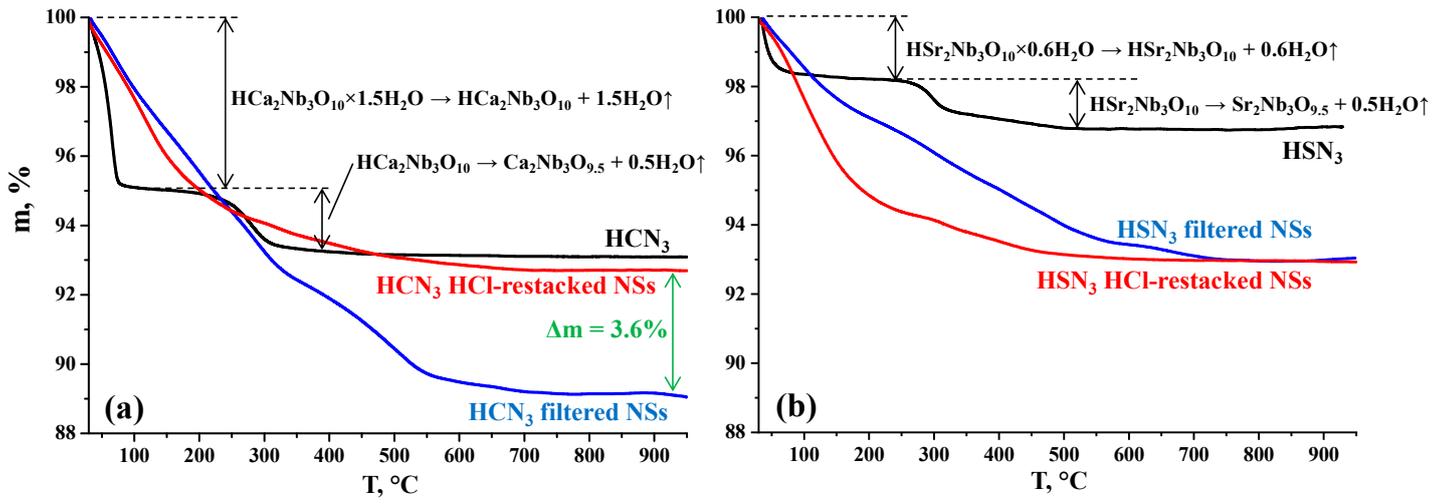


Figure S2

Images of the niobate nanosheets obtained by TEM (a,b), HR-TEM (c,d) and SAED patterns with main interplanar distances (e,f)

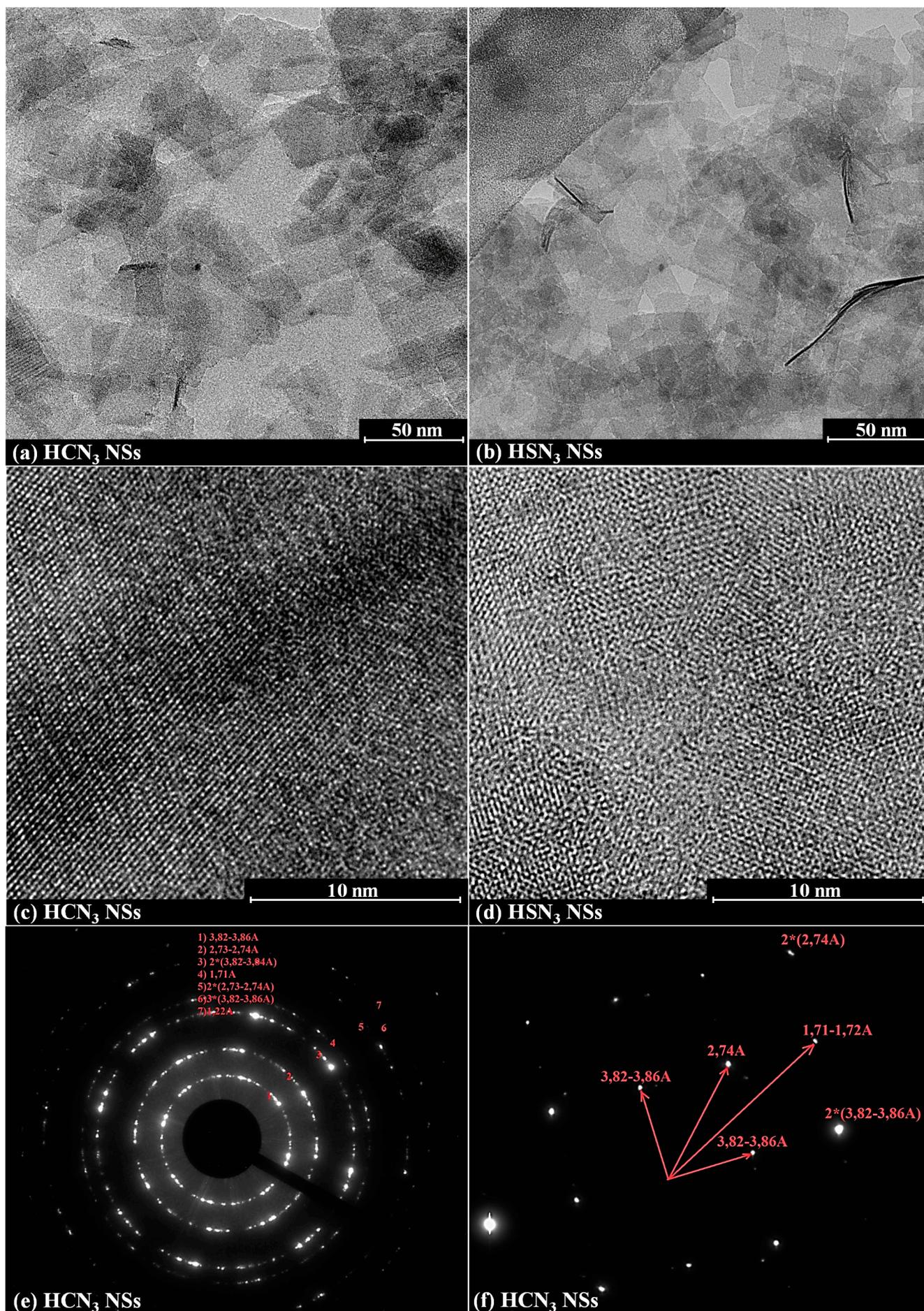


Figure S3

Kinetic curves of photocatalytic hydrogen evolution from 1 mol.% aqueous methanol in the presence of 0.004 M TBAOH over pristine and Pt-loaded HCN₃ nanosheets without medium acidification

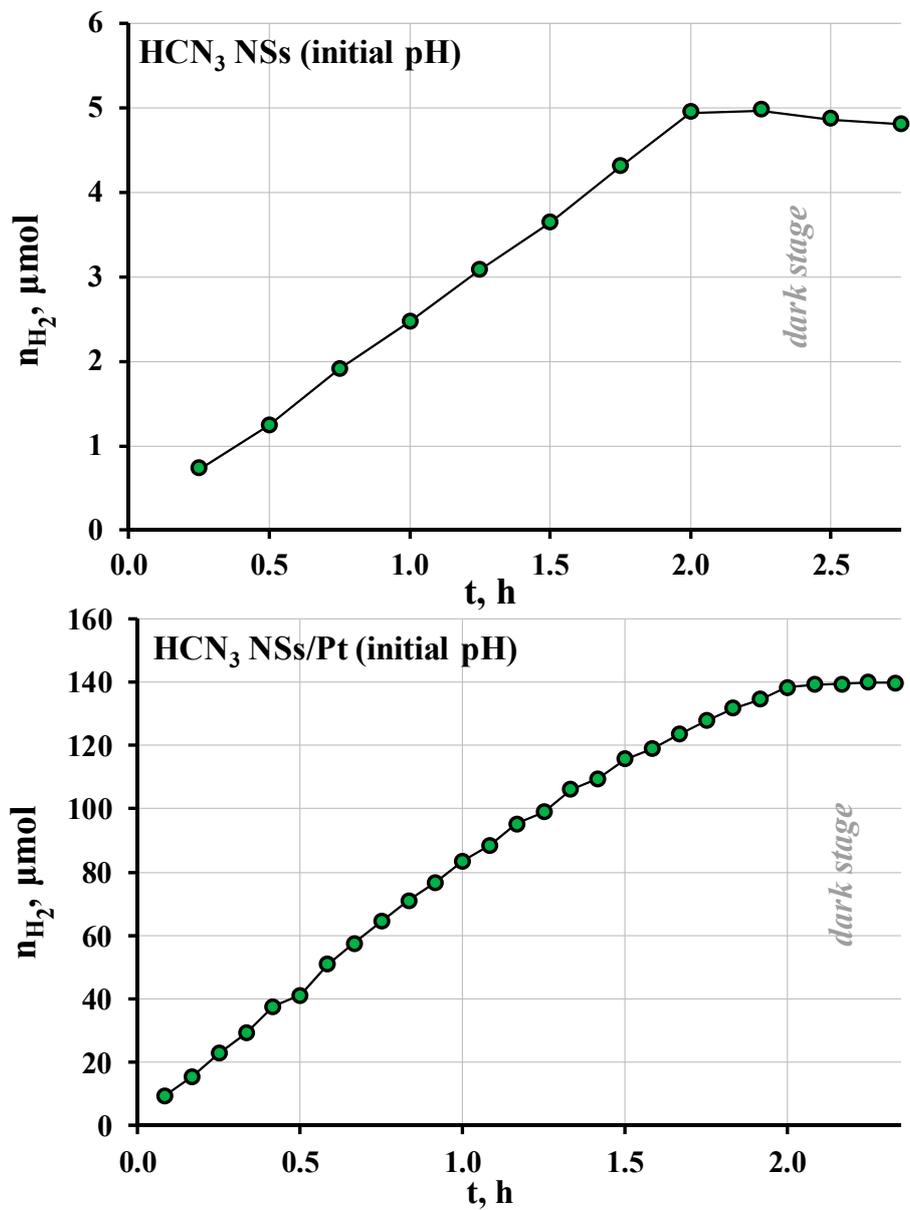


Figure S4

Full kinetic curves of photocatalytic hydrogen evolution from 1 mol.% aqueous methanol over Pt-loaded HBN₃ nanosheets

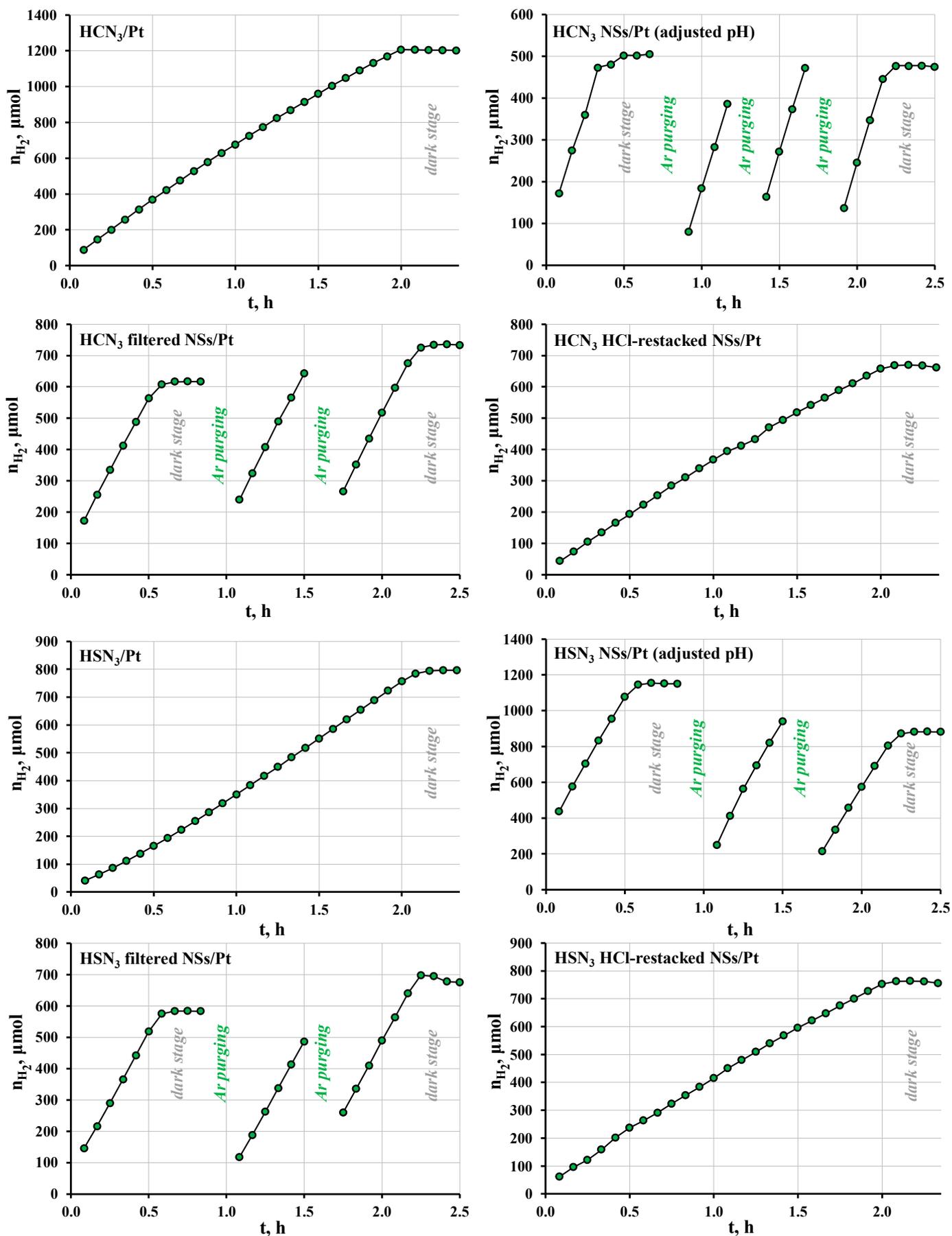


Figure S5

Kinetic curves of photocatalytic hydrogen evolution from water over initial and Pt-loaded protonated niobates HBN_3

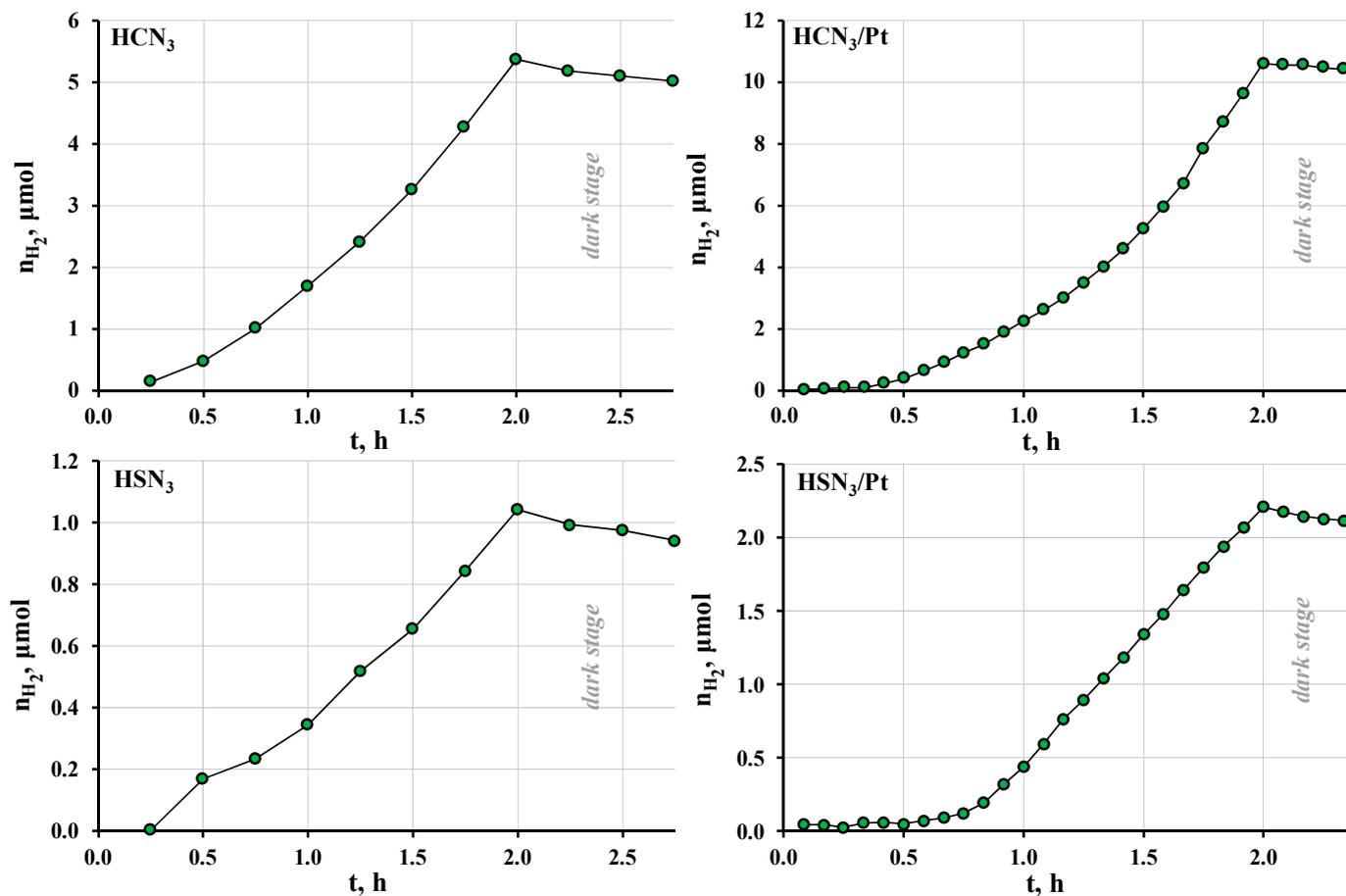


Figure S6

Kinetic curves of photocatalytic hydrogen evolution from water over HCN₃ nanosheet-based photocatalysts

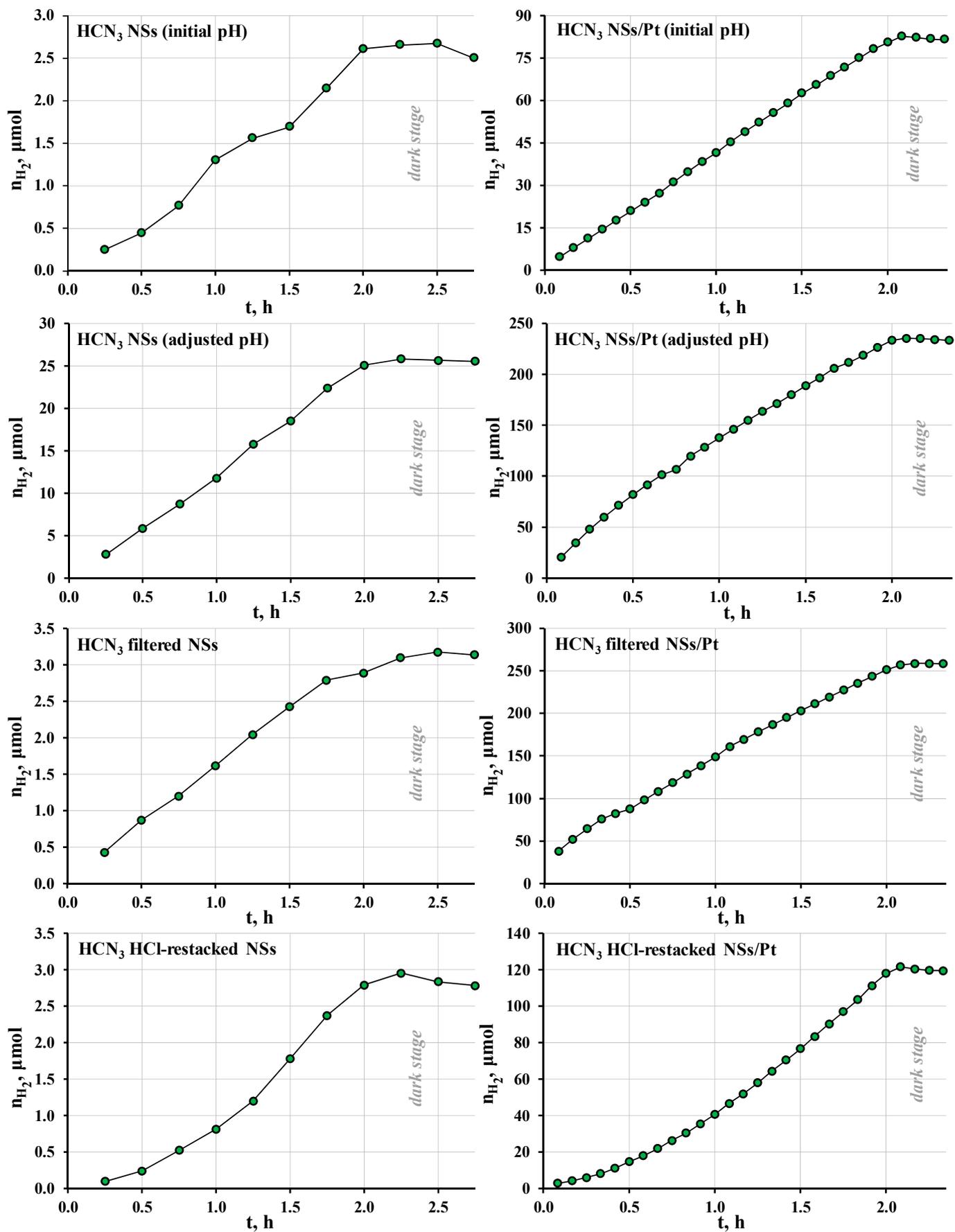


Figure S7

Kinetic curves of photocatalytic hydrogen evolution from water over HSN₃ nanosheet-based photocatalysts

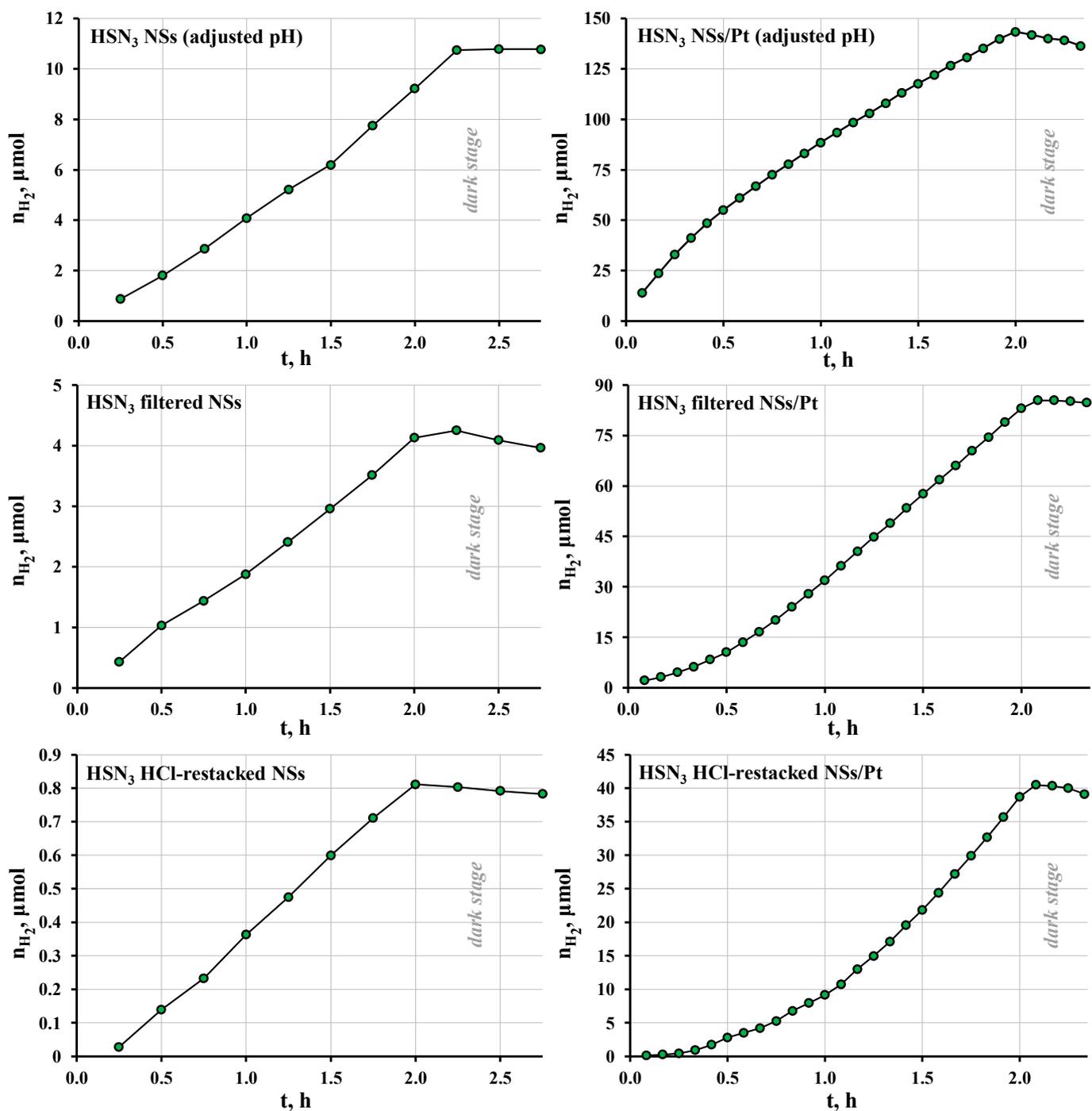


Figure S8

Hydrogen generation rate from 1 mol.% aqueous methanol over Pt-loaded HBN₃ nanosheet-based photocatalysts after several running cycles

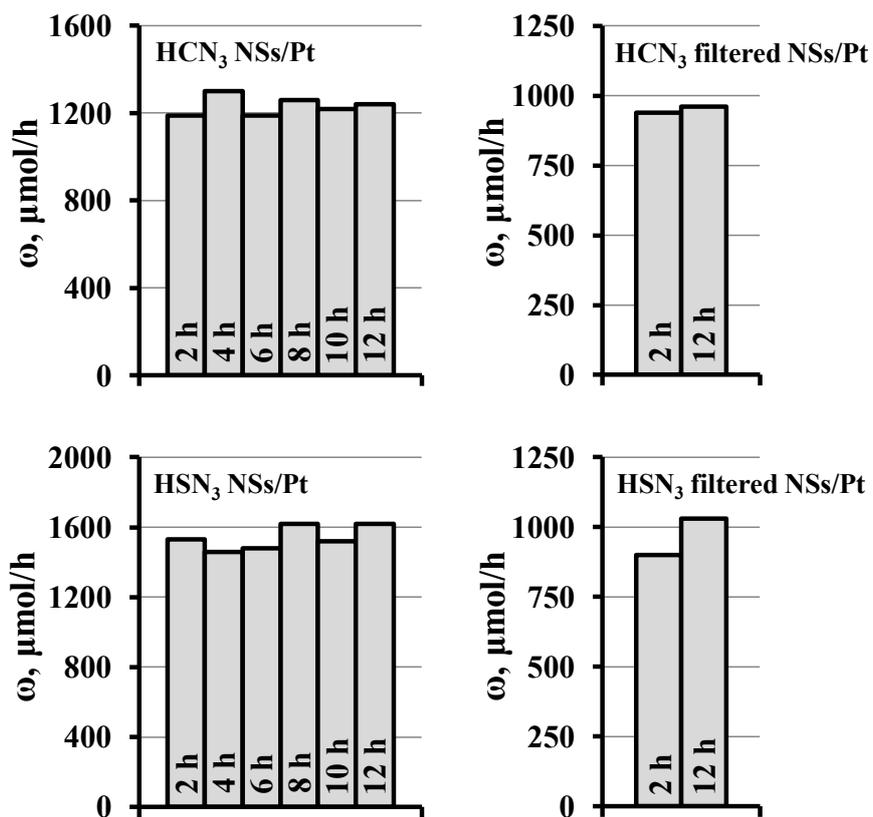


Figure S9

XRD patterns of the reassembled nanosheets before and after photocatalysis (PC)

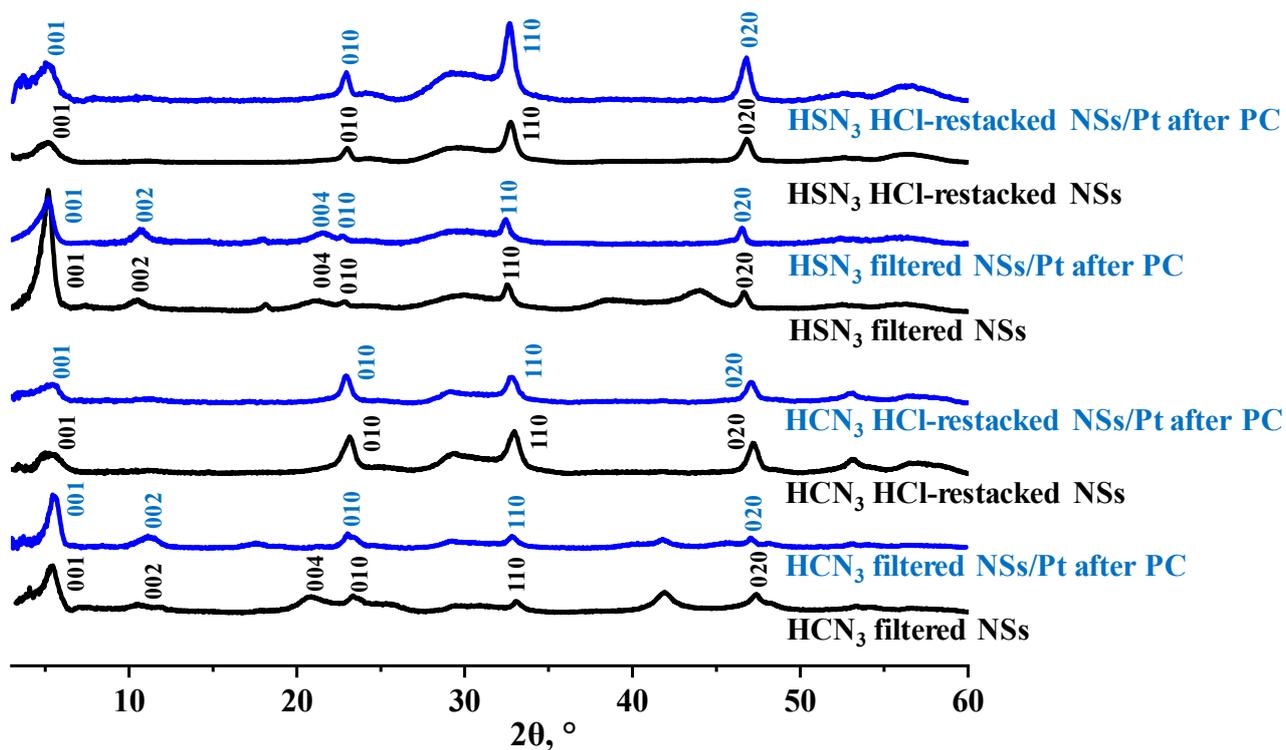


Figure S10

SEM images of the reassembled nanosheets before and after photocatalysis (PC)

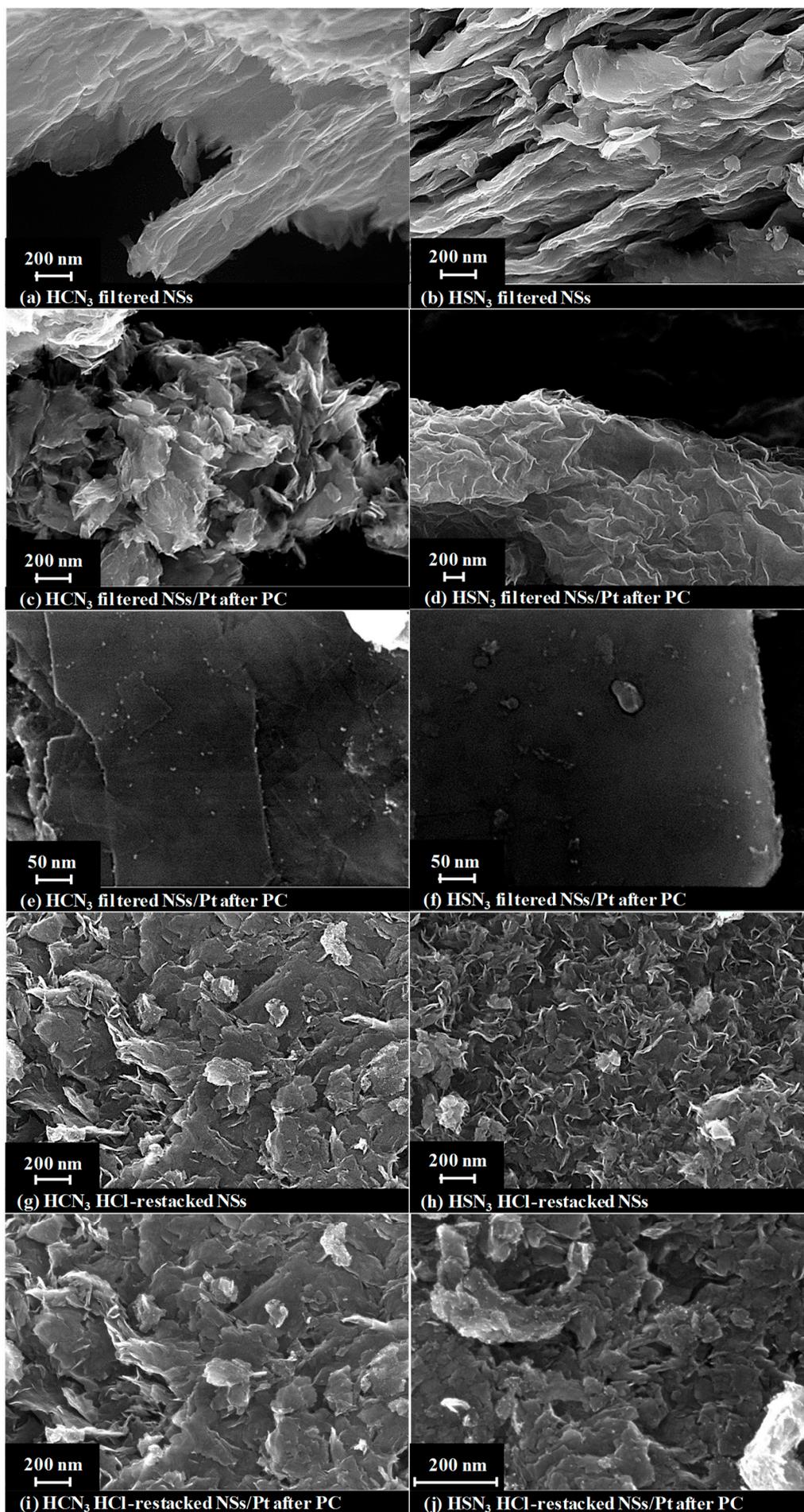
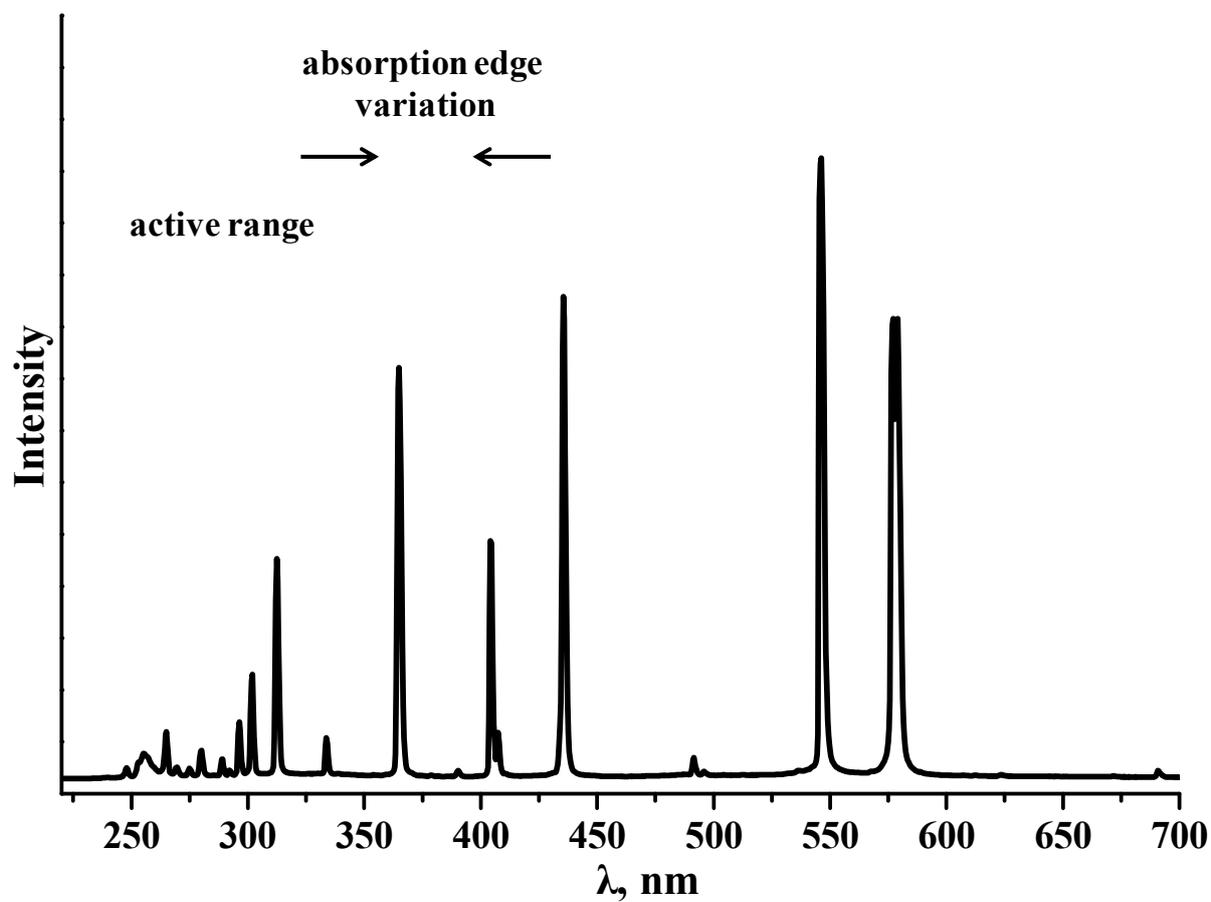


Figure S11

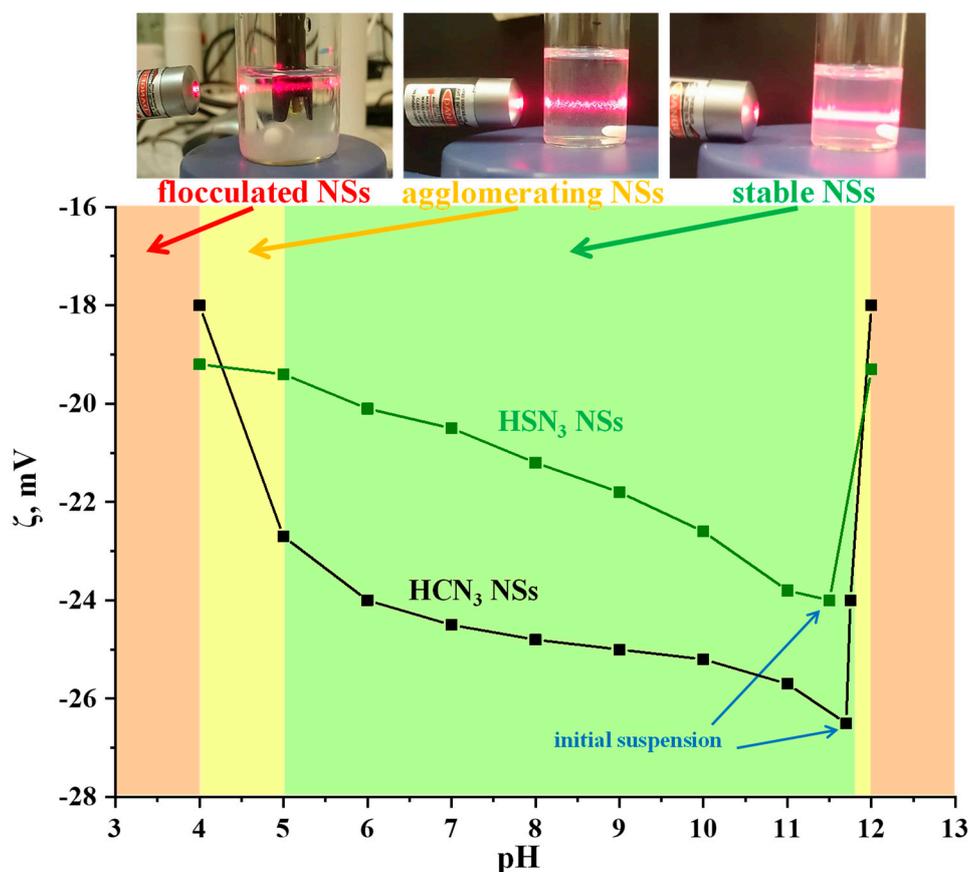
Emission spectrum of the DRT-125 mercury lamp compared with the absorption regions of the photocatalysts under study



Information S1

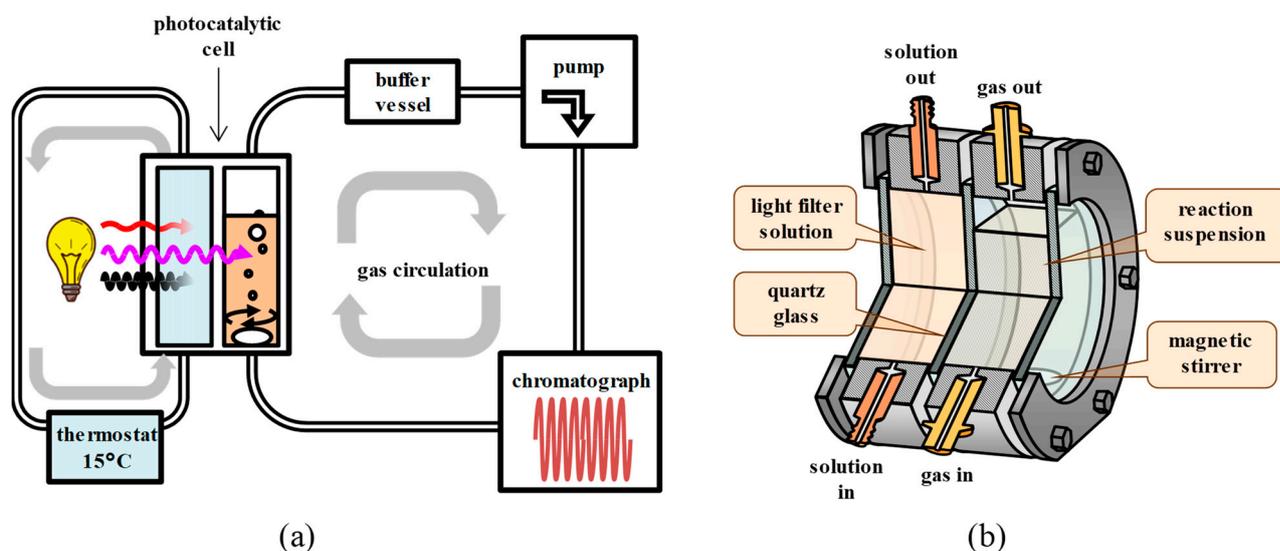
Stability of the as-prepared nanosheet suspensions relative to fast flocculation upon pH shifts

To find the pH range of stability, the initial suspensions of HBN₃ NSs (pH ≈ 11.65) were gradually acidified or alkalized under continuous stirring being illuminated with a red laser beam. When the nanosheet suspension is stable, the scattered light of the laser (a Tyndall effect) looks homogeneous and does not allow one to see individual scattering particles with the naked eye. As the stability limit is being approached, separate sparkles become notable in the scattered light indicating aggregation of the nanosheets. Concentration of the aggregates continues rising until the critical pH is reached when the suspension undergoes fast flocculation. The latter is observed as a sharp increase in the suspension turbidity due to the active formation of flakes that easily settle to the bottom immediately after the stirrer is turned off. The experiments conducted in this way showed HBN₃ NSs to be stable upon the acidification to pH ≈ 5. Further pH decreasing is accompanied by the severe nanosheet agglomeration and, when pH ≈ 4 is reached, the suspension is immediately flocculating. The same occurs when pH ≥ 12. Thus, the range of the suspension stability with respect to fast flocculation is 5 ≤ pH ≤ 11.75 (shown on a green background in the figure below). Samples of all the suspensions from this pH range were additionally analyzed by DLS to determine ζ-potentials. It was found that the initial suspension of HCN₃ NSs exhibits ζ = -26.5 mV and its absolute value decreases upon the acidification or alkalization due the double layer contraction. Clear signs of the nanosheet agglomeration are already observed at ζ = -23 mV and ζ > -20 mV results in the fast flocculation. In the case of HSN₃ NSs, the initial suspension shows ζ = -24 mV and remains stable until ζ < -20 mV.



Information S2

Scheme and operation principle of the photocatalytic setting



Photocatalytic measurements were performed on the laboratory photocatalytic setting (a), consisting of an arc mercury tube lamp DRT-125 (125 W), photocatalytic cell (b), online gas chromatograph and closed gas circulation system, connecting the last two components. The lamp emission spectrum is presented in Supporting Information S8 and the method for the calculation of its photon flux is described in Supporting Information S9. The self-made photocatalytic cell represents an external irradiation reactor, including two compartments equipped with branch pipes for the supply and removal of solutions and gases. The compartment closest to the lamp is filled with a light filtering solution thermostated at 15 °C (aqueous NaBr and KCl, 6 g/L of each salt, cutting off $\lambda < 220$ nm). The compartment farthest from the lamp is for the reaction suspension, being intensively stirred during the experiment. When the reaction cell is irradiated, gaseous reaction products come from the cell into the gas circulation system. Their detection is conducted according to a specified program at fixed time intervals by a Shimadzu GC-2014 gas chromatograph (Kyoto, Japan) equipped with a 30 m long Rt-MSieve 5A capillary column, thermal conductivity detector and using argon as a carrier gas.

Information S3

Method for the calculation of apparent quantum efficiency

Apparent quantum efficiency φ of photocatalytic hydrogen generation was calculated using the following formula:

$$\varphi = \frac{2\omega}{f} \cdot 100\% \quad (1)$$

where ω is the hydrogen evolution rate (mmol/h) and f is the photon flux in the photocatalyst absorption range (mmol/h).

The photon flux was measured previously in accordance with the ferrioxalate actinometry technique. Briefly, 3 g of potassium ferrioxalate $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ was dissolved in 1 L of 0.05 M sulfuric acid. 50 mL of the photosensitive solution prepared was pumped into the reaction compartment of the photocatalytic cell and irradiated by the DRT-125 lamp through the NaBr + KCl light filter (transmission $\lambda > 220$ nm) for 20 s. Then 0.5 mL of the irradiated solution was sampled from the cell, mixed with 2 mL of an acetate buffer and 1 mL of 0.1% 1,10-phenanthroline and made up to the 25 mL mark with distilled water in a volumetric flask. Amount of Fe^{2+} in the final solution was determined spectrophotometrically using a previously built calibration plot. To measure the photon flux in the range of 220–340 nm, the similar experiment was conducted using a KNO_3 light filter and irradiation time 30 s (transmission $\lambda > 340$ nm). Each series of measurements was repeated 3 times and Fe^{2+} contents were averaged. Assuming the quantum yield of the Fe^{2+} formation from potassium ferrioxalate is 100%, we calculated the photon flux f in accordance with the formula:

$$f = V \cdot \left(\frac{c}{t} - \frac{c'}{t'} \right) \quad (2)$$

where V is a volume of the photosensitive solution in the cell (L), c is concentration of Fe^{2+} (mM) in the photosensitive solution after its irradiation through the NaBr + KCl light filter for the time t (h), c' is concentration of Fe^{2+} (mM) in the photosensitive solution after its irradiation through the KNO_3 light filter for the time t' (h). To measure the photon flux in the range of 220–400 nm, a NaNO_2 light filtering solution (transmission $\lambda > 400$ nm) was used instead of KNO_3 and the single irradiation duration was 120 s. All other experimental and calculational procedures were the same.

Information S4

Detailed procedure for the investigation of photocatalytic activity

To study the activity of powder photocatalysts (protonated niobates, filtered NSs and HCl-restacked NSs) in a bare state (without a cocatalyst), 27 mg of the sample was placed into a round-bottom flask containing 54 mL of 1 mol. % aqueous methanol or pure distilled water. The flask was sealed, shaken and sonicated in an Elmasonic S10H bath (Elma, Singen, Germany) for 10 min. The suspension obtained was pumped into the reaction compartment of the cell, after which the light filter, lamp, magnetic stirrer and argon purging through the suspension were switched on. After 15 min, 4 mL of the suspension was taken from the cell to measure a UV-vis spectrum and pH of the medium before the photocatalytic experiment. 15 min later, the argon purging was switched off to allow the hydrogen to start accumulating in the gas circulation system. At the same time, a 2 h photocatalytic activity measurement was started, consisting in a chromatographic analysis of the gaseous phase every 15 min. Afterwards, the dark stage was organized via turning off the lamp and monitoring potential dark activity of the sample for 45 min. Thereafter, 4 mL of the suspension was sampled to measure a UV-vis spectrum and pH of the medium after the photocatalytic experiment. When studying the activity of the powder samples with a Pt cocatalyst, the volume of the suspension for loading into the reaction compartment was 53 mL. After 15 min from the moment the light filter, lamp, magnetic stirrer and argon purging were switched on, 1.1 mL of the 1.27 mM H_2PtCl_6 aqueous solution was injected into the reaction suspension to perform in situ photocatalytic platinization. The solution volume was calculated to provide a mass fraction of Pt in the final photocatalyst of 1% assuming its full reduction. The gaseous phase was analyzed every 5 min and the dark stage duration was 20 min. If the hydrogen evolution rate exceeded 500 $\mu\text{mol/h}$, the photocatalytic measurement program was divided into 30 min sections, separated by a 10 min argon purging to release the accumulated hydrogen and reduce pressure in the system, and included an additional dark stage after the first section. Other experimental conditions and procedures were the same.

The activity of pristine nanosheets without reassembly (HBN₃ NSs) was investigated using the TBAOH-containing suspensions after the exfoliation. The experiments were conducted both at the initial pH of the suspensions (pH \approx 11.6–11.7) and after their acidification with 1 M hydrochloric acid to achieve the pH characteristic of the initial protonated niobates (pH \approx 4–5). A typical experimental procedure included the dilution of the suspension to the nanosheet concentration of 500 mg/L and, if necessary, addition of hydrochloric acid and methanol to provide the same concentration of the latter as in the aforementioned experiments with the powder samples. The suspension obtained was pumped into the reaction cell and, if necessary, platinized via the H_2PtCl_6 reduction. Other experimental conditions and procedures were the same as described above.

Information S5

Spectrophotometric calibration plots for express measurement of nanosheet concentrations in suspensions

The suspensions of HBN₃ NSs in 0.004 M TBAOH were prepared as described in the main body of the article. Concentrations of the NSs in the suspensions were measured by ICP-AES after their preliminary acid digestion. To obtain the calibration plot $A - c$ (mg/L) for each niobate, UV-vis spectra for the series of the diluted suspensions were recorded, analytical wavelength $\lambda = 230$ nm (HCN₃) or $\lambda = 255$ nm (HSN₃) was selected and the linear approximation of the experimental dependence $A_\lambda = A_\lambda(c)$ was found using the least-squares method.

