Supporting Information

Photodegradation Behavior and Antibacterial Activity of Light Transition Metal-based Tetranapthalene Porphyrin/C_3N_5 Heterojunction

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Sample preparation

Preparation of C_3N_5 nanosheets. The C_3N_5 was synthesized using 3-amino-1,2,4-triazole and thiourea as precursors through a thermal polymerization method. Firstly, the precursors were thoroughly ground into powder with a mass ratio of 2:8, then heated up to 500 °C for 3 h under argon (Ar) atmosphere in a quartz tube furnace, with a heating rate of 5 °C/min^{-1}. The sample were recorded as bulk C_3N_5. Next, the bulk C_3N_5 underwent a re-pyrolysis at 500 °C for 3 h with a heating rate of 5 °C/min^{-1} to obtain C_3N_5 nanosheets.

Preparation of tetranapthalene porphyrin, [$(Np)_4H_2P$]. Building upon the work of previous researchers, the experimental method has been slightly modified [21]. Propionic acid (100 mL) was taken in a 250 mL round bottom flask and heated for 15 min followed by the addition of 2-naphthaldehyde (15.62 g, 0.1 mol) and pyrrole (6.71 g, 0.1 mol). The contents were then refluxed for 12 h under an Ar atmosphere. After the reaction, the solvent was evaporated by distillation under reduced pressure, and the resulting solids were purified through column chromatography using an eluate mixture of dichloromethane and petroleum ether in a ratio of 6/1. Collect purple liquid and steam dry to get pure products.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.9 (s, 8H, β-pyrrole-H), 8.7 (m, 4H, phenyl-H), 8.44 (m, 4H, phenyl-H), 8.23 (m, 8H, phenyl-H), 8.12 (m, 4H, phenyl-H), 7.76 (m, 8H, phenyl-H), -2.61 (s, 2H, imino-H). (as shown in Fig. S2a and b)

Preparation of copper tetranapthalene porphyrin, [$(Np)_4CuP$]. $Cu(NO_3)_2\cdot xH_2O$ (0.368 mmol) and tetranapthalene porphyrin (0.368 mmol) were dissolved in N,N-Dimethylformamide and refluxed for 12 h under Ar gas. The solvent (cold trap liquid nitrogen protection) was removed under reduced pressure distillation, and the obtained solids were purified by column chromatography with a dichloromethane/petroleum ether (6/1) eluent. The red liquid that was collected was dried using steam to obtain the pure product. The preparation of $(Np)_4NiP$ and $(Np)_4ZnP$ is similar to that of $(Np)_4CuP$.

Preparation of copper Tetranapthalene porphyrin/C_3N_5-x, [$(Np)_4CuP$/CN-x]. Nanomaterials were synthesized into $(Np)_4CuP$/CN-x composites by a straightforward wet grinding method. C_3N_5 nanosheets and porphyrin were mixed in a mortar according to a certain mass ratio, with an appropriate amount of absolute ethyl alcohol added during grinding process to ensure fully mixing. Subsequently, the gotten product was collected and dried via oven at 60 ℃ for 4 h to obtain the target compounds. $(Np)_4$NiP/CN-x and $(Np)_4$ZnP/CN-x are prepared in the same way as $(Np)_4$CuP/CN-x.

Characterization

Scanning electron microscopes (SEM; ZEISS, MERLIN Compact, Germany) and transmission electron microscopy (TEM; FEI, tecnai F20) were used to explore the morphology and microstructure. The samples were analyzed for phase composition using an X-ray diffractometer (XRD; Rigaku, SmartLab 9 Kw, Japan). The ^{1}H NMR spectra were obtained on a Quantum-1 400 MHz spectrometer (Q. One Instruments Ltd., Quantum-1, China). High resolution mass spectrometry (HRMS) was obtained by ultra-high performance liquid chromatography (ACQUITY UPLC I-Class PLUS, Waters, America) tandem quadrupole-time-of-flight mass spectrometer (Qtof, Xevo G2-XS, Waters, America). The Fourier transform-infrared (FT-IR; Thermo Nicolet iS5) spectrometer was employed for surface-functional groups analysis of the catalysts. X-ray photoelectron spectroscopy (XPS; Thermofisher escalab 250xi) was performed to ascertain the chemical states of C_3N_5、$(Np)_4$CuP and $(Np)_4$CuP/CN-0.5. A BrunauerEmmett-Teller (BET;) analysis using the Micromeritics 3 Flex Version 5.00 was conducted to assess the influence of surface area on the efficiency of photocatalytic degradation. This analysis involved the measurement of surface area by means of the adsorption and desorption of nitrogen gas molecules. The UV-visible diffuse reflectance spectrophotometer (UV-vis DRS, Shimadzu 3600-plus) was used to investigated the optical properties of the prepared samples, with $BaSO_4$ serving as the reference material. Solid state photoluminescence (PL) spectra were acquired on an Edinburgh FLS-1000 fluorescence spectrophotometer (λex = 395 nm)

Electrochemical measurements

The Mott-Schottky (M-S) curves, electrochemical impedance spectroscopy (EIS) and transient photocurrent response (i-t curves) were measured by the electrochemical workstation (CHI660C Apparatuses). During the experiments, the counter electrode is constructed from Pt foil, the working electrode consists of photocatalysts coated on FTO glass, and the reference electrode is an Ag/AgCl electrode. The process of preparing the working electrode included dispersing 2 mg of the catalyst in 200 μL of DMF. Following this, 10 μL of nafion was added, and the mixture was sonicated for 1 h. Subsequently, 200 μL of the slurry was applied to 1×2 cm^2 FTO glass and allowed to dry naturally. The electrolyte in the experiment was 0.1 M Na_2SO_4.

Photocatalytic bacteriostasis experiment

Bacterial Culture

Prepare the culture medium: Select an appropriate culture medium according to the type of bacteria to be cultured. For example, LB medium is used for the culture of common bacteria such as Escherichia coli. Add the culture medium powder to an appropriate amount of distilled water according to the instructions, stir well, and then perform sterilization treatment. Usually, the autoclaving method is adopted, and sterilization is carried out at 121 °C and a pressure of 1.05 kg/cm^2 for 20 min.

Inoculate the bacteria: On an aseptic workbench, use a pipette to take an appropriate amount of bacterial liquid and inoculate it into a sterilized solid culture medium that has been cooled to an appropriate temperature. The spread plate method is used to evenly distribute the bacteria on the surface of the culture medium.

Culture the bacteria: Place the inoculated culture medium under suitable culture conditions. Escherichia coli is cultured in a constant-temperature incubator at 37 °C for 18 h, and Staphylococcus aureus is cultured at 37 °C for 24 h.

Initial Bacterial Concentration Calibration Method

Plate Count Method

Prepare diluted bacterial solutions: Take a certain amount of the bacterial liquid to be calibrated and perform gradient dilution with sterile physiological saline. Dilute it into bacterial solutions with different dilution factors such as 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-7} in sequence.

Spread the plates: Take 0.1 mL of bacterial solutions with different dilution factors respectively and evenly spread them on solid culture medium plates. Prepare 3 parallel plates for each dilution factor.

Culture and count: Put the plates into an incubator and observe the growth of colonies on the plates after culturing at an appropriate temperature for a certain period. Select the plates with the number of colonies between 30 and 300 for counting, and calculate the average number of colonies on each plate. Calculate the concentration of bacteria in the original bacterial liquid based on the dilution factor and the volume of the spread bacterial liquid. For example, if the average number of colonies on a certain plate is 50, and the spread bacterial liquid is 0.1 mL of the 10^{-4} dilution factor, then the concentration of the original bacterial liquid is $50 \div 0.1 \times 10^4 = 5 \times 10^6$ CFU/mL.

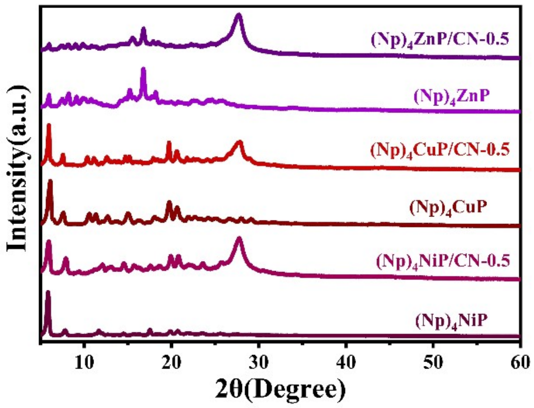

Figure S1. XRD patterns of $(Np)_4MP$ and $(Np)_4MP/CN-0.5$ (M=Ni, Cu, Zn).

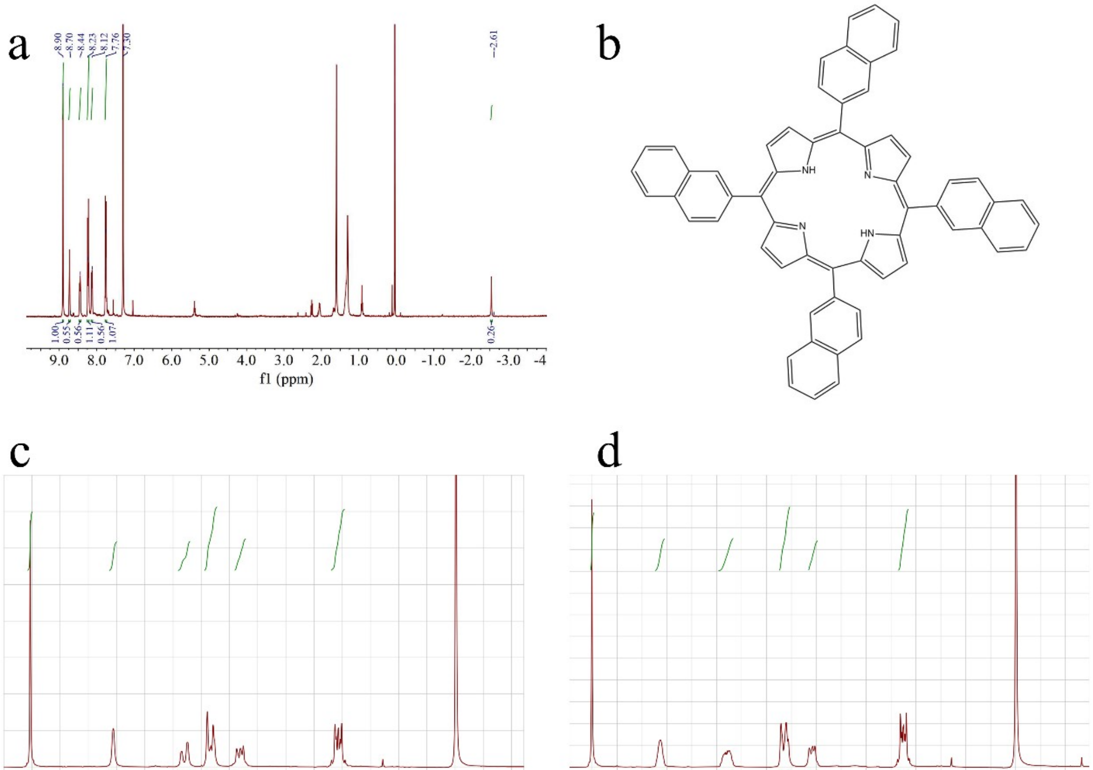

Figure S2. 400 MHz ^1H NMR spectrum of (a) $(Np)_4H_2P$ (c) $(Np)_4NiP$ and (d) $(Np)_4ZnP$; structure diagram of (b) $(Np)_4H_2P$.

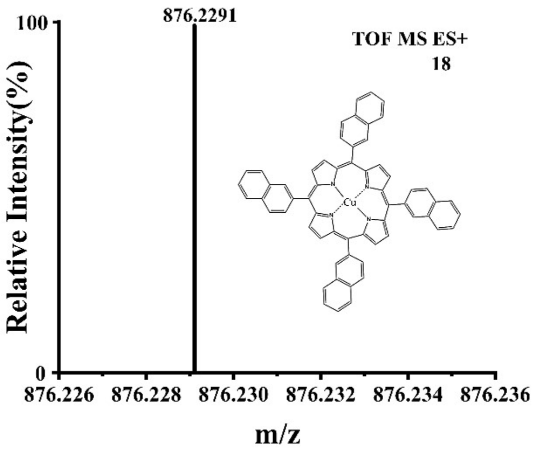

Figure S3. HRMS spectra of $(Np)_4CuP$.

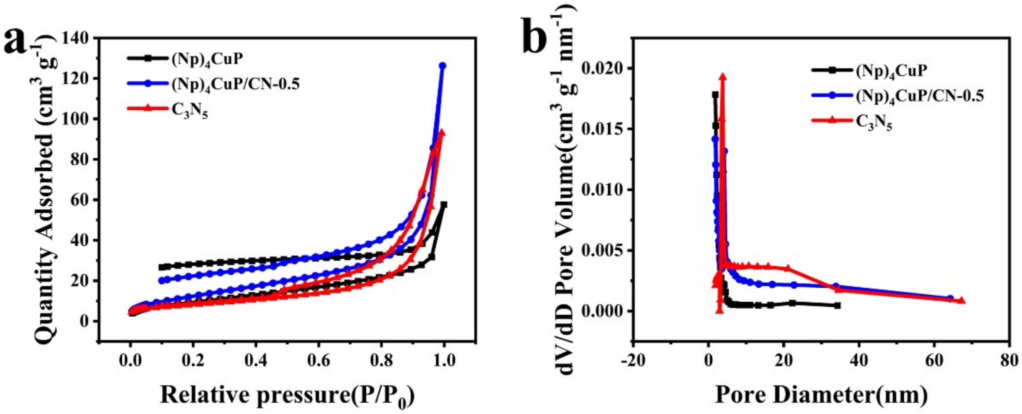

Figure S4. (a) N_2 adsorption-desorption isotherms curves of C_3N_5, $(Np)_4CuP$ and $(Np)_4CuP/CN-0.5$; (b) pore size distribution curves of C_3N_5, $(Np)_4CuP$ and $(Np)_4CuP$ /CN-0.5.

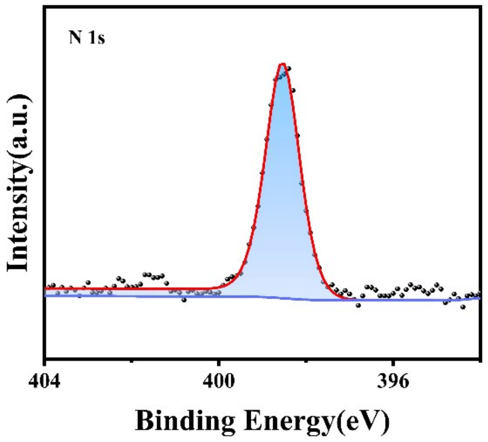

Figure S5. High-resolution XPS spectra of N 1s in $(Np)_4CuP$.

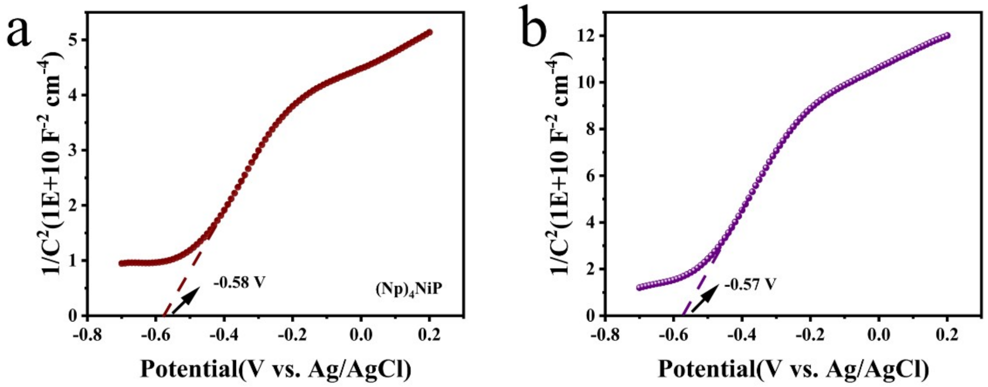

Figure S6. Mott-Schottky curves of (a) $(Np)_4NiP$ and (b) $(Np)_4ZnP$.

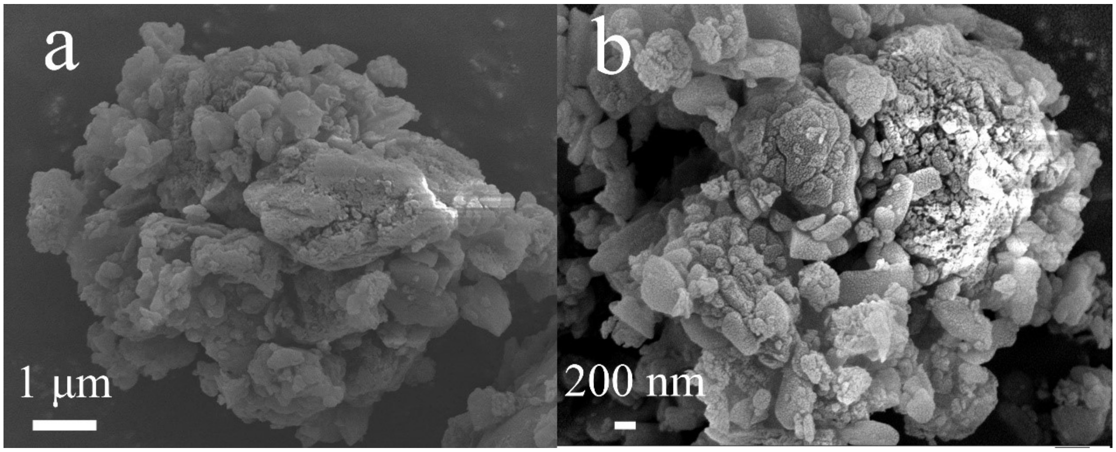

Figure S7. SEM images of $(Np)_4CuP$ catalyst before (a) and after (b) catalysis.

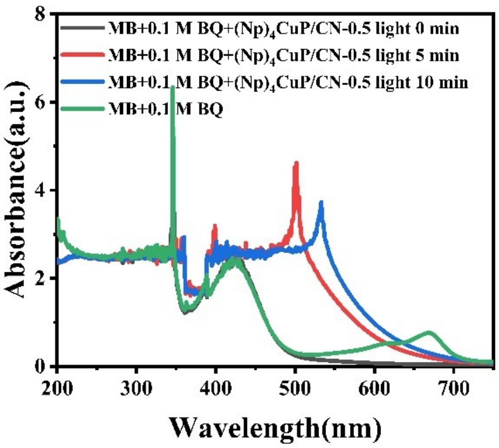

Figure S8. UV-vis absorption spectra of 20 ppm MB + 0.1 M BQ and 20 ppm MB + 0.1 M BQ + catalyst at different illumination times.

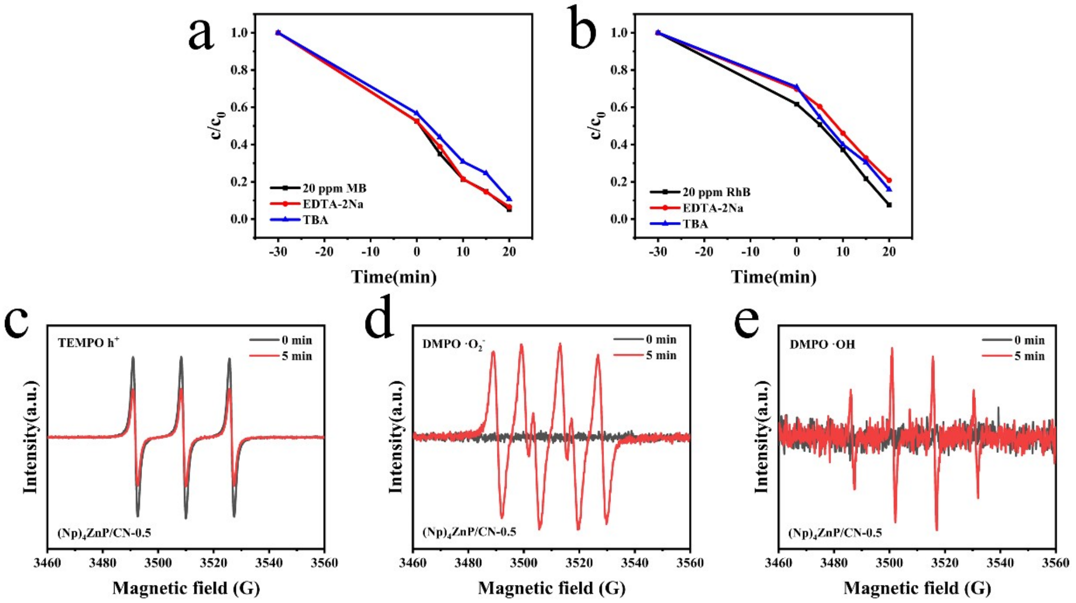

Figure S9. Photocatalytic degradation curves of (Np)$_4$ZnP/CN-0.5 for MB (a) and RhB (b) under different scavengers; The EPR spectra of (Np)$_4$ZnP/CN-0.5 under light and dark with TEMPO dispersed in water for h$^+$ (c), DMPO dispersed in water for ·O$_2^-$ (d) and ·OH (e).

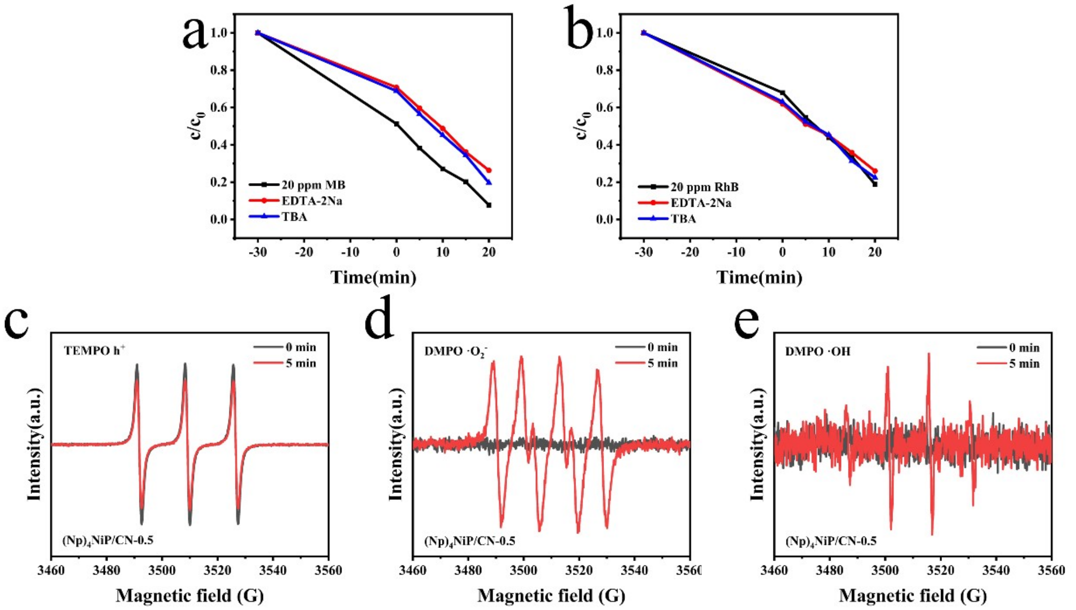

Figure S10. Photocatalytic degradation curves of (Np)$_4$NiP/CN-0.5 for MB (a) and RhB (b) under different scavengers; The EPR spectra of (Np)$_4$NiP/CN-0.5 under light and dark with TEMPO dispersed in water for h$^+$(c), DMPO dispersed in water for ·O$_2^-$ (d) and ·OH (e).

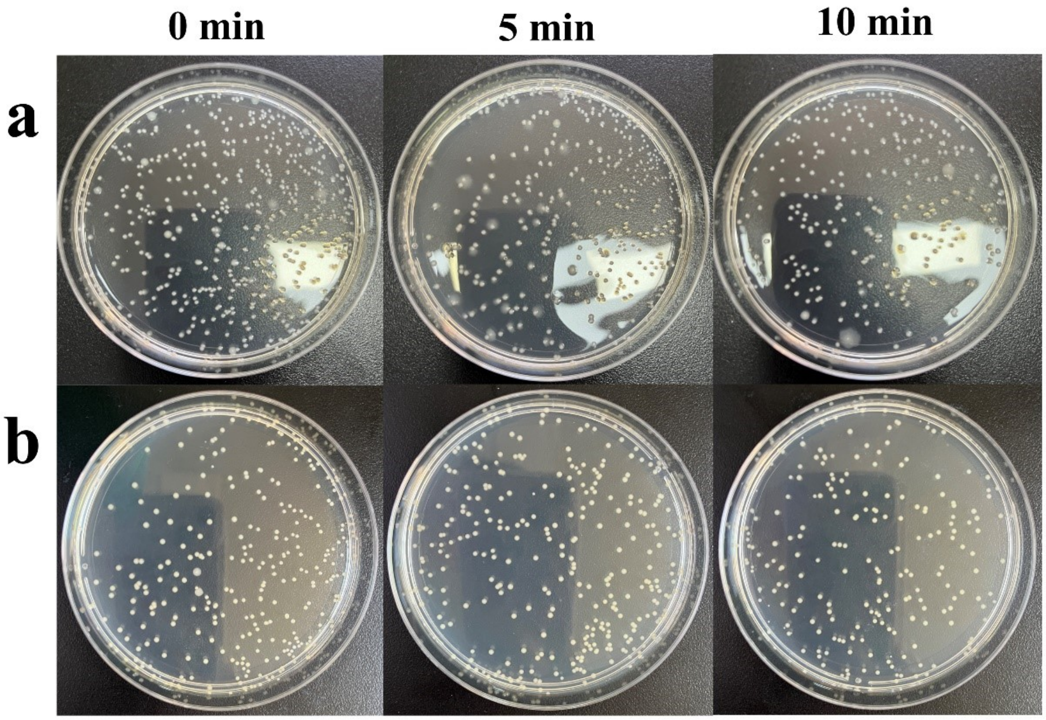

Figure S11. Effect of light on (a) *E. coli* and (b) *S. aureus* at different time.

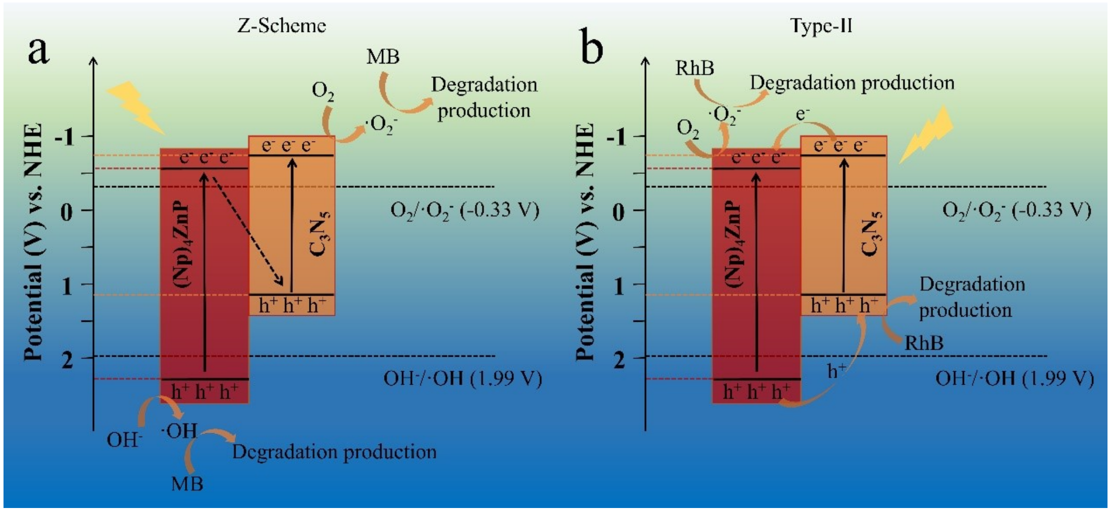

Figure S12. (a) Z-scheme mechanism of MB degradation and (b) type-II mechanism of RhB degradation under visible light illumination by $(Np)_4ZnP/CN-0.5$.

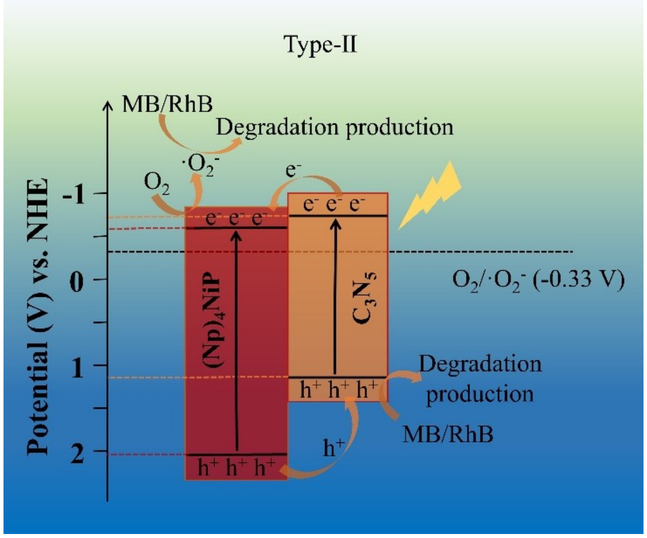

Figure S13. Possible type-II mechanism of MB/RhB degradation under visible light illumination by $(Np)_4NiP$/CN-0.5 composite materials.

$(Np)_4NiP$/CN-0.5 Mechanism of photocatalytic degradation of dyes. On the base of the above information, a type-II mechanism for the dyes photodegradation using the $(Np)_4NiP$ hybridized C_3N_5 photocatalyst is proposed as illustrated in Figure S11. The CB edges of C_3N_5 and $(Np)_4NiP$ are −0.698 V and −0.58 V respectively, while the VB edges of C_3N_5 and $(Np)_4NiP$ are +1.092 V and +2.02 V respectively. Both the C_3N_5 and $(Np)_4NiP$ can be excited by visible light and produce photogenerated electrons and holes. Since the CB position of $(Np)_4NiP$ is lower than that of C_3N_5, the photoinduced electrons on the CB of C_3N_5 can directly transfer to the CB of $(Np)_4NiP$. Consequently, the photoinduced electrons in CB of $(Np)_4NiP$ are reducing agents that could capture the adsorbed O_2 onto the composite catalyst surface and reduce it to $\cdot O_2^-$. Subsequently, dyes can be degraded by oxidation reaction with $\cdot O_2^-$. Meanwhile, the corresponding VB potential of C_3N_5 is less than that of $(Np)_4NiP$, the photogenerated h^+ on the VB of $(Np)_4NiP$ can spontaneously immigrate to the VB of C_3N_5. The h^+ on VB of C_3N_5 can directly degrade the organic compounds under visible light irradiation. Hence, the traditional type-II heterojunction is conducive to the degradation of MB/RhB. The possible mechanism of $(Np)_4NiP$/CN-0.5 material decomposition of dyes is as follows:

$$(Np)_4NiP/CN\text{-}0.5 \rightarrow h^+ + e^- \quad (1)$$

$$e^{-} + O_2 \rightarrow \cdot O_2^{-} \quad (2)$$

$$\cdot O_2^{-} + \text{MB/RhB} \rightarrow \text{Degradation product} \quad (3)$$

$$h^{+} + \text{MB/RhB} \rightarrow \text{Degradation product} \quad (4)$$