Electronic Supplementary Information (ESI) For

Photocatalytic Oxidation of Water by Polymeric Carbon Nitride Nanohybrids made of Sustainable Elements

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Supporting Information

Synthesis of Carbon Nitride: CNS sample was synthesized by directly heating trithiocyanuric acid (2g) at 650°C for 2 h under flowing nitrogen gas (10 mL/min). g-C_3N_4 sample was synthesized by using melamine as the precursor at and heating at 600 °C for 4h under flowing nitrogen gas (10 mL/min). Mesoporous graphitic carbon nitride (mpg-C_3N_4) was synthesized by using 12-nm SiO_2 particles (Ludox HS40, Aldrich) as the template and the mass rate of silica/cyanamide was controlled as 1:1. After heating at 550°C for 4h, the resulting brown-yellow powder was treated with 4M NH_4HF_2 for 24 h to remove the silica template.

Synthesis of Monodispersed Co_3O_4 Nanoparticles: Cobalt(II) acetate tetrahydrate ($Co(CH_3COO)_2.4H_2O$) (0.5 g) was dissolved in a mixture of water (2 ml) and ethanol (23 ml) under magnetic stirring at 45 ºC. After complete dissolution of the salt, ammonia was dropwise added (2.5 ml, 33%) under magnetic stirring at 45 ºC. Formation of the cobalt oxide nanoparticles takes place at 80 ºC, during 3 hours. To wash nanoparticles, acetone (100 ml) was added into 27 ml of cobalt oxide crude product, and the solution immediately became turbid. After centrifugation at 4500 rpm for 20 min, the precipitate of Co_3O_4 NPs was obtained and reddish supernatant containing unreacted cobalt salt was discarded. In the second step of washing, Acetone (120 ml) was added into Co_3O_4 NPs solution (12 ml in methanol), followed by centrifugation (4500 rpm, 20 min). Remaining nanoparticles were redispersed in methanol (20 ml). Final product of cobalt oxide nanoparticles (120 mg) was obtained by complete evaporation of the methanol.

Modification of Carbon Nitride with Cocatalyst:

(a)Loading Cocattalyst by Impregnation Method: Cr_2O_3, RuO_2, CuO, Fe_2O_3, NiO, Mn_3O_4, Ir_2O_3, Rh_2O_3 and Co_xO_y were loaded on to carbon nitride powder by impregnation from the solution of $CrCl_2$, $RuCl_3$, $Cu(NO_3)_2.2.5H_2O$, $FeCl_3.6H_2O$, $NiCl_2.6H_2O$, $Mn(NO_3)_2.H_2O$, $IrCl_4.2HCl.6H_2O$, Na_3RhCl_6, and $CoCl_2.6H_2O$, respectively. For a typical preparation: 0.1g carbon nitride powder was impregnated into 4 ml water containing certain amount of desired metal salt and the resulting solution was kept in ultrasonic bath for 10 second. After drying, the resulting mixture was calcined in air at 300°C for 1h. The loading amount was based on the metal specie.

(b)Loading Co_3O_4 by Coating Method: Co_3O_4 nanoparticles were previously dispersed in methanol with the desired concentration (0.5mg.mL^{-1}), which was then subject to ultrasonic treatment for 30 min to promote the dispersion of Co_3O_4 in the solution. Carbon nitride powder was first dispersed in 5mL methanol, and then a certain amount of the Co_3O_4 solution was added to the mixture. After drying in oil bath, the mixture was transferred to a vacuum oven and kept at 60°C overnight to remove the methanol. To strengthen the interaction between Co_3O_4 nanoparticles and the carbon nitride matrix, the resulting mixture was further treated at 150°C for 2h in air. The loading amount was based on cobalt oxide.

(c) Calculating the number of Co_3O_4 on CNS: Number of cobalt oxide nanoparticles used in the photocatalysis was calculated by assuming that each particle has spherical shape, as determine from TEM analysis. Using Co_3O_4 NPs with radius equal to 3.03 nm gives 14.57 nm^3 of one particle volume. Taking 6.11 g/cm^3 as Co_3O_4 density gives 8.88×10^{-20} g of one particle weight. Therefore, dividing total weight of Co_3O_4 NPs (0.0015g) by weight of one particle, become 1.69×10^{16} particles used in the photocatalytic process.

Characterization: Powder X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance diffractometer with CuKα1 radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized AlKα line source (200W). All binding energies were referenced to the C1s peak at 284.6 eV. The UV-Vis diffuse reflectance spectra (DRS) and liquid UV-Vis absorption spectra were performed on Varian Cary 500 Scan UV-visible system and Varian Cary 50 Scan UV-visible system, respectively. Nitrogen adsorption-desorption isotherms were collected at 77 K using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Fourier transformed infrared (FTIR) spectra were recorded on BioRad FTS 6000 spectrometer. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained by JEOL model JEM 2010 EX instrument at the accelerating voltage of 200 kV. The photoluminescence spectra (PL) were surveyed by Edinburgh FL/FSTCSPC920 spectrophotometer. The concentration of Co species in the reaction solution was analyzed by Inductively Coupled Plasma (ICP) OES spectrometer (Ultima2). TG was performed on TG209 (NETZSCH Co.).

***Photocatalytic Test*:** Photocatalytic O_2 production was carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. For each reaction, 50 mg catalyst powder was well dispersed in an aqueous solution (100 mL) containing $AgNO_3$ (0.01M) as an electron acceptor and La_2O_3 (0.2g) as a pH buffer agent. The reactant solution was evacuated several times to remove air completely prior to irradiation under a 300 W Xe lamp and a water-cooling filter. The wavelength of the incident light was controlled by using an appropriate long pass cut-off filter. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector. The apparent quantum yield (AQY) for O_2 evolution was measured using a similar experimental setup but with a band pass filter (λ = 420.5 nm), and was estimated as:

$$\text{AQY (\%)} = (8\times R/I)\times 100$$

where R, and I represent the rates of O_2 evolution and incident photons, respectively. The total number of incident photons (49.4 mW) was measured using a calibrated silicon photodiode

Electrochemical Analysis: For electrochemical measurement, catalysts were transformed from powders into film electrodes. And this kind of film electrodes were made by dip-coating the catalyst slurry ($25mg.ml^{-1}$ in DMF) onto fluoride-tin oxide (FTO) conductor glass and the area was controlled as $0.25cm^{-2}$. After heating at 350°C in air, the uncoated part of FTO electrode was isolated. Electrochemical performances were performed in a conventional three electrode cell, using a Pt plate and an Ag/AgCl electrode (3 M KCl) as counter electrode and reference electrode, respectively. A 0.2 M Na_2SO_4 aqueous solution (pH6.6) without additive was chosen as the supporting electrolyte and was purged with nitrogen to remove O_2 before any measurements. The current-voltage measurements were conducted with a CHI 660d workstation, with the working electrodes irradiated from the back side in order to minimize the influence of thickness of the semiconductor layer. The visible light was generated by a 300 W Xe lamp with 420 nm and IR cut-off filters, and was chopped manually.

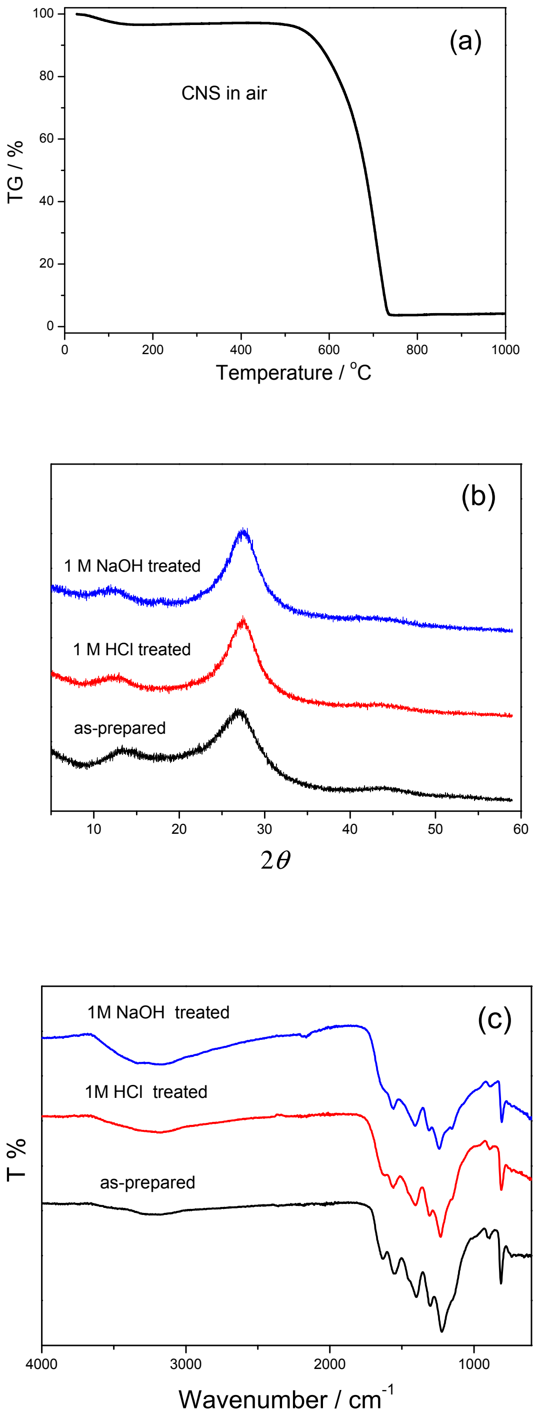


Figure S1. Stability test of carbon nitride: (a) TG curve in air of CNS indicating the excellent thermal stability up to 550^{o}C against oxidation. Powder X-ray diffraction pattern (b) and Fourier transformed infrared spectra (c) of CNS before and after HCl (1 M) or NaOH (1M) treatments.

Table S1. Photocatalytic Activities of CNS Loaded with Various Cocatalysts under UV Irradiation (λ > 300 nm)

			Photocatalytic activity		
Entry	Cocatalyst	wt. %	O_2 (μmol h^{-1})	N_2 (μmol h^{-1})	O_2 selectivity[a]
1	none	0	18.8	8.6	68.6
2	CuO	3	2.4	3.0	44.4
3	Cr_2O_3	3	3.5	4.3	44.9
4	Mn_3O_4	3	4.1	3.5	54.0
5	RuO_2	3	4.9	8.6	36.3
6	Fe_2O_3	3	5.8	4.5	56.3
7	NiO	3	10.5	6.5	61.8
8	Ir_2O_3	3	12.6	6.7	65.3
9	Rh_2O_3	3	22.4	5.0	81.8
10	Co_xO_y	1	41.9	4.2	90.9
11	Co_xO_y	2	42.3	4.3	90.8
12	Co_xO_y	3	53.7	4.1	92.9
13	Co_xO_y	5	11.8	4.0	74.7
14	[b]Co_xO_y	3	41.2	4.1	91.0
15	[c]Co_3O_4	3	31.5	1.6	95.2
16	[d]$Co(NO_3)_2$	3	33.0	4.2	88.7

a. O_2 selectivity was calculated by $100[M_{O2}/(M_{O2}+M_{N2})]$ (Where M = Molar quantity).

b. Co_xO_y prepared from $Co(NO_3)_2.6H_2O$.

c. Co_3O_4 was purchased from Alfa Aesar.

d. Just using $Co(NO_3)_2$ as cocatalyst.

Table S2. Ubiquity Enhanced Activities of Photocatalysis Water Oxidation Promoted by Co_xO_y for Carbon Nitride Based Photocatalysts. Reactions were Taken under UV Irradiation (λ > 300 nm)

		Photocatalytic activity		
Entry	Catalyst	O_2 (μmol h^{-1})	N_2 (μmol h^{-1})	O_2 selectivity[a]
1	CNS	18.8	8.6	68.6
2	3%wt. Co_xO_y/CNS	53.7	4.1	92.9
3	g-C_3N_4	2.9	1.9	60.4
4	3%wt. Co_xO_y/g-C_3N_4	41.1	3.1	93.0
5	*3%wt. RuO_2/g-C_3N_4	6.3	3.1	67.0
6	#mpg-C_3N_4	4.2	17.2	19.6
7	3%wt. Co_xO_y /mpg-C_3N_4	13.2	5.9	69.1

* RuO_2 was taken as the reference.

[#] mesoporous graphitic carbon nitride.

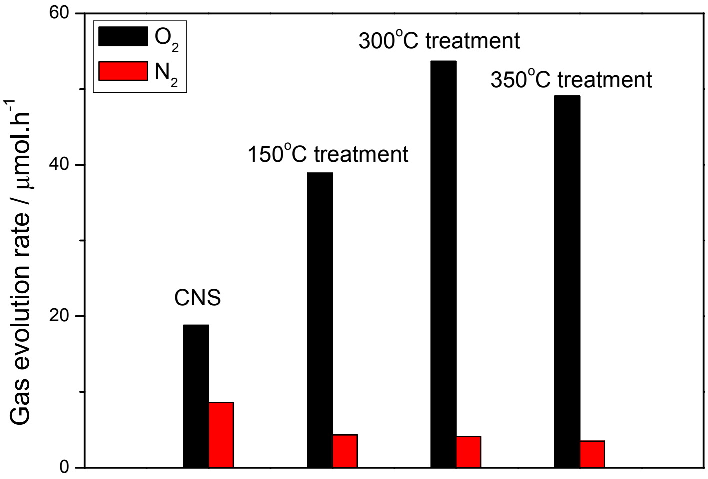


Figure S2. The relationship between the temperature of heat treatment and the photocatalytic activities of 3wt.% Co_xO_y/CNS sample.

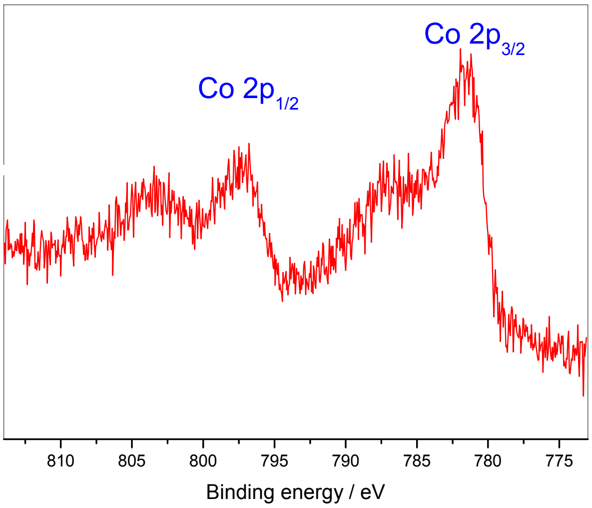


Figure S3. XPS spectrum of Co lines obtained from 3%wt.Co_xO_y/CNS sample.

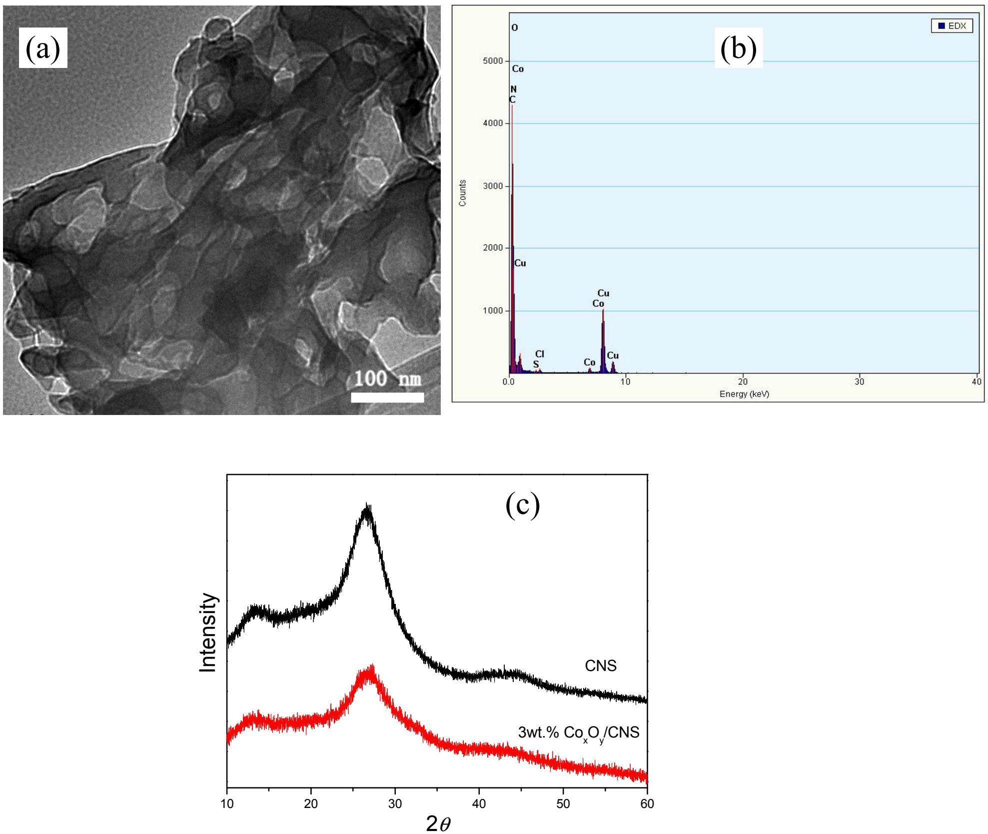


Figure S4. TEM image (a) and the corresponding EDX spectra (b) of 3%wt.Co_xO_y/CNS. (c) Powder X-ray diffraction pattern of CNS and 3%wt. Co_xO_y/CNS. No solid-state cobalt species can be found with TEM and XRD investigations, but the result of EDX analysis confirmed the presence of cobalt in CNS matrix, which was further realized as Co(III) and Co(II) species by XPS analysis (Figure S3).

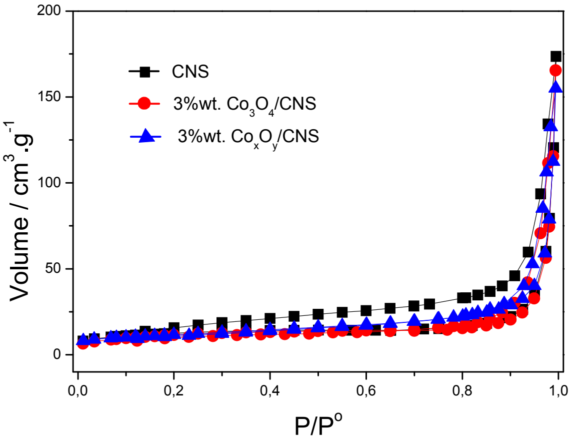


Figure S5. Nitrogen adsorption-desorption isotherms of CNS, 3%wt. Co_3O_4/CNS and 3%wt. Co_xO_y/CNS.

Table S3. Physicochemical properties of CNS, 3%wt. Co_3O_4/CNS and 3%wt. Co_xO_y/CNS samples from Nitrogen adsorption-desorption analysis.

Sample	Surface area / $m^2.g^{-1}$	Pore volume / $cm^3.g^{-1}$	Average pore size / nm
CNS	45	0.26	41.1
3%wt. Co_3O_4/CNS	42	0.25	38.6
3%wt. Co_xO_y/CNS	40	0.24	26.4

As shown in Figure S5 and Table S3, the loading of cocatalyst did not significantly influence the BET surface area of CNS matrix.

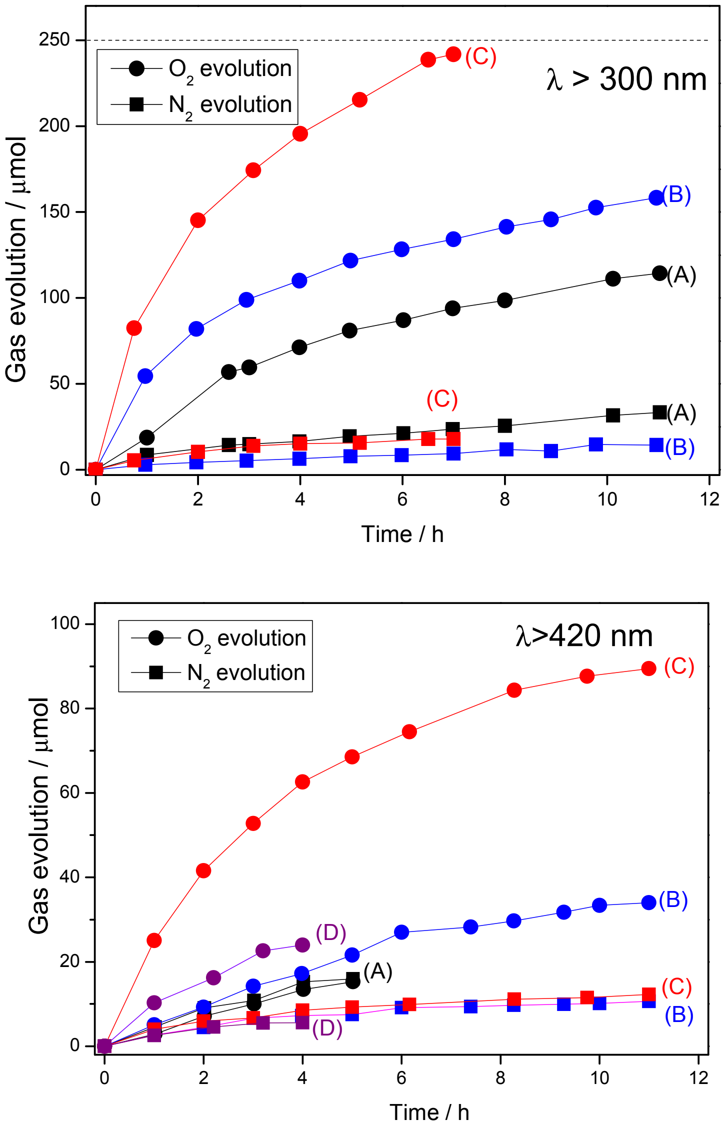


Figure S6. Photocatalytic water oxidation by CNS (A), 3%wt. Co_xO_y/CNS (B), 3%wt. Co_3O_4/CNS (C) and physical mixture of 3%wt.Co_3O_4 and CNS (D), as a function of time under UV and visible light illumination.

Table S4. The Corresponding Initial (First Hour) Rates of Photocatalytic Water Oxidation in Figure S6 were summarized as below.

			Photocatalytic activity		
Entry	Samples	Light	O_2 (μmol h^{-1})	N_2 (μmol h^{-1})	O_2 selectivity[a]
1	CNS	λ>300 nm	18.8	8.6	68.6
2	3%wt.Co_xO_y/CNS	λ>300 nm	53.7	4.1	92.9
3	3%wt.Co_3O_4/CNS	λ>300 nm	110	7.4	93.7
4	CNS	λ>420 nm	2.8	4.6	37.8
5	3%wt.Co_xO_y/CNS	λ>420 nm	5.0	2.6	65.8
6	3%wt.Co_3O_4/CNS	λ>420 nm	25.1	4.0	86.3
7	*3%wt.Co_3O_4 + CNS	λ>420 nm	10.3	2.6	79.8

*3%wt. Co_3O_4 + CNS: physical mixture of CNS powder and Co_3O_4.

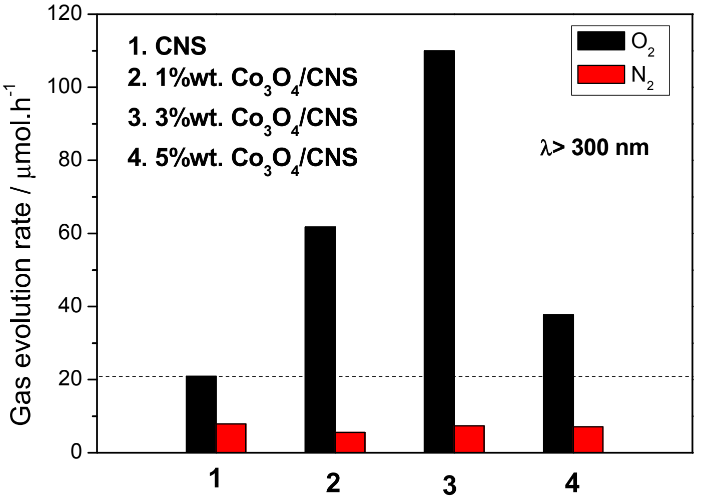


Figure S7. Influence of loading amount of Co_3O_4 on photocatalytic water oxidation.

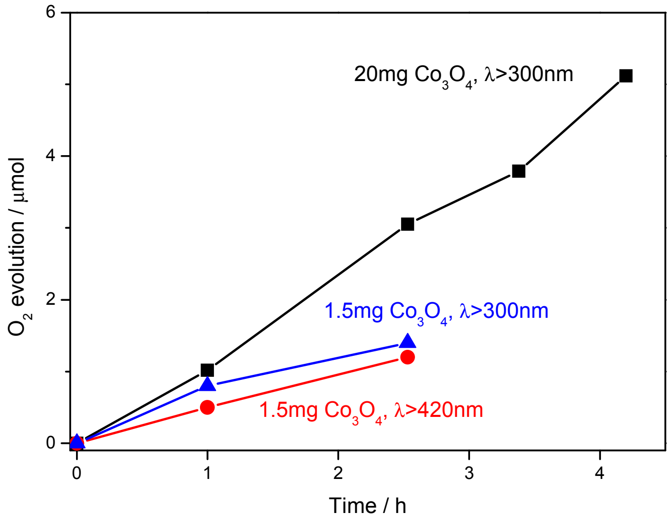


Figure S8. Photocatalytic water oxidation by Co_3O_4 nanoparticles (~3nm).

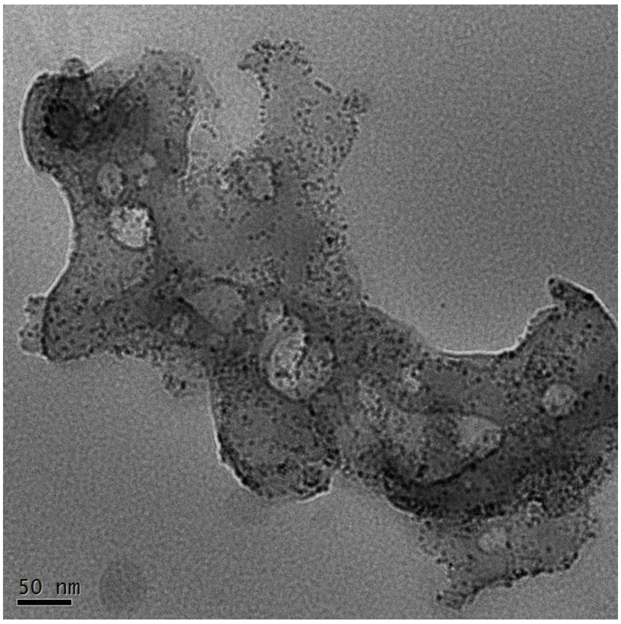
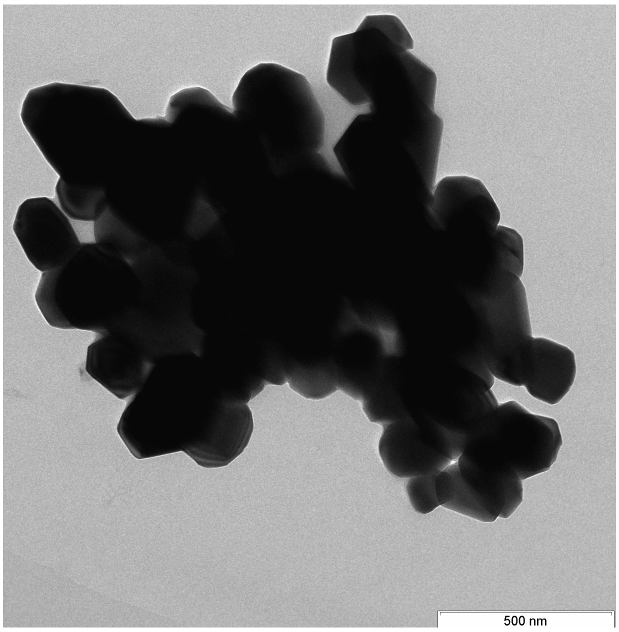


Figure S9. Typical TEM image of 3%wt.Co_3O_4/CNS. Co_3O_4 nanoparticles were found to be well dispersed on the CNS matrix.



5 **Figure S10.** Typical TEM image of bulk, commercial Co_3O_4, showing big Co_3O_4 crystals with size of ~250 nm.

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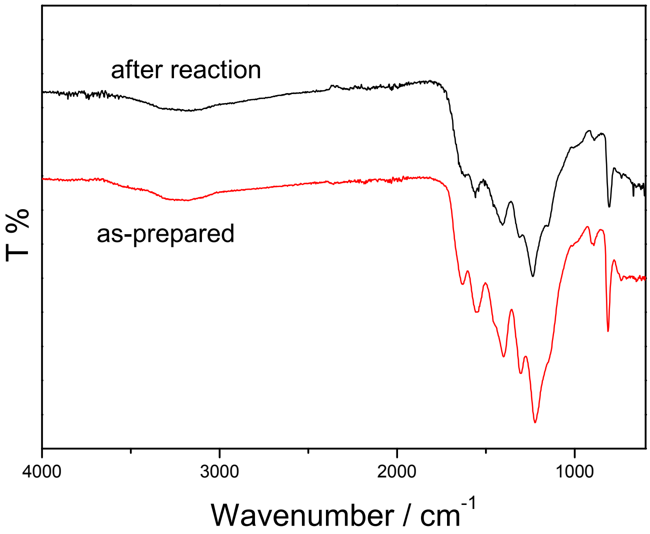

Figure S11. FT-IR spectra of 3%wt.Co_3O_4/CNS before and after the photocatalytic water oxidation reaction. The catalyst after the reaction was treated with aqua regia and ammonia to remove La_2O_3, Co_3O_4, and Ag 15 particles

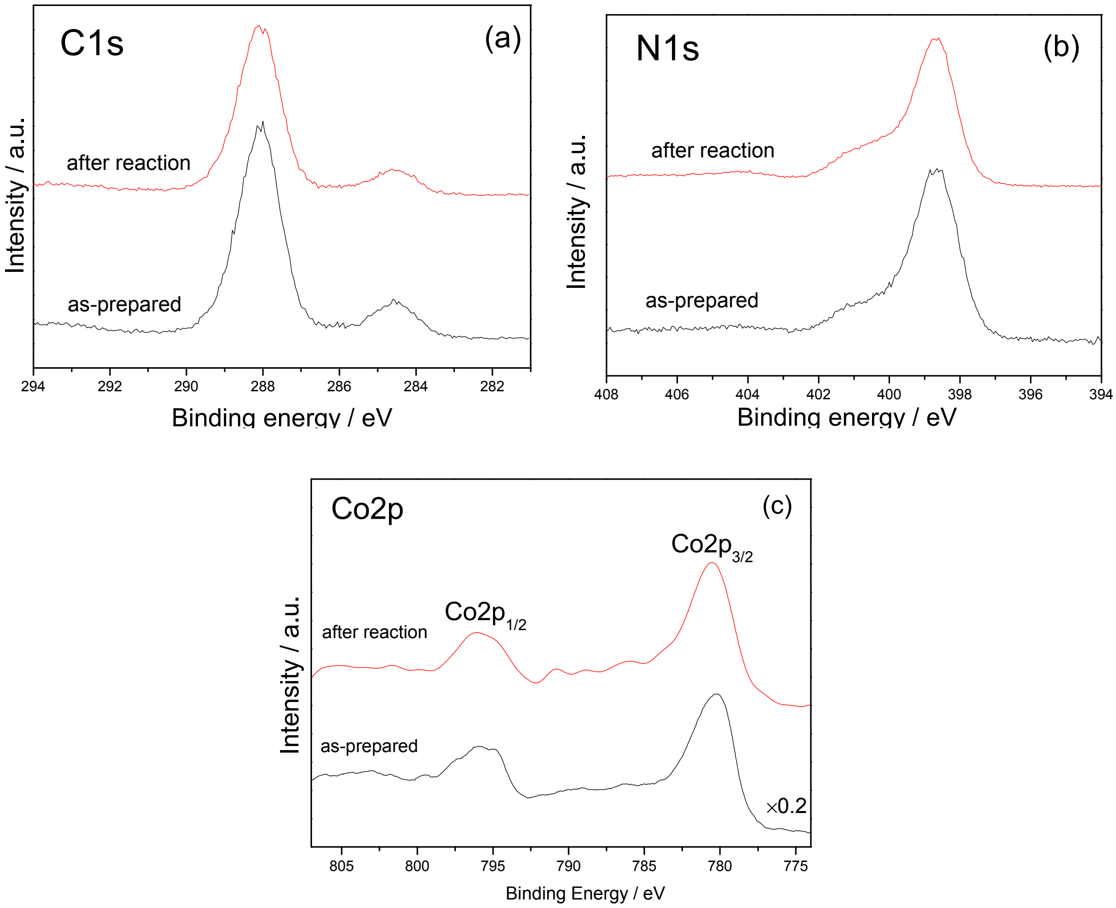

Figure S12. XPS analysis of 3%wt.Co_3O_4/CNS before and after the photocatalytic water oxidation reaction. No significant alternations can be found from the C1s (a), N1s (b) and Co2p (c) spectra before and after the reaction.