

Electronic Supplementary Information

An insight towards the photo-generation of H₂ and multifarious carbon fuel additive from biomass-derived ethanol: Boosting the bio-chemical economy

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1. Experimental section

1.1. Materials

Urea was purchased from Sigma Aldrich, Niobium oxide (Nb₂O₅) was purchased from CDH, Cyanamide (CA) was purchased from Sigma Aldrich, and ethanol (99.99%) of analytical grade was purchased from Changshu Hongsheng Fine Chemicals. Triethanolamine (TEOA) and H₂PtCl₆ · 6H₂O were also purchased from Sigma Aldrich. All the chemicals were used without further purification.

1.2. Synthesis procedure of UCN

Crystalline urea of 20 g was weighed and kept in a crucible with lid and calcined in a Nabertherm box furnace at 550 °C for 3 h with a heating rate of 5 °C min⁻¹ under the flow of N₂. For the comparison view point, the prepared UCN was further treated thermally at 550 °C for 30 min with heating rate of 10 °C min⁻¹ under the flow of N₂, which was denoted as UCN-550 °C.

1.3. Synthesis procedure of UCN/Nb₂O₅

The synthesis procedure of UCN/Nb₂O₅ is as follows: first 200 mg of as prepared UCN was taken and ground uniformly in quartz mortar with varied amount of Nb₂O₅-(x) (x= 1 (50 mg), 2 (100 mg), 3 (150 mg), and 4 (200 mg)). The resultant powder was further, kept inside the box furnace and calcined at 550 °C for 30 min with heating rate of 10 °C min⁻¹ under the flow of N₂. The obtained materials were mentioned as UCN/Nb₂O₅-(1), UCN/Nb₂O₅-(2), UCN/Nb₂O₅-(3), and UCN/Nb₂O₅-(4). Amid all synthesized composite, UCN/Nb₂O₅-(2) showed excellent photo performance after Pt deposition, based on this, UCN/Nb₂O₅-(2) composite was characterized only for sake of clarity throughout manuscript. Notably, pure Nb₂O₅ was also thermally treated separately at 550 °C under the same conditions and denoted as Nb₂O₅-550 °C.

1.4. Synthesis procedure of Pt/UCN/Nb₂O₅-(2)

Pt a co-catalyst over the surface of UCN/Nb₂O₅-(2) was loaded under the light irradiation via photo-deposition method. Firstly, a certain amount of UCN/Nb₂O₅-(2) was taken in a 100 ml round bottom (RB) flask which was already charged with water and TEOA (80:20, 60 ml). To that solution mixture H₂PtCl₆. 6H₂O was added in such a manner to vary the Pt loading in Pt/UCN/Nb₂O₅-(2) from 1 wt %-5 wt %. Thenceforth, the resulting solution mixture was evacuated and purged with inert Argon gas for 30 min to supersede the dissolved O₂ completely in the system and kept under the solar simulator (AM 1.5) for 3 h. After the suspended Pt/UCN/Nb₂O₅-(2) was recovered through centrifugation, washed with plenty of D.I water and dried at 80 °C in the oven.

1.5. Analytical techniques

The diffraction patterns were determined by powder XRD using Bruker D8 Advance diffractometer equipped with a scintillation counter detector, with Cu-K α radiation ($\lambda = 0.15418$ nm) source operating at 40 kV and 40 mA. Diffuse reflectance spectra of the solid sample was recorded on an UV-visible spectrophotometer (Shimadzu UV-2600), which was operated in a solid state mode with barium sulfate as reference. BET surface area and pore size distribution were estimated by the Brauner-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method on the Autosorb iQ3 instrument (Quantachrome), respectively. Transmission electron microscope (TEM) analysis was carried out using JEOL operated at an accelerating voltage of 200 kV. The presence of acidic sites over the surface of the photocatalyst was estimated by conducting ammonia-Temperature Programmed Desorption (NH₃-TPD) analysis (TPD Standard 10% NH₃ balanced He) with the help of AutoChem HP 2950 V3.02A instrument. X-ray photoelectron spectroscopy (XPS) was further corroborated to realize the chemical states and elemental compositions of the sample by using the PHI 5000 Versaprobe II instrument. Electron paramagnetic resonance (EPR) was performed to ensure the vacancies and structure-activity relation between photocatalyst and ethanol by using Bruker EMX Microx spectrometer over the frequency of 100 kHz and modulation amplitude of 0.2 G. (Photo)-electrochemical analysis was performed in a standard three-electrode, platinum electrode, Ag/AgCl (in saturated KCl) electrode, and glassy carbon electrode as a counter, reference and working electrode, respectively. The measurement was recorded via Metrohm Autolab (M204 multichannel potentiostat galvanostat). After the reaction, an estimation of the gaseous product (H₂) was done by Gas Chromatography (Perkin Elmer Clarus 680) and the analysis of the liquid samples were estimated by Shimadzu Gas Chromatography- Mass Spectrometer (GC-MS) equipped with Stabilwax-MS column.

1.6. General reaction procedure

The PD of ethanol was performed in a glass round bottom (RB) flask under a solar simulator (AM 1.5), 100 mW.cm⁻². In a typical reaction, a certain amount of Pt/UCN/Nb₂O₅-(2) photocatalyst (Pt loading 1wt% - 5wt %) was pre-mixed in 3 ml of ethanol (TEM grade). Furthermore, the solution containing sealed RB was purged with inert Argon gas for 30 min to ensure the complete removal of dissolved O₂ and kept under the solar simulator (AM 1.5), 100 mW cm⁻². After the different periods of time, the gaseous product H₂ was analyzed and quantified by Gas Chromatography (Perkin Elmer Clarus 680, TCD detector, Argon as carrier gas). The liquid ethanol mixture was centrifuged and segregated from the suspended catalyst and analyzed by Shimadzu Gas Chromatography-Mass Spectrometer (GC-MS). Moreover, the separated catalyst was collected and washed with copious amounts of water followed by ethanol. Subsequently the washed catalyst was dried in the oven and utilized for the recycling experiments. Notably, owing to the highest photocatalytic activity of 3 wt% Pt loading over UCN/Nb₂O₅-(2) (**Figure S5a**), the sample was mentioned as Pt/UCN/Nb₂O₅-(2) and discussed throughout the manuscript.

Table S1. Comparison of Pt/UCN/Nb₂O₅-(2) and other reported photocatalysts for ethanol valorization into H₂, DEE, and CH₃CHO.

| S. no | Catalyst | Conditions | Production rate (μmol.h ⁻¹ .g ⁻¹) | | Selectivity (%) | | Ref. |
|-------|--------------------------------------|--|--|-------------------------------------|-----------------|---------------------|--------------|
| | | | H ₂ | Oxidized products | DEE | CH ₃ CHO | |
| 1. | CoTiO ₃ /TiO ₂ | 2 mg photocatalyst, 10 % ethanol water mixture, UV light | 3700 | CH ₃ CHO (N.A.) | - | 100 | ¹ |
| 2. | Pt/TiO ₂ | 100 mg photocatalyst, 100 ml neat ethanol, UV light | N.A. | DEE, and CH ₃ CHO (N.A.) | N.A. | N.A. | ² |
| 3. | Au/anatase-rutile TiO ₂ | 300 mg photocatalyst, 1 ml ethanol, 6 h, and UV light. | N.A. | DEE, and CH ₃ CHO (N.A.) | 92.8 | 2.1 | ³ |
| 4. | Pt/TiO ₂ | 100 mg, 20 ml ethanol, 12 h, and UV light | N.A. | DEE (N.A.) | >99 | | ⁴ |
| 5. | PdPSA-CdS | 10 mg photocatalyst, 100 ml ethanol, 0.05 ml H₂SO₄ , Xe lamp (λ >420 nm, 2200 mW*cm⁻²) | | DEE (35100) | 100 | | ⁵ |
| 6. | CdS/Ni-MoS ₂ | 5 mg photocatalyst, 20 ml ethanol, 0.03 mmol H₂SO₄ , Xe lamp (λ >420 nm, 300 W Xe lamp), 12 h | 52100 | DEE (52100) | 99.2 | | ⁶ |
| 7. | TNS-Pd | 15 mg photocatalyst, 2 ml ethanol, | 51500 | DEE (7700) CH ₃ CHO | 92 | 8 | ⁷ |

| | | | | | | | |
|----|---------------------------------------|---|-----|--|----|----|-----------------|
| | | HCl ($1 \cdot 10^{-3}$ mol L ⁻¹), UV-vis light, 12 h | | (N.A.) | | | |
| 8. | Pt/UCN/Nb ₂ O ₅ | 10 mg, 3 ml ethanol, (solar simulator, AM 1.5 G, 100 mW/cm ²), 12 h, without external acid fractions. | 632 | DEE (594) CH ₃ CHO (289) | 72 | 28 | Our work |

Note: N.A. = Not available

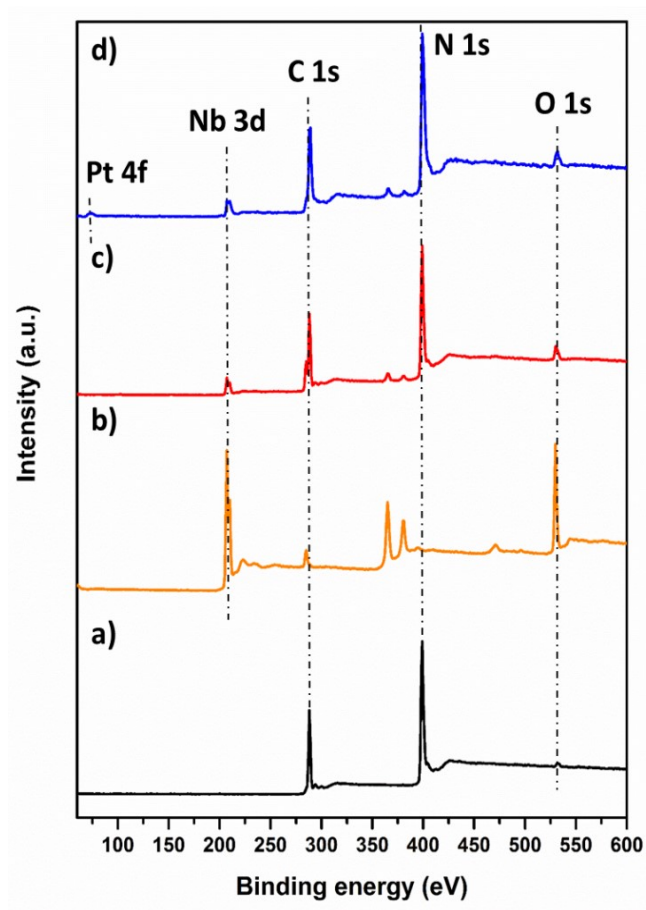


Figure S1. XPS survey scan (a) UCN, (b) Nb₂O₅, (c) UCN/Nb₂O₅-(2), and (d) Pt/UCN/Nb₂O₅-(2).

Table S2. XPS-determined surface atomic percentage (%) and C/N ratio of UCN, UCN/Nb₂O₅-(2) and Pt/UCN/Nb₂O₅-(2).

| Catalyst | Elements | | | | | |
|--|----------|-------|------|------|------|------|
| | C | N | O | Nb | Pt | C/N |
| UCN | 40.13 | 58.74 | 1.13 | - | - | 0.68 |
| UCN/Nb ₂ O ₅ -(2) | 44.95 | 47.54 | 5.74 | 1.79 | - | 0.94 |
| Pt/UCN/Nb ₂ O ₅ -(2) | 41.09 | 50.33 | 4.37 | 1.28 | 2.94 | 0.81 |

Table S3. Relative ratios of N-C=N, N-(C)₃, -NH_x and π-excitation estimated by N1s XPS spectra.

| Samples | N-C=N | N-(C) ₃ | -NH _x | π-excitations |
|---|---------|--------------------|------------------|---------------|
| UCN | 71.80 % | 15.36 % | 9.46 % | 3.38 % |
| UCN/Nb ₂ O ₅ -(2) | 75.21 % | 8.92 % | 12.44 % | 3.43 % |

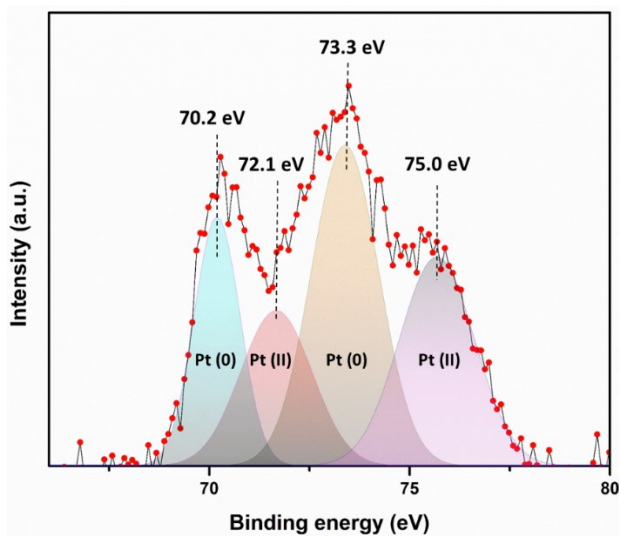


Figure S2. High resolution 4f Pt XPS spectra.

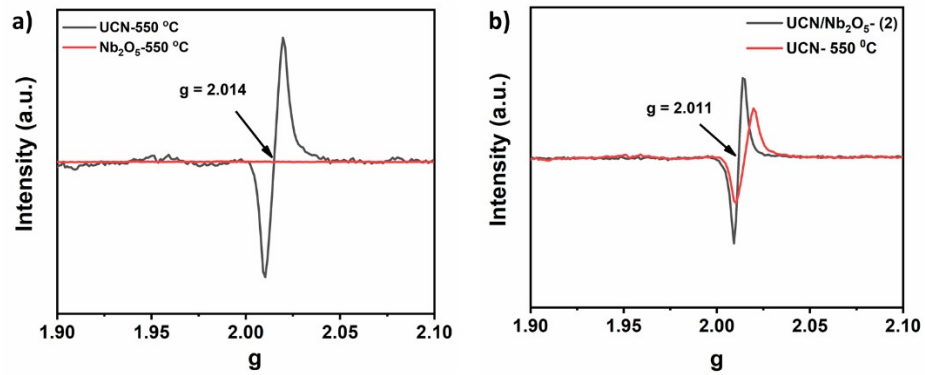


Figure S3. Solid state EPR spectra of a) post thermal treated UCN-550 °C and Nb₂O₅-550 °C b)UCN/Nb₂O₅-(2) and UCN-550 °C.

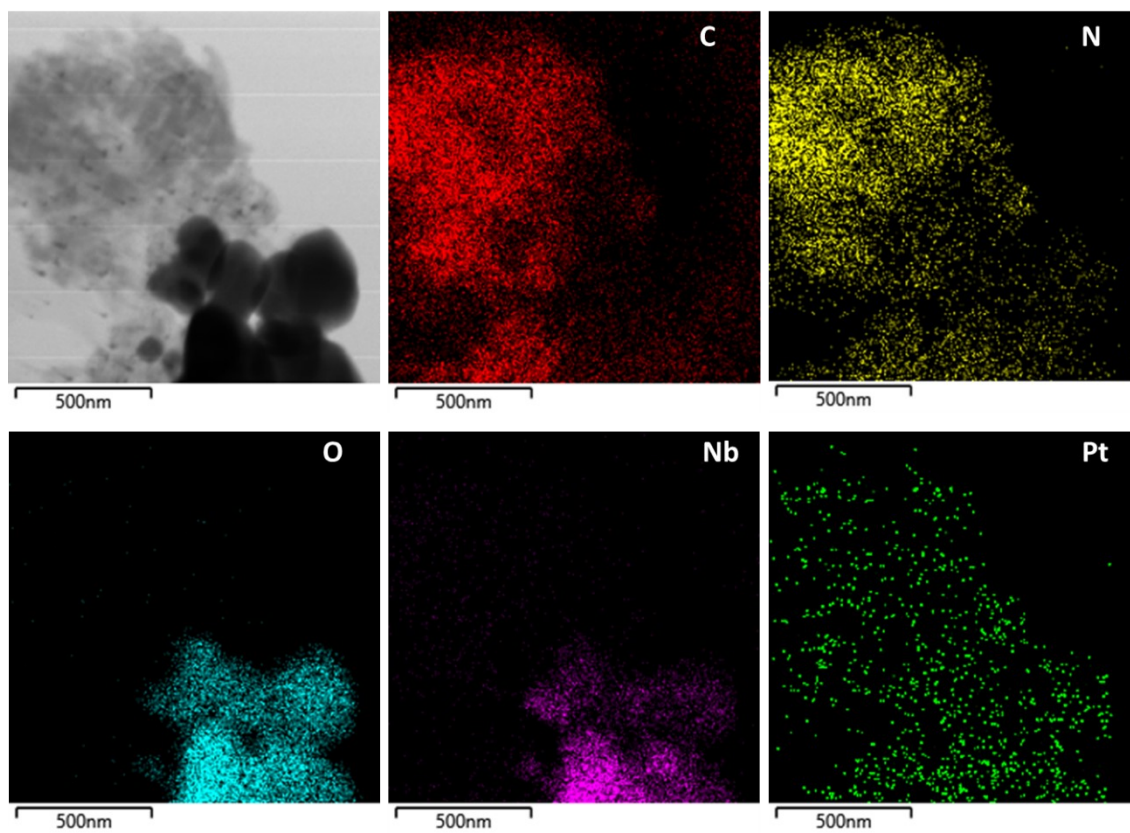


Figure S4. TEM elemental mapping of Pt/UCN/Nb₂O₅-(2) showing existence of C, N, O, Nb, and Pt elements.

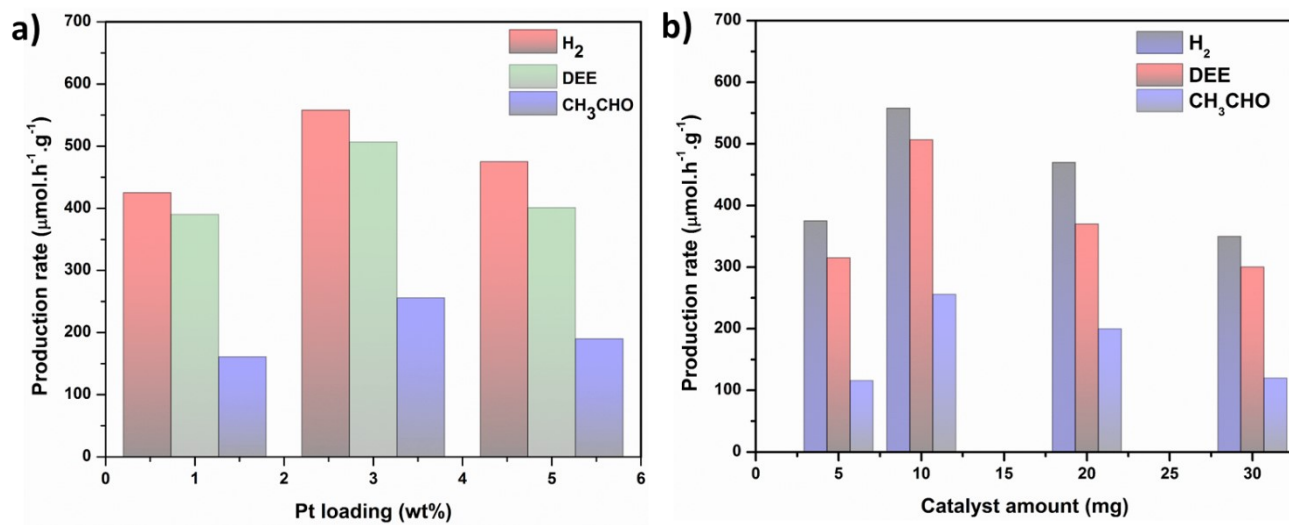


Figure S5. (a) Effect of Pt loading over the production rates of DEE and H_2 during ethanol valorization. (b) Effect of catalyst amount over the production rates of DEE and H_2 during ethanol valorization.

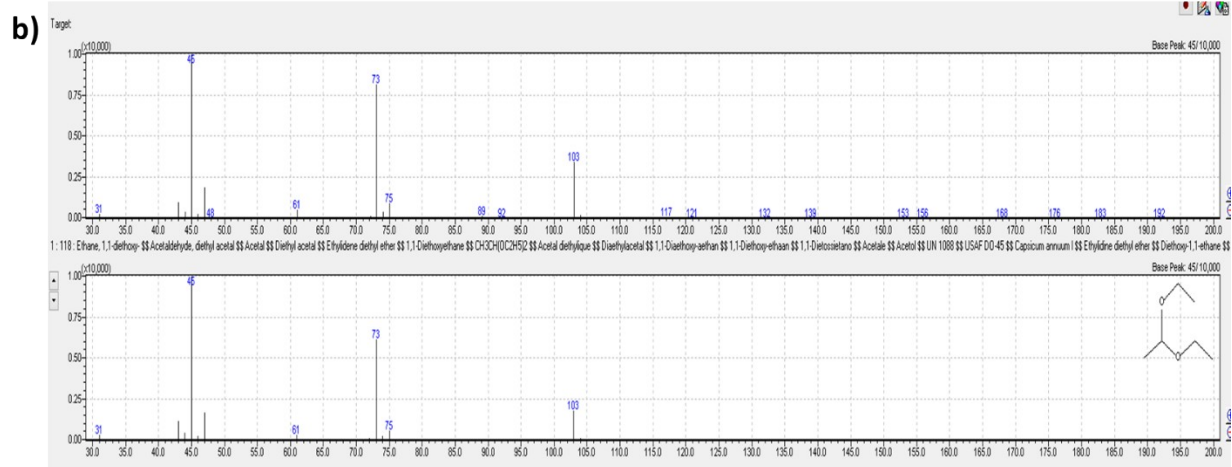
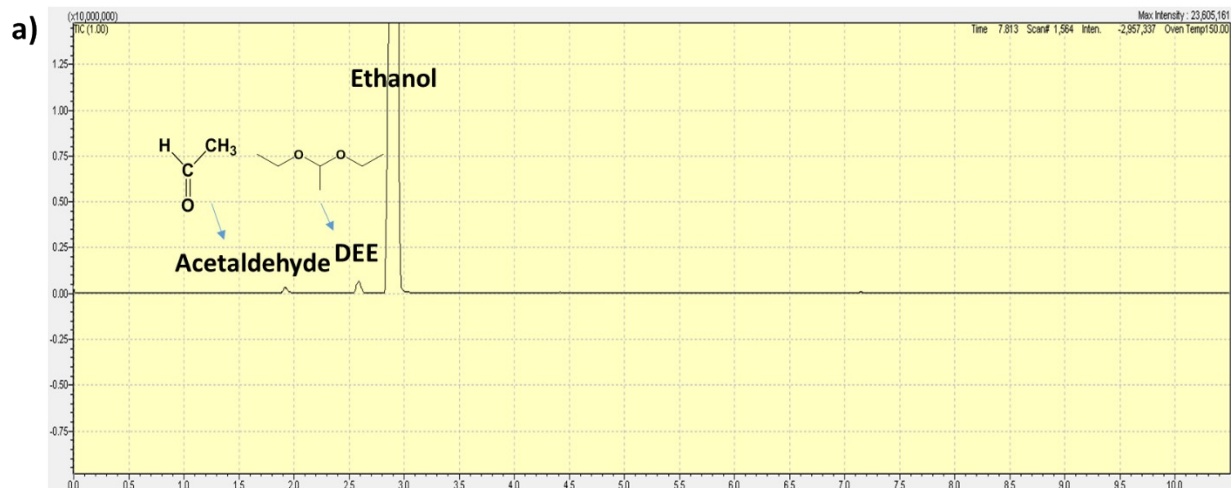


Figure S6. (a) GC-MS snap-shot of Pt/UCN/Nb₂O₅-(2) catalyzed ethanol valorization after 12 h, showing the production of DEE along with acetaldehyde. (b) Mass spectrum of DEE.

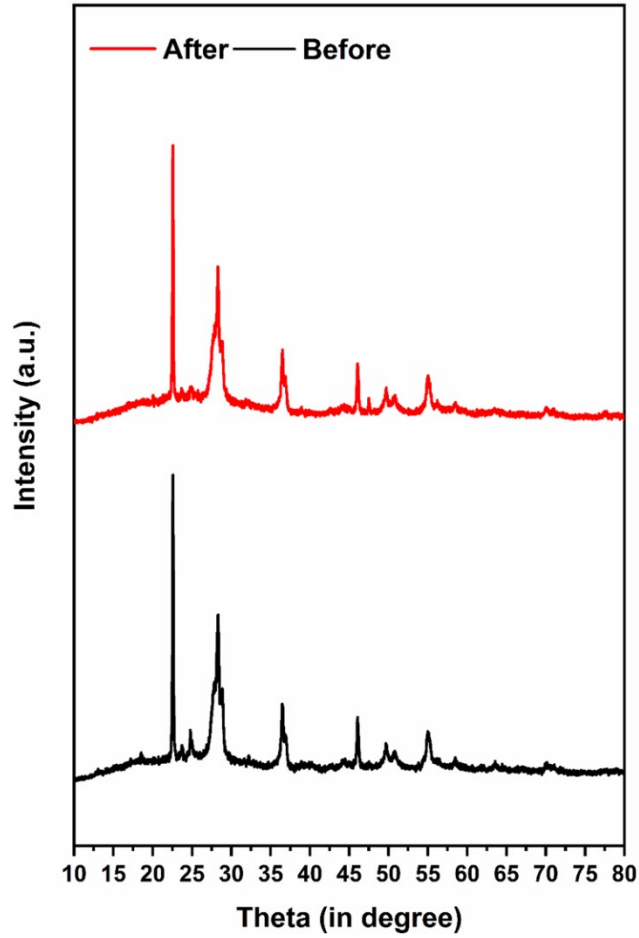


Figure S7. XRD pattern of Pt/UCN/Nb₂O₅-(2) before and after recycling experiments.

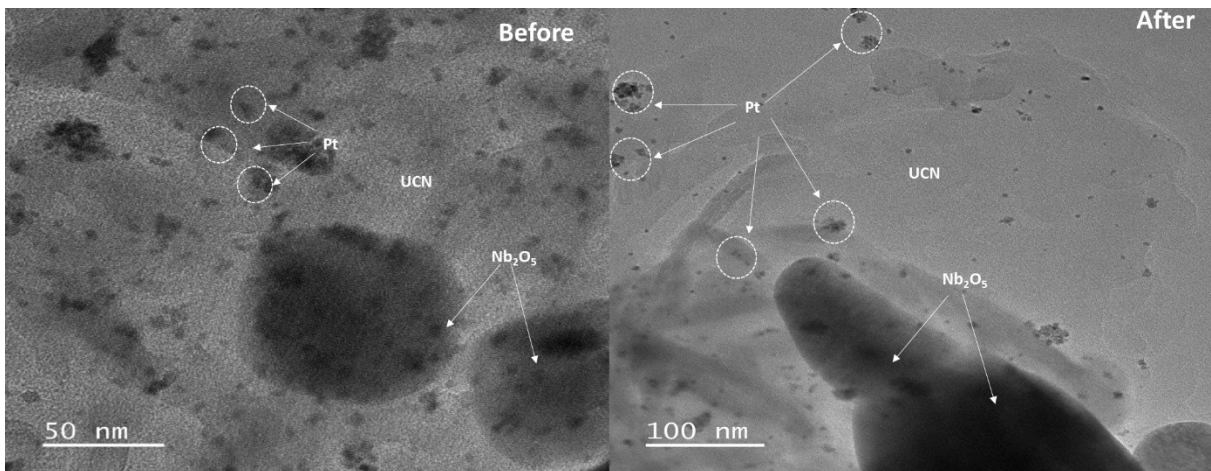


Figure S8. TEM image of Pt/UCN/Nb₂O₅-(2) before and after recycling experiments.

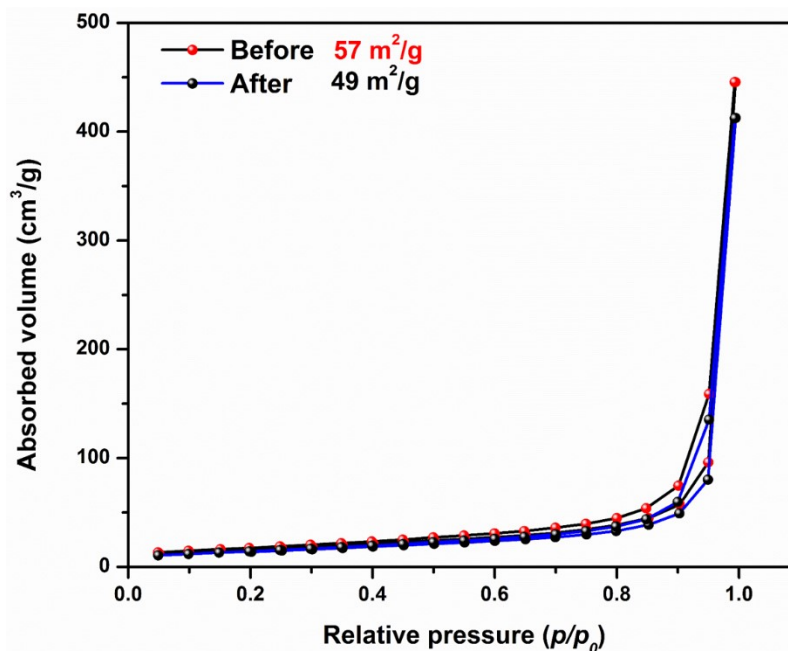


Figure S9. N₂ physisorption isotherm of Pt/UCN/Nb₂O₅-(2) before and recycling experiments

Table S4. XPS-determined surface atomic percentage (%) of Pt/UCN/Nb₂O₅-(2) before and after recycling experiments.

| Catalyst | Elements | | | | |
|--|----------|-------|------|------|------|
| | C | N | O | Nb | Pt |
| Pt/ UCN/Nb ₂ O ₅ -(2) – Before catalysis | 41.09 | 50.33 | 4.37 | 1.28 | 2.94 |
| Pt/ UCN/Nb ₂ O ₅ -(2) – After catalysis | 39.74 | 51.62 | 4.52 | 1.33 | 2.79 |

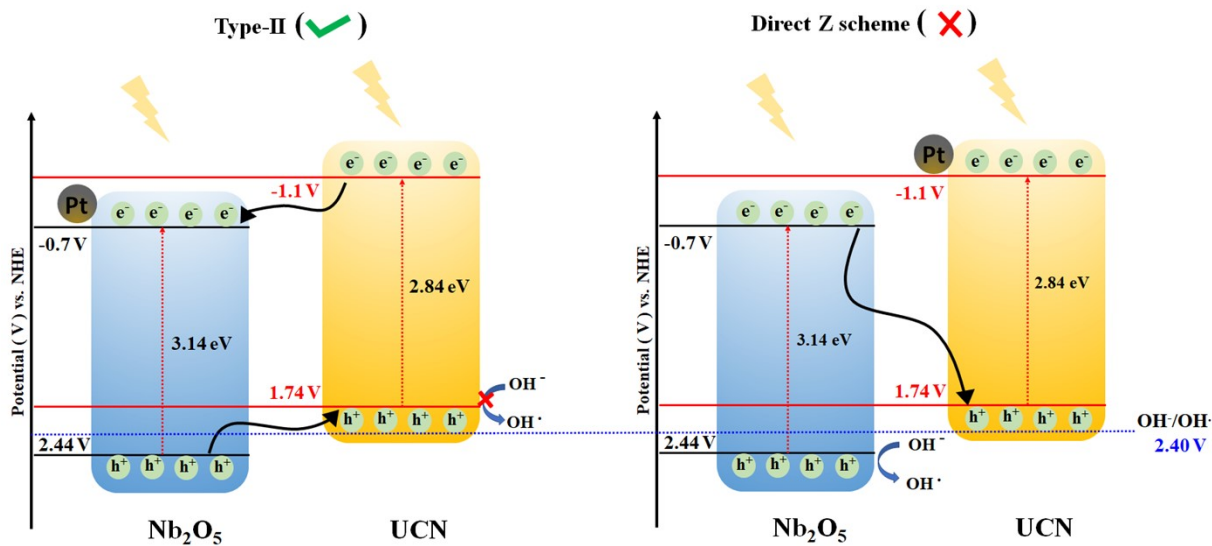


Figure S10. Schematic illustration of the migration pathway of photogenerated electrons and holes in accordance with type-II and direct Z-scheme system of the Pt/UCN/Nb₂O₅-(2) indicating the inhibition of the formation of hydroxyl radical in type -II pathway.

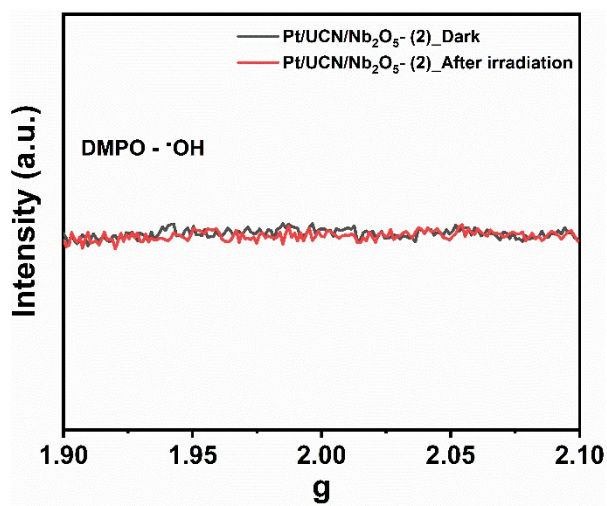


Figure S11. Electron paramagnetic resonance (EPR) spectra of UCN/Nb₂O₅-(2) in water in the presence of DMPO as a spin-trapping agent before and after light irradiation.

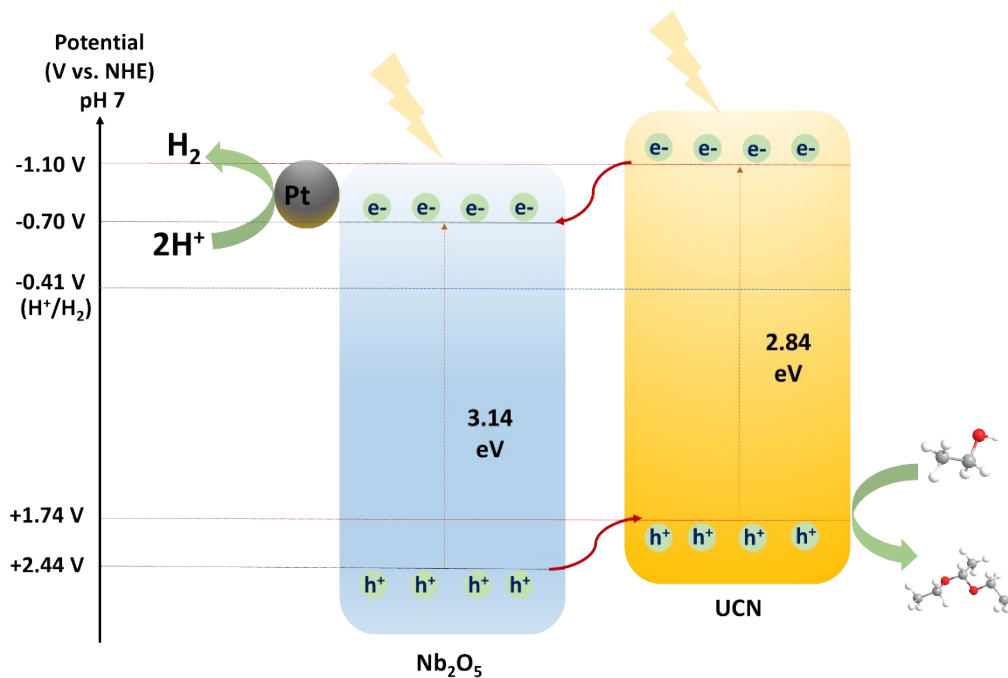


Figure S12. PD of ethanol illustrating the efficient charge transfer mechanism via type (II) process in order to produce H₂ and DEE.

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