Characterization

A Bruker AXS D8-Focus diffractometer with Cu Ka radiation (Germany) was used to record the X-ray powder diffraction (XRD) patterns. Scanning electron microscopy (SEM, Sirion) and transmission electron microscopy (TEM, G220 FEI) were used to observe the morphology and microstructure. Fourier transform infrared spectroscopy (FTIR) was measured by a TENSOR27 infrared spectrometer from Bruker, Germany. Electron spin resonance (ESR) experiments were performed on a Bruker A300 spectrometer (Germany). XPS measurements were performed on a Kratos AXIS Ultra DLD spectrometer with a monochromatic Alka X-ray source. Element analysis (EA) was performed on Vario MICRO. The photoluminescence (PL) measurements were performed on an RF-5301PC spectrofluorophotometer with an excitation wavelength of 400 nm. Ultraviolet-visible (UV-vis) absorption spectra and UV-vis diffuse reflectance spectra were recorded on a Shimadzu UV-3600 spectrophotometer. The chromatographic determination was carried out on an Agilent 1260 Infinity series HPLC/DAD system (Agilent Technologies, CA, USA).

Photoelectrochemical measurements

Electrochemical measurements were performed on a CHI 660D electrochemical workstation using a standard three-electrode cell with a working electrode, a standard Ag/AgCl electrode as the reference electrode, and a Pt electrode as the counter electrode. An aqueous solution of 0.5 M Na_2SO_4 was used as an electrolyte and the working electrode was prepared as below: 5 mg of photocatalyst was dispersed in 1 mL of ethanolic solution contained Nafion (3 v/v%) and then sonicated for 30 min to give a homogenous suspension. Then, the mixed solution was dropped on 2.5 × 2.5 cm FTO (Fluorine doped tin oxide) substrate by spin coating technique and left under the air to be dried.

Density functional theory (DFT) calculations

The Cambridge Sequential Total Energy Package (CASTEP) is used to calculate the structure optimization, adsorption and other related electronic structure properties in this work. Generalized gradient approximation of the PBE functional (GGA-PBE) method was used to describe the exchange-correlation

energy of electrons and the ultrasoft pseudopotential in the Vanderbilt form was taken to describe ion-electron interaction.

Table S1. Element distribution of as-synthesized samples from XPS data and EA.

Samples	C/at %	N/at %	O/at %	C:N(C/N)[a]
CN	42.35	56.45	1.20	3:4(0.73)
Nv-CN	44.67	50.47	4.86	3.54:4(0.85)
Cv-CN	38.96	58.82	2.22	2.65:4(0.66)

a) EA value in parentheses.
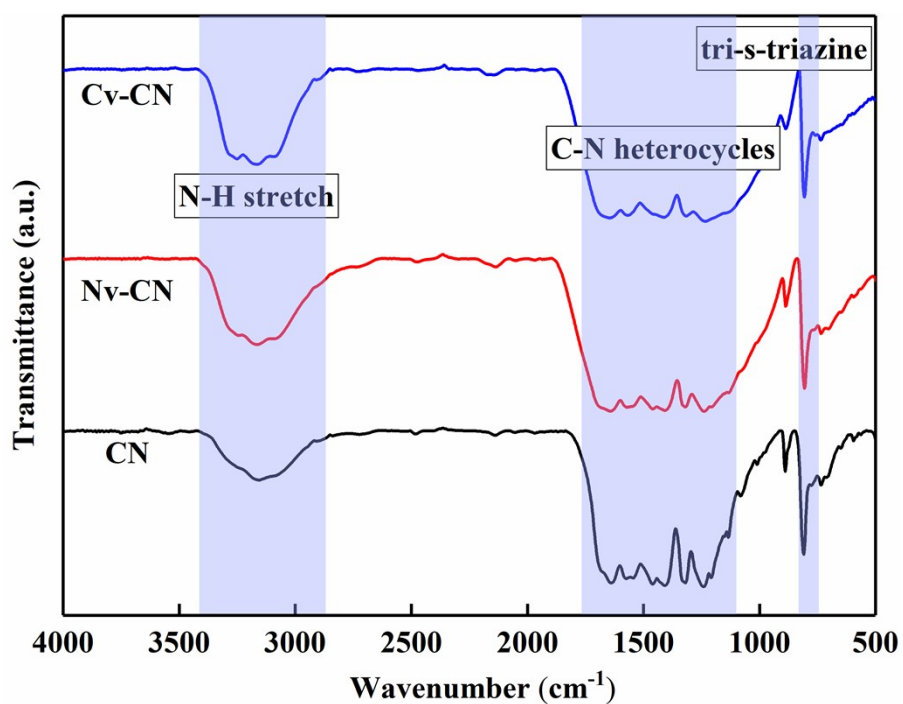
Fig. S1. FTIR patterns.
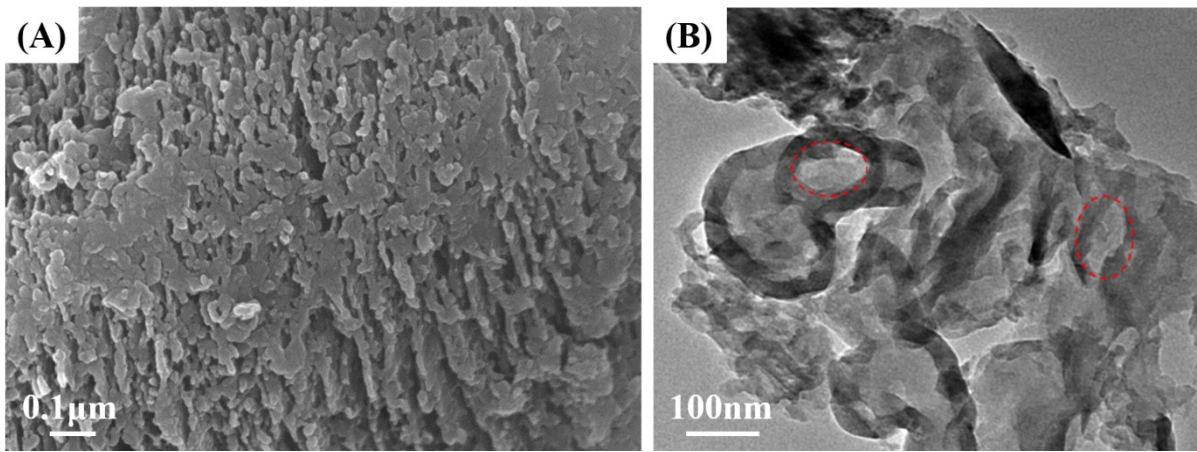
Fig. S2. (A) SEM image of Nv-CN, (B) TEM image of Nv-CN.
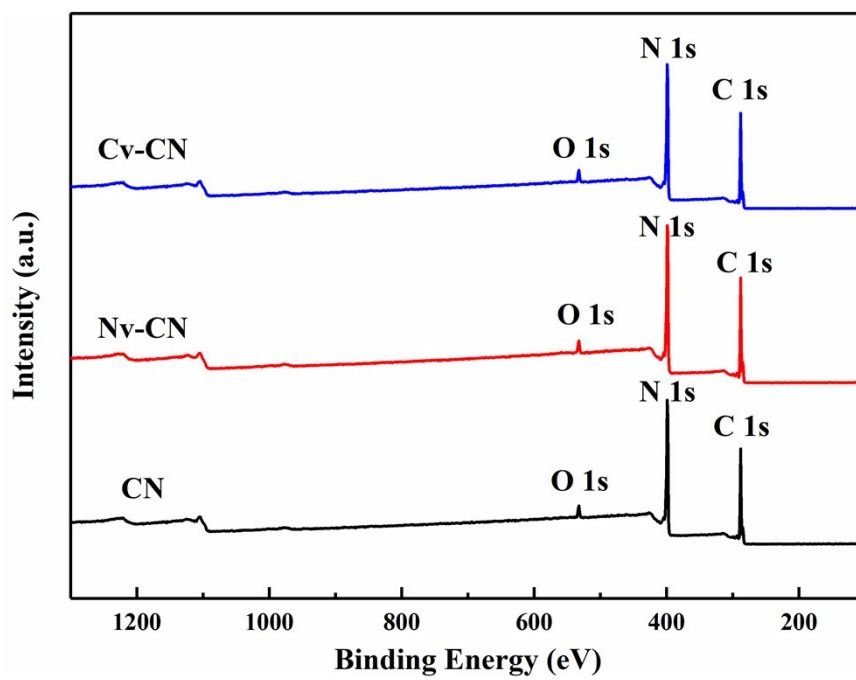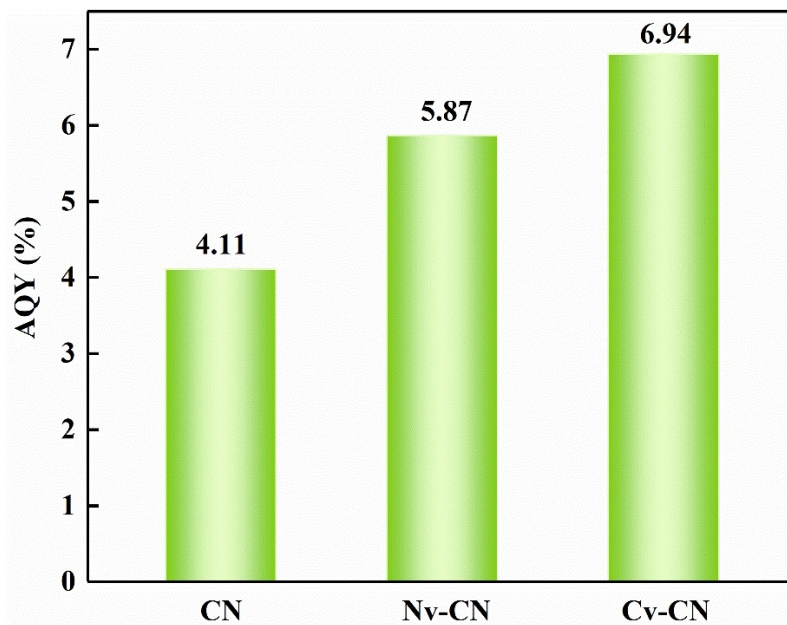
Fig. S3. XPS survey spectra of CN, Nv-CN and Cv-CN.

Fig. S4. Comparison of the AQY (H_2O_2) values at $\lambda=420$nm.
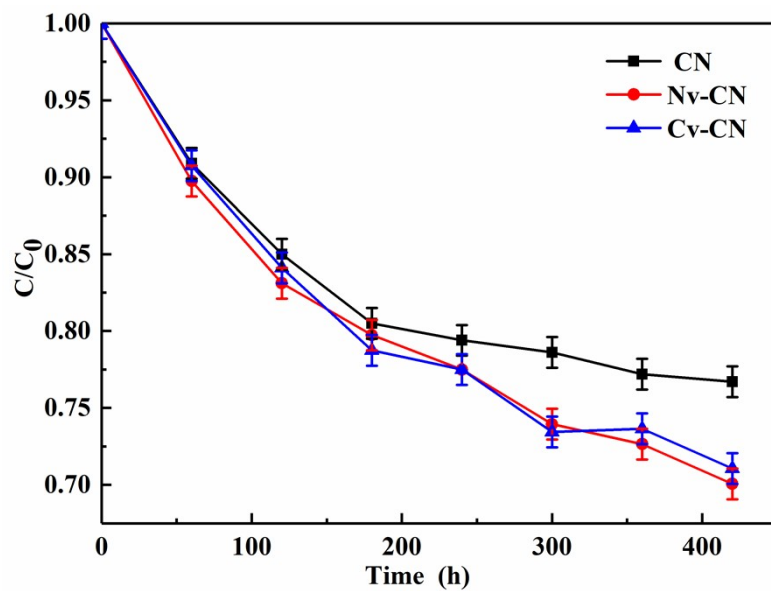
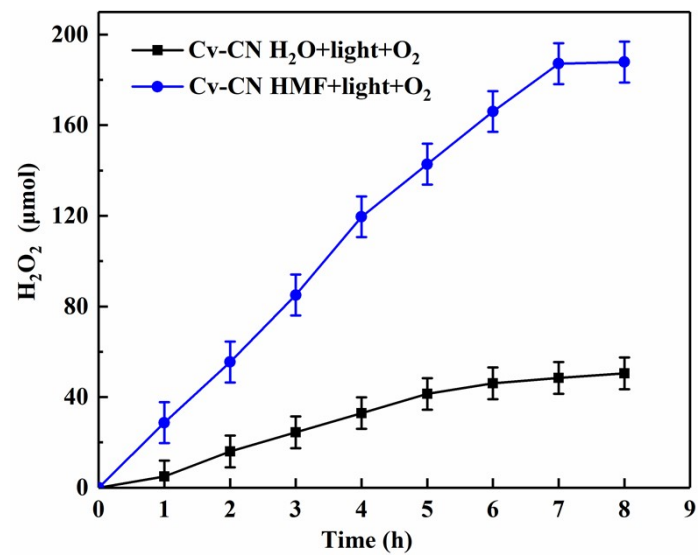**Fig. S5.** Experimental results of catalytic decomposition of H_2O_2.

Fig. S6. Results of catalytic of H_2O_2 by Cv-CN under different conditions.
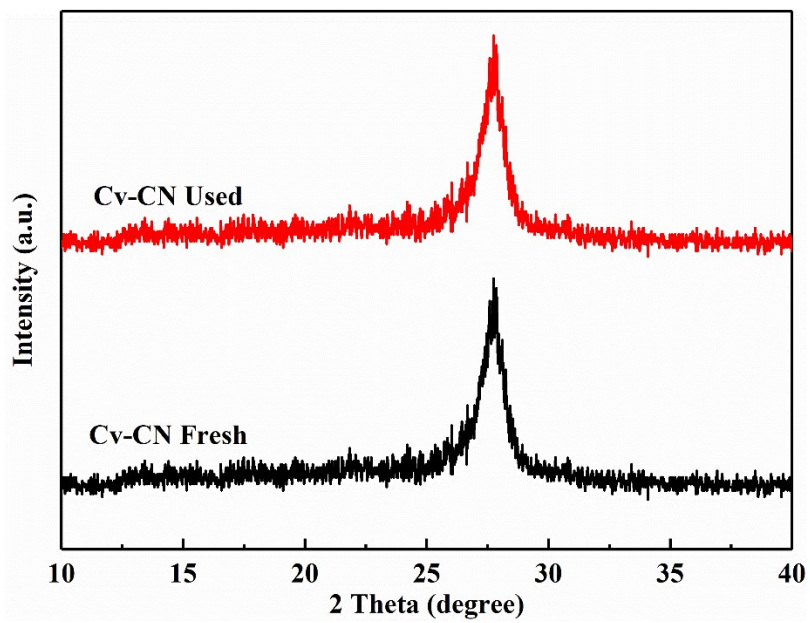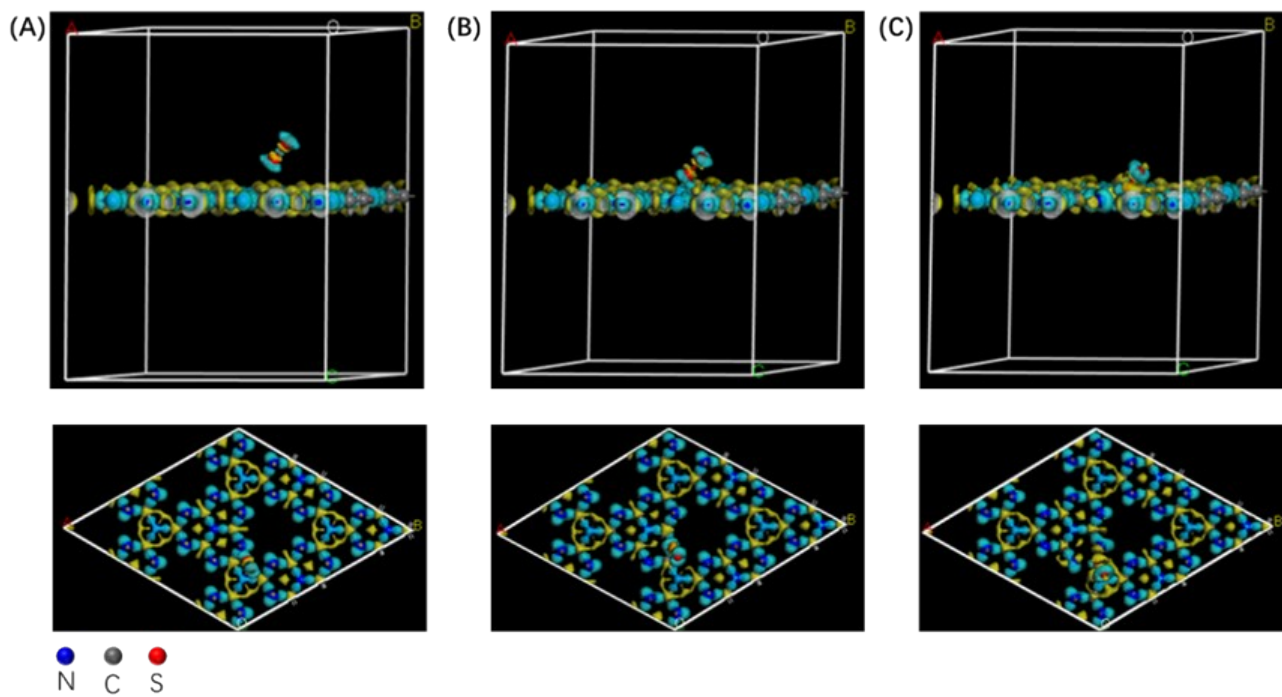
Fig. S7. XRD patterns of fresh and used Cv-CN.

Fig. S8. Differential charge diagram of oxygen adsorption by (A) CN (B) Nv-CN and (B) Cv-CN, with yellow and grayish blue portions representing accumulated and depleted electrons, respectively.