Steam reforming of formaldehyde for generating hydrogen and coproducing carbon nanotubes for enhanced photosynthesis

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Materials and chemicals

Nickel chloride (AR) and ammonium molybdate tetrahydrate (AR) were purchased from *Sinopharm Chemical Reagent Co., Ltd* (Shanghai, China). Deionized water (AR) was purchased from *Nanjing Wanqing Chemical Galss Instrument Co., Ltd* (Jiangsu, China). All chemicals were of analytical grade and used without further processing.

Catalysis measurement

One gram catalyst without pre-treatment was placed in the fixed-bed reactor for the steam reforming of formaldehyde, and the gaseous hourly space velocity (GHSV) was 10,000 h^{-1}. The formaldehyde solution (38 wt.%) is fed through a peristaltic pump and heated into a gas in the preheating unit (200 °C). The flow rate of formaldehyde was 10 mL h^{-1} while the molar ratio of CH_2O/H_2O was equal to 2:3 according to Eq. (1). N_2 was the carrier gas and the inner substance for internal standard method of gas chromatograph. The reaction temperature was adjusted from 300 to 600 °C, and the test time for each reaction temperature was 1.5 h.

$$CH_2O + H_2O \rightarrow CO_2 + 2H_2 \qquad \text{Eq. (1)}$$

The products were analyzed by gas chromatograph (GC-2014). The gases were tested by a Thermal Conductivity Detector (TCD as abbreviation) equipped with a TDX-01collumn, and the liquids were tested by a Flame Ionization Detector (FID as abbreviation) equipped with a PEQ capillary column. The catalytic performance of the catalysts was evaluated by selectivity of H_2, CO and CO_2. The formaldehyde conversion was abbreviated as X_F, and the selectivity of H_2, CO and CO_2 was abbreviated as S_{H2}, S_{CO} and S_{CO2}. The selectivity of H_2, CO and CO_2 was abbreviated as S_{H2}, S_{CO} and S_{CO2}, and the formaldehyde conversion was abbreviated as X_F.

$$S_{H_2} = \frac{mol_{H_2}}{2\times mol_F} \times 100\% \qquad \text{Eq. (2)}$$

$$S_{CO} = \frac{mol_{CO}}{mol_F} \times 100\% \qquad \text{Eq. (3)}$$

$$S_{CO_2} = \frac{mol_{CO_2}}{mol_F} \times 100\% \qquad \text{Eq. (4)}$$

$$X_F = \frac{mol_{F_{out}}}{mol_{F_{in}}} \times 100\% \quad \text{Eq. (5)}$$

Photosynthesis experiment

Chloroplast Isolation Assay. Chloroplast was isolated from 3 weeks spinach leaves cultivated under Hoagland nutrient solution by a mechanical method according to Weise et al [1]. Firstly, 4-5 spinach leaves were cut into 0.5cm wide strips vertical to the main vein after remove the main veins, then quickly moved them into an ice-cold mortar. The ice-cold buffer in the mortar consists of 30 mM HEPES buffer (pH 7.6) with 350 mM mannitol, 3 mM EDTA, and 0.05 g of acetone-washed fraction-V BSA. When grinding, the muller is not allowed to directly contact the wall of the mortar to prevent the chloroplast from breaking. After two minutes of grinding, the chloroplasts were fully released from the leaves and transferred to a 50 ml centrifuge tube through four layers of cheesecloth, followed centrifugation at 100 g for 2 minutes in a 4 ℃ centrifuge. After removing the supernatant using a pipette, the chloroplasts at the bottom of the tube were re-suspended in solution consisting of 30 mM Hepes buffer (pH 7.6) with 350 mM mannitol, 2.5 mM $MgCl_2$, 5 mM KH_2PO_4 and 2.5 mg per ml BSA. Finally, counting chloroplasts using a hemocytometer.

Hill reaction. The chloroplast and material coexist for 2 hours. Then 20 μl water solution with 1.36 μg DCPIP (Aladdin) was transferred to a 96-well plate, followed by add 200 μl chloroplasts or chloroplasts/material into it. The absorbance is initially measured under dark conditions, and then the absorbance is measured under 200 μM cm^{-2} s^{-1} illumination every two minutes at 600nm using Microplate reader (Thermo Fisher 3020) until the curve is stable. The chloroplast content is 10^7 per ml.

ATP production. The extracted chloroplasts were allowed to stand in the dark for 30 minutes in order to consume excess ATP. Then chloroplast co-culture with the CNTs or Ni/MoO_3, then placed at 200 μM cm^{-2} s^{-1} light for 30 minutes. ATP content determination method reference reagent instructions.

Characterization

X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (Smartlab TM 9Kw, Rigaku, Japan). The 2θ scans covered the range 5-85 °, and the accelerating voltage and applying current were 45 kV and 200 mA, respectively. The microstructural natures and element mapping of the catalysts have been investigated using a transmission electron microscope (JEOL, JEM-2100F). Visible Raman spectra of the catalysts were collected at room temperature on the LabRAMHR800 (Horiba Jobin Yvon). A 514 nm diode-pumped solid-state semiconductor laser was used as the excitation source with a power output of 30 mW. The specific surface area and average pore diameter (BET method) of the samples were measured by N_2 adsorption/desorption isotherms at -196 ℃ using a surface-area analyzer (Micromeritics, 2020M V3.00H). All of the samples were degassed at 350 ℃ under vacuum for 3 h prior to the adsorption experiments. The X-ray photoelectron spectroscopy (XPS) patterns were acquired by the PHI 5600 spectrometer with a hemispherical energy analyzer (Mg-K_α radiation, 1253.6 eV at 100 Watts), and the vacuum degree was maintained at 10^{-7} Pa. The samples were dried at 80 ℃ for 24 h to remove moisture and then were tested without surface treatment. Curve fitting was performed by utilizing XPSPEAK 4.1 with a Shirley-type background. The temperature programmed desorption of ammonia (NH_3-TPD) was conducted on the CHEMBET-3000 (Quantachrome) to obtain the surface acid properties. All the catalysts were preheated at 450 ℃ under a helium stream for 1 h, and then cooled to 50 ℃ for the ammonia adsorption. Afterwards, ammonia was desorbed from 50 ℃ to 900 ℃ at a heating rate of 10 ℃ min^{-1}. The Semiautomatic Micromeritics TPD/TPR 2900 instrument was used for the temperature programmed reduction of hydrogen (H_2-TPR). All the catalyst carriers were preheated to 400 ℃ under an argon stream for 1 h, and cooled to 50 ℃. Then 5% H_2/Ar flow was switched, and the temperature increased from 50 ℃ to 900 ℃ at a 10 ℃ min^{-1} heating rate. The data were collected throughout the whole temperature range. *In situ* Diffuse Reflectance Infrared Fourier Transform Spectra (*in situ* DRIFTS) were collected by a Nicolet IS50 spectrometer. All the catalysts were preheated at 400 ℃ under a N_2 stream for 2 h, and then cooled to the desired temperature. The formaldehyde, water vapor and nitrogen were pumped into the system for 10 min when the temperature was cooled to 100 ℃. After that, formaldehyde and water vapor were stopped and pure nitrogen was pumped into the system for 10 min. Then formaldehyde and water vapor were pumped into the system and the temperature increased to 400 ℃ and kept for 10 min.

[1]. Weise, S. E.; Weber, A. P. M.; Sharkey, T. D., Maltose is the major form of carbon exported from the chloroplast at night. *Planta* **2004,** *218*, (3), 474-482.

Fig.S1

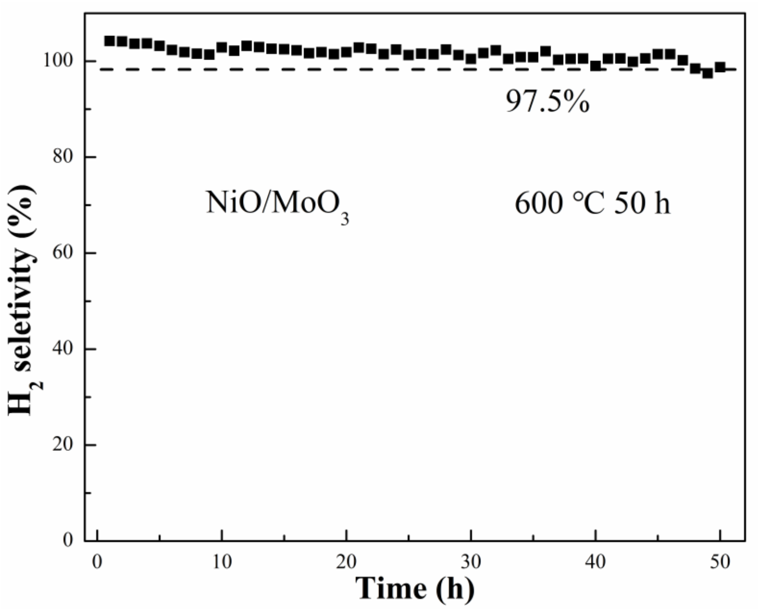

Fig.S1 H$_2$ selectivity versus reaction time (50 h) for NiO/MoO$_3$ catalyst.

Fig.S2

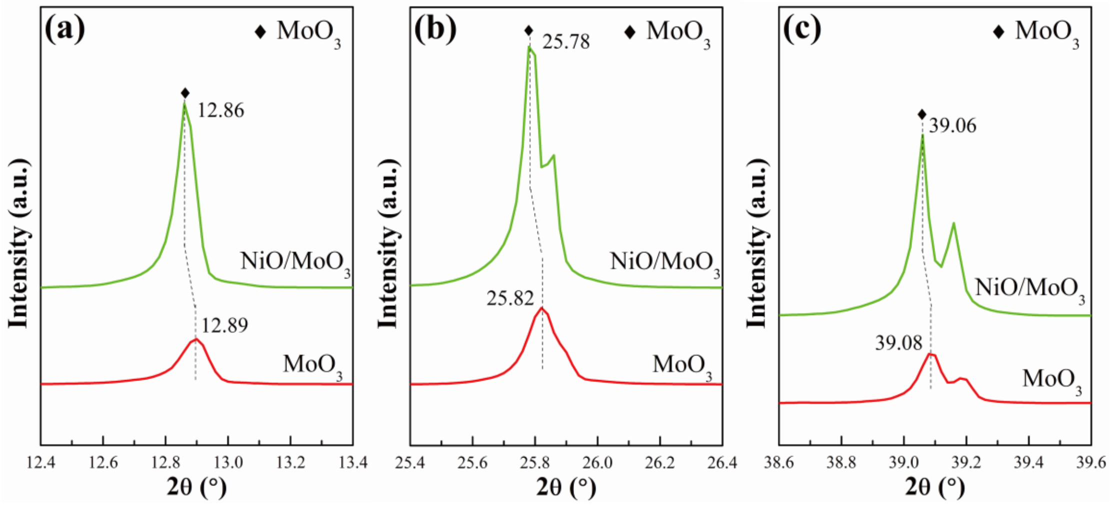

Fig.S2 The details of XRD patterns for MoO_3 and NiO/MoO_3.

Table S1

Table S1 X-ray fluorescence results of NiO/MoO_3 catalyst

Sample	NiO (wt.%)	MoO_3 (wt.%)	MgO (wt.%)
NiO/MoO_3	6.053	93.901	467.3 ppm

Fig.S3

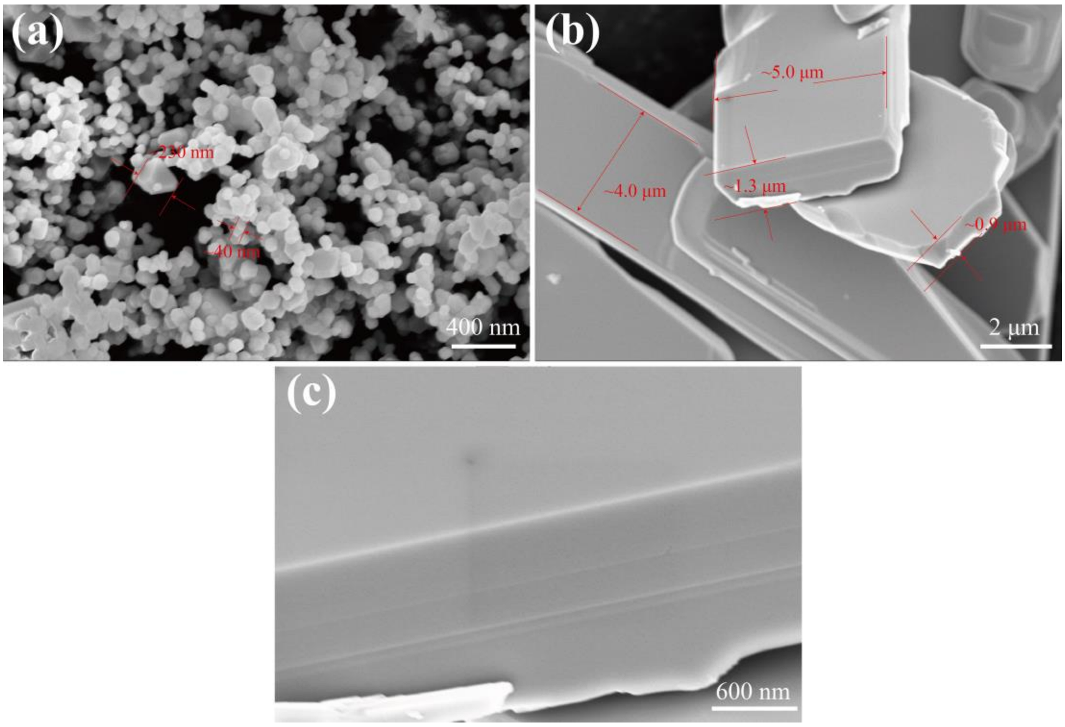

Fig.S3 The FE-SEM images of (a) NiO, (b) MoO_3 and (c) detail image of MoO_3.

Fig.S4

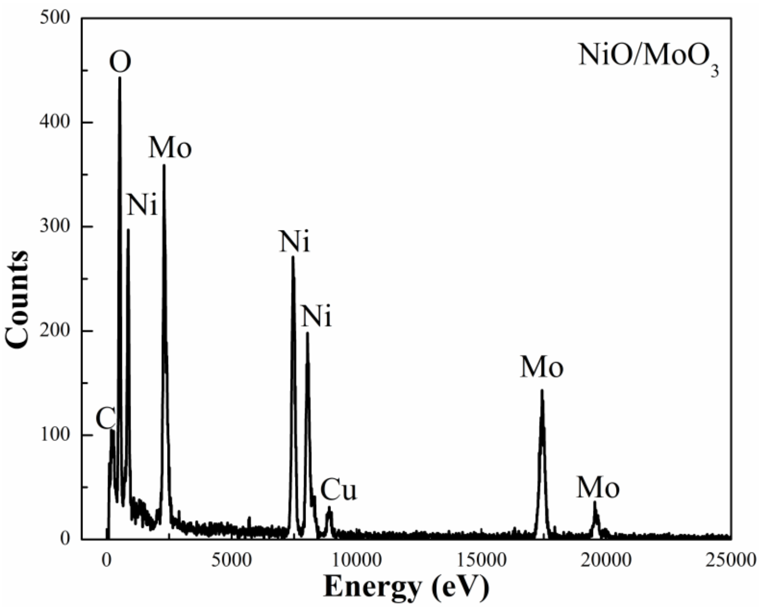

Fig.S5 EDX spectrum of NiO/MoO_3.

Fig.S5

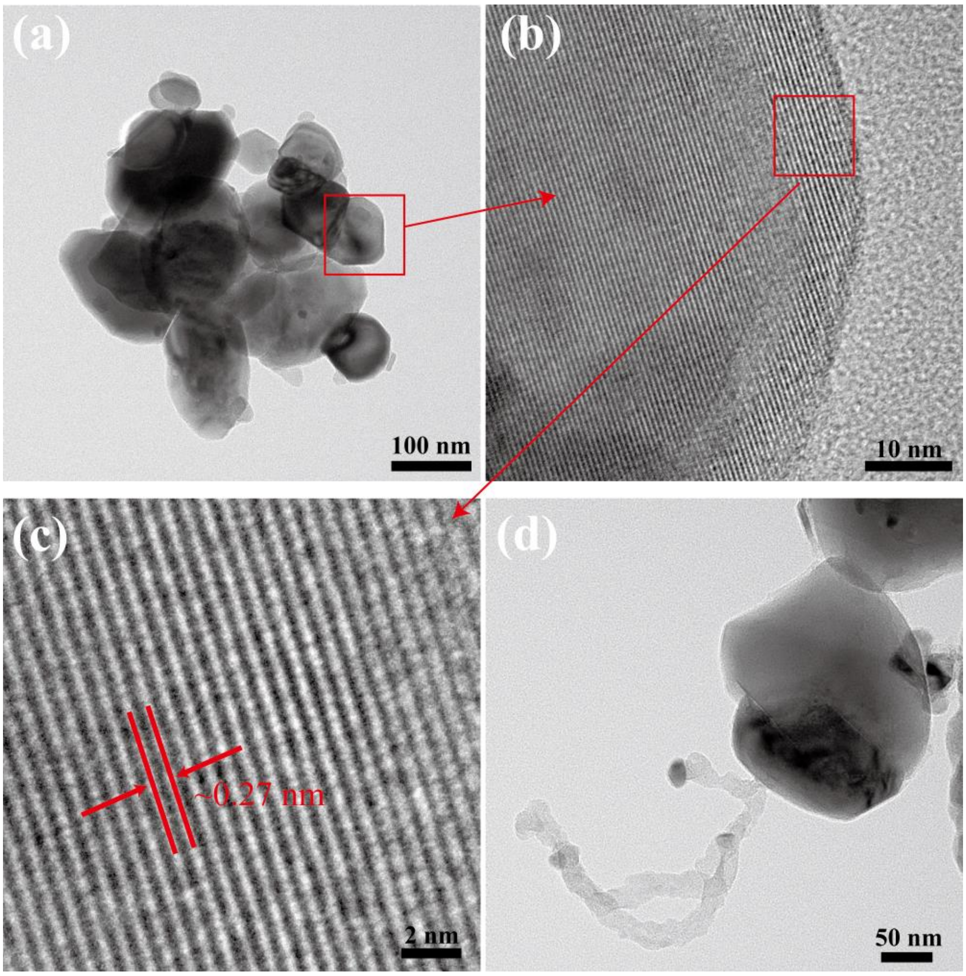

Fig.S5 TEM micrograph and element mapping of used NiO/MoO_3 catalyst.

Fig.S6

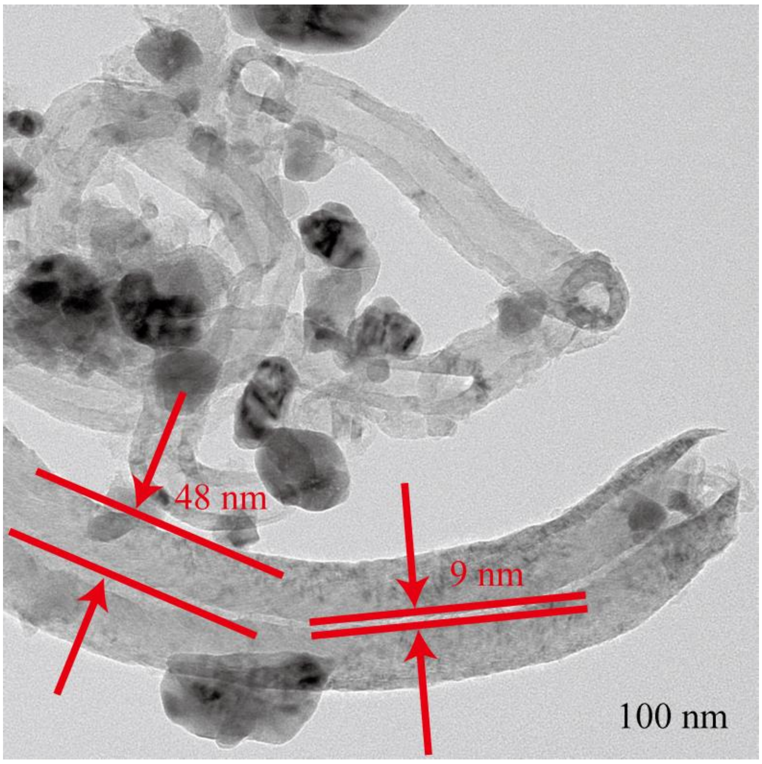

Fig.S6 TEM micrograph of CNTs obtained after the catalytic reaction.

Table S2

Table S2 Physical properties of different catalysts.

Samples	S_{BET}/(m^2 g^{-1})	V_{Pore}/(cm^3 g^{-1})	D_{pore}/nm
NiO	5.6	0.174	93.5
MoO_3	1.2	0.004	14.9
NiO/MoO_3	3.6	0.031	24.4

Fig.S7

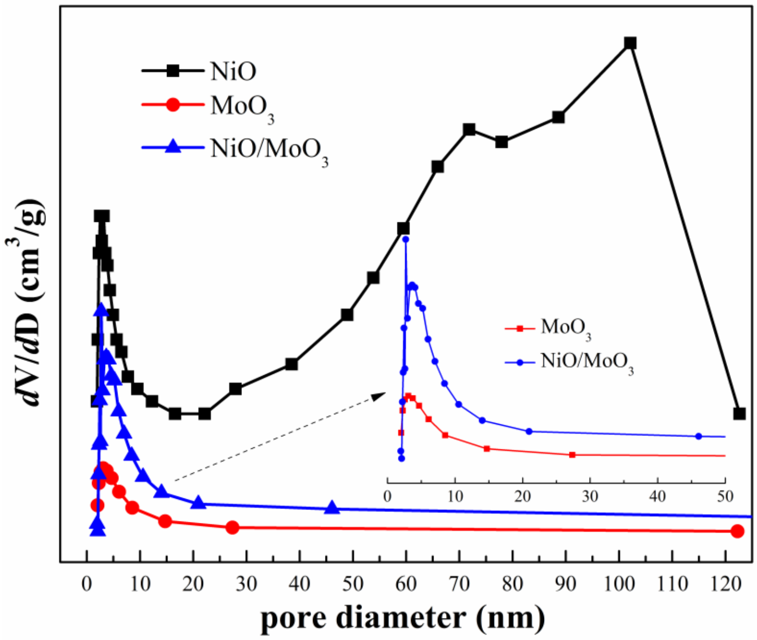

Fig.S7 Pore size distribution of NiO, MoO_3 and NiO/MoO_3.

Fig.S8

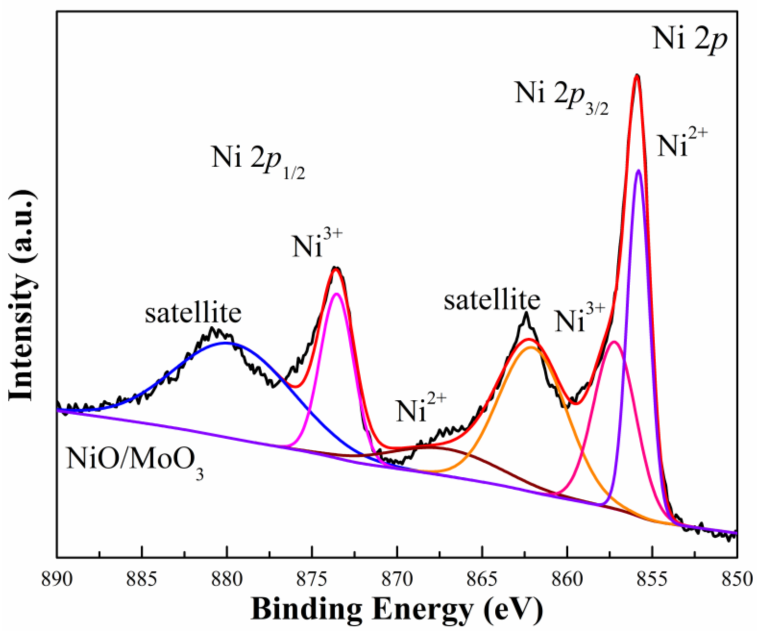

Fig.S8 The detail information of Ni 2*p* XPS high-resolution scans spectra for NiO/MoO_3 catalyst.

Fig.S9

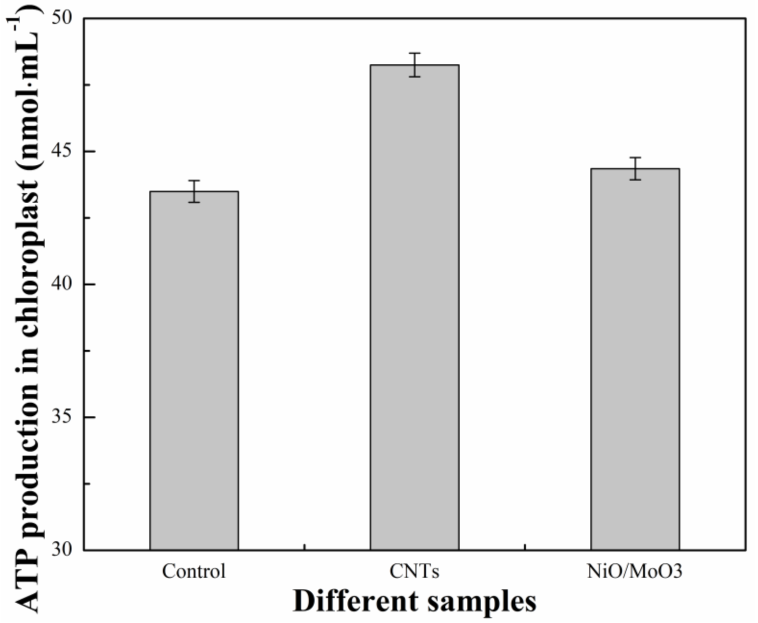

Fig.S9 ATP production of chloroplasts as affected by different samples.