

Fabrication of Cu₂O-loaded TiO₂ nanotubes with heterojunctions via an electrochemical method: Enhanced photocatalytic activity

Peng Qiao,^a Xueqin Wang,^{*a,d} Jiangling Liu,^b Yanxiu Liu,^{*a} Man Dai,^c Rui Piao,^a Ying Liu,^a
Wenyi Wang,^a Yuanyuan Wang,^a and Hua Song^{a,d}

a.College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, P.R. of China.

b.Shuguang Oil Production Plant , Petrochina Liaohe Oilfield Company, Panjin 124109, P.R. of China.

c.Daqing Petrochemical Research Center, Daqing 163318, P.R. of China

d.Provincial Key Laboratory of Oil & Gas Chemical Technology, Northeast Petroleum University, Daqing 163318,
P.R. of China.

*Corresponding Author: wangji624@163.com

Figure S1 shows the energy-dispersive X-ray spectroscopy (EDS) of pristine TiO₂ NTs, and Cu₂O-TiO₂ NTs obtained at Cu deposition voltages of 1V, 2V, 3V, 4V, and 5V. As shown in Fig. S1 and Table 1, pristine TiO₂ NTs were composed of three elements: Ti, O, and C. The Ti:O atomic ratio was approximately 2:1, and C originated from external pollution. After the electrochemical deposition of Cu to form Cu₂O-TiO₂ NTs, the characteristic peak of Cu gradually intensified with the increase in the deposition voltage. The atomic percentage of Cu gradually increased from 1.75 to 4.85% with the increase in the deposition voltage from 1 to 5 V. No other elements were detected, which confirmed that the Cu₂O-TiO₂ NTs prepared by the electrochemical deposition process were of high purity and no other impurities were generated.

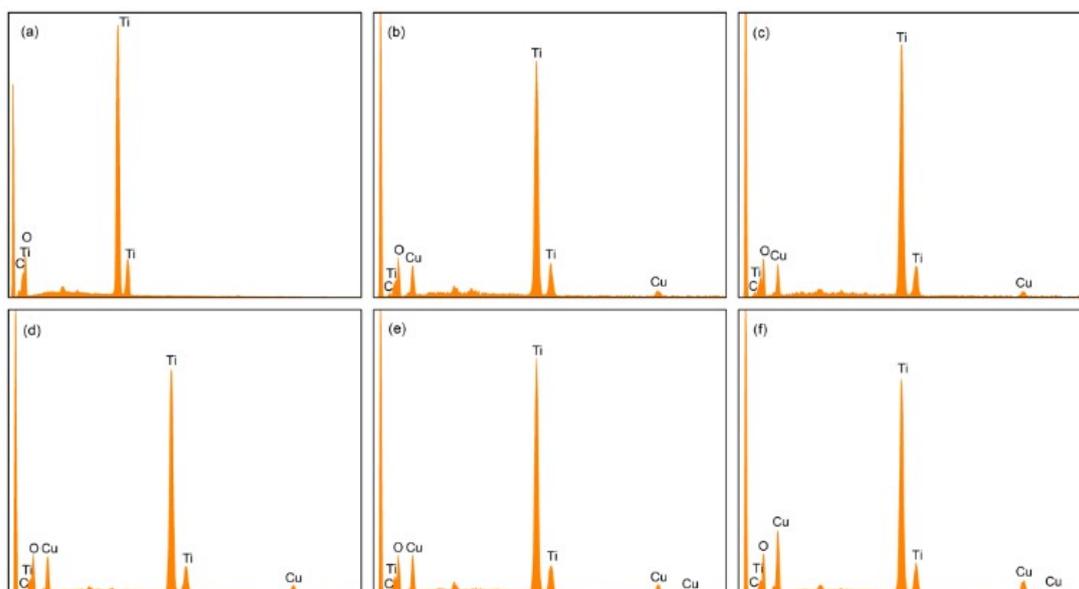


Fig. S1 EDS profiles of different samples: (a) pristine TiO₂ NTs, (b–f) Cu₂O-TiO₂ NTs obtained at Cu deposition voltages of 1V, 2V, 3V, 4V, and 5V, respectively

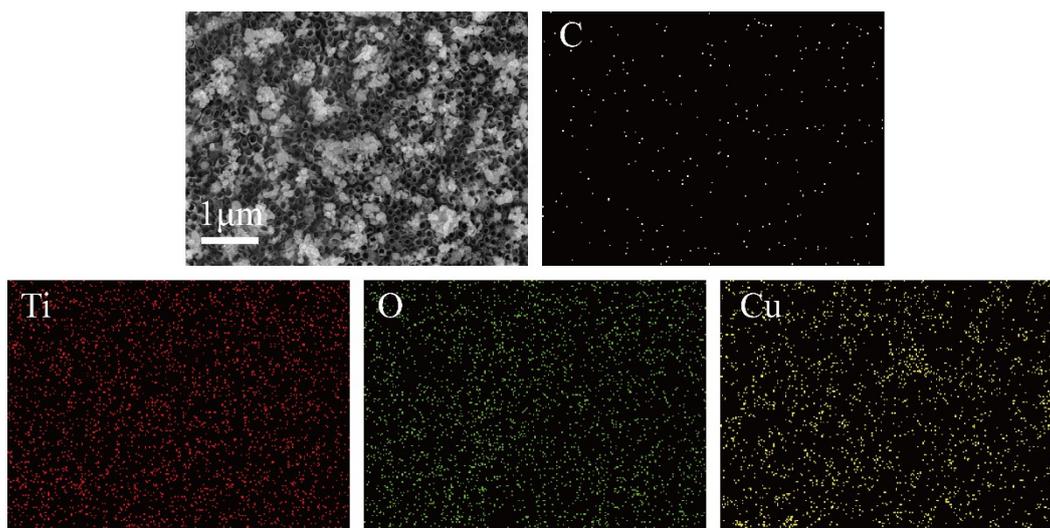


Fig. S2 EDS mapping of $\text{Cu}_2\text{O-TiO}_2$ NTs

Figure S2 shows the EDS mapping of the $\text{Cu}_2\text{O-TiO}_2$ NTs. As shown that the distribution of Cu, Ti, O, C is uniform, and there is no obvious aggregation phenomenon. The as-prepared Cu_2O nanoparticles loading TiO_2 NTs are homogeneous and crack-free. It can be concluded that after electrochemical deposition Cu element is also uniformly distributed on the surface of TiO_2 NTs.

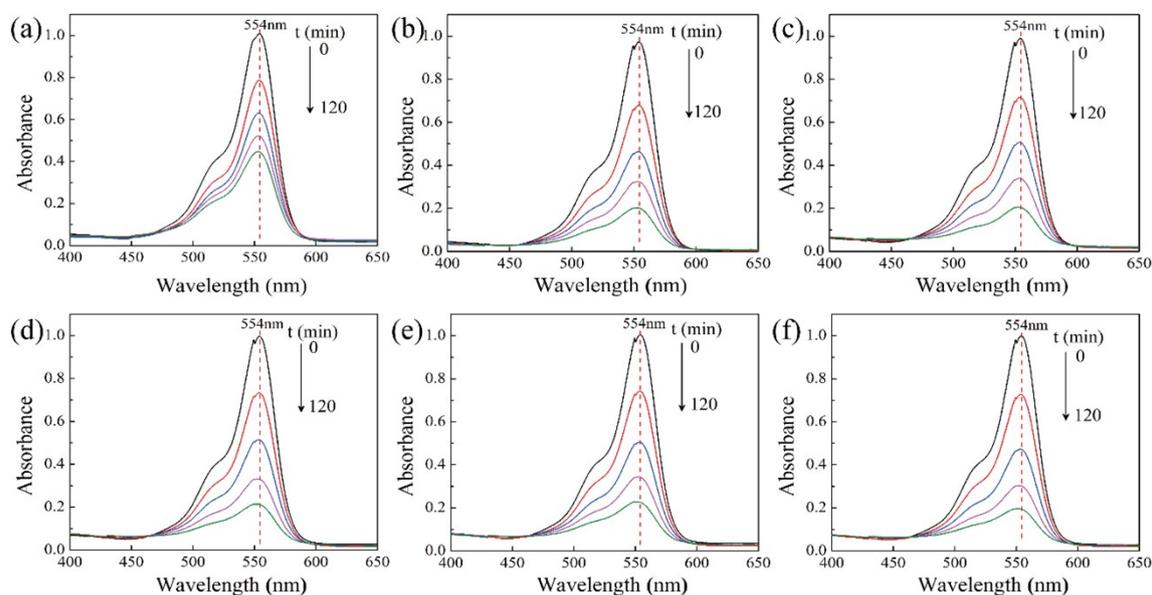


Fig. S3 UV-vis absorption spectra recorded during RhB degradation using different samples as catalysts: (a) pristine TiO_2 NTs, (b–f) $\text{Cu}_2\text{O-TiO}_2$ NTs obtained at Cu deposition voltages of 1V, 2V, 3V, 4V, and 5 V, respectively

Quantum efficiency (QE) is the ratio of the photochemical reaction rate to the absorbed photon flux in a specific wavelength range; And photon flux is the number of photons radiated by the light source and unit time interval, and is a function of wavelength λ .

The QE was calculated by the following formula:

$$QE = \frac{\text{reaction rate}}{q_p} = \frac{K \cdot n(H_2)}{IA\lambda/hc} \times 100\%$$

Among them, K is the number of transferred electrons (2 in this work), I is the optical power density, $1.5 \cdot 10^{-4} \text{ W} \cdot \text{cm}^{-2}$; A is the area of light exposure, 1 cm^2 ; λ is $3.65 \cdot 10^{-11} \text{ m}$; h is the Planck's constant, $6.626 \cdot 10^{-34}$; and c is the speed of light, $3 \cdot 10^8$. The calculation result was shown in Fig. S4.

The maximum QE of $\sim 22.08\%$ is obtained at 3V $\text{Cu}_2\text{O-TiO}_2$ NTs, which is consistent with the maximum IPCE of $\sim 22.08\%$.

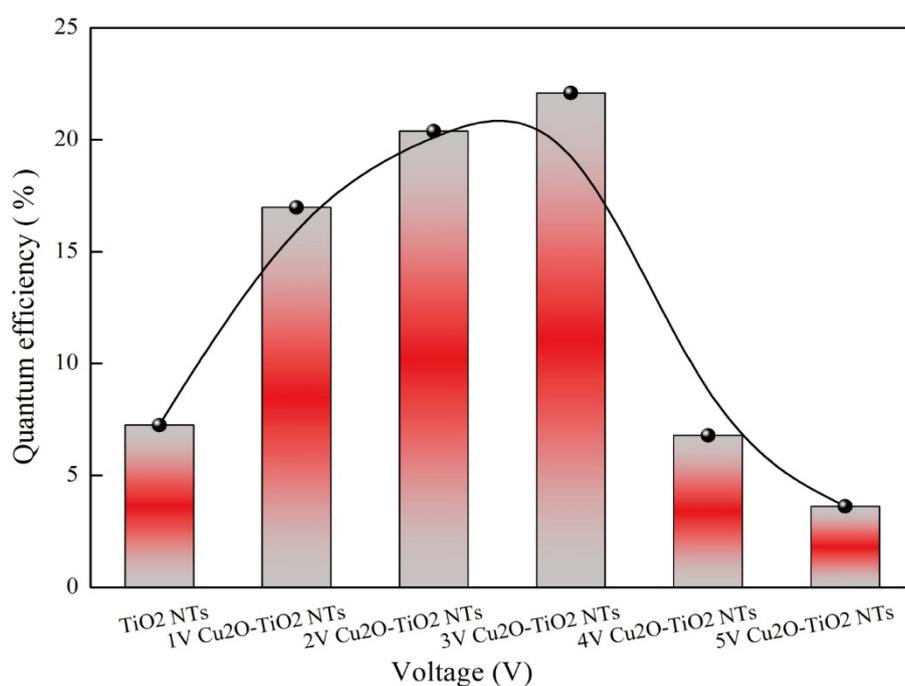


Fig. S4 Quantum efficiency of pristine TiO_2 NTs and $\text{Cu}_2\text{O-TiO}_2$ NT samples prepared using different Cu deposition voltages under UV illumination

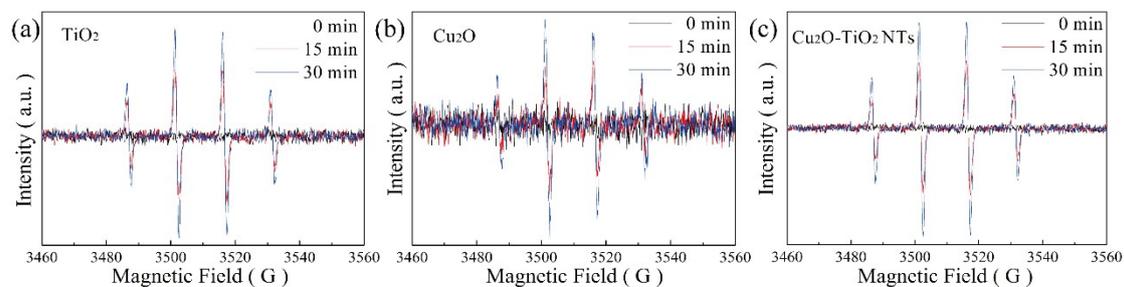


Fig. S5 EPR spectra under UV light irradiation: (a) pristine TiO_2 NTs, (b) Cu_2O and (c) 3V $\text{Cu}_2\text{O-TiO}_2$ NTs

Fig. S5 exhibits the electron paramagnetic resonance (EPR) spectra of pristine TiO_2 NTs, Cu_2O ,

and 3V Cu₂O-TiO₂ NTs with UV light irradiation at 0 min, 15 min and 30 min. At 0 min irradiation, none of the three samples showed characteristic peaks under the magnetic field. After 15 min and 30 min irradiation, the intensities of the characteristic peaks significantly arise at different magnetic field intensity for all the samples, which meaning more hydroxyl radical (\cdot OH) be obtained under UV irradiation.