## **Electronic Supplementary Information**

## Cu<sub>2</sub>O sensitized flexible 3D-TiO<sub>2</sub> nanotube arrays for enhancing

## visible photo-electrochemical performance

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Fig.S1 indicates that five peaks appear at 36.52°, 42.42°, 61.55°, 73.73° and 77.61° in the samples T(400) and T(400)-1 besides Ti peaks, which can be assigned to (111), (200), (220), (311) and (222) crystal faces of cubic Cu2O (JCPDS, card no: 77-0199), T(400) and T(400)-1 have nearly the same Cu2O peak position and intensity, indicating that Cu2O is stable after the degradation experiment. No CuO diffraction peak is found in these samples.



Fig.S2. The XPS spectra of CT(400): XPS survey spectrum (A), high resolution XPS spectra of Ti2p (B) and Cu2p (C)

Fig.S2 gives the XPS spectra of CT(400) in order to further clarify the chemical states of Cu. Fig.S2(A) indicates that the sample contains Cu, Ti, O and C elements. The small amount of carbon could have resulted from adventitious hydrocarbons from the XPS instrument itself and can be taken as the standard signal for the correction of other peaks. The binding energy of the superfluous carbon in our detection is C 1s = 284.8 eV, the same as the standard value. Fig.S2(B) indicates that two main peaks exist at bonding energies of 458.5 and 464.3 eV, which are consistent with that of Ti4+ 2p3/2 and Ti4+ 2p1/2, respectively. [1.2] Fig.S2(C) indicates the existence of Cu 2p3/2 and Cu 2p1/2. Peak Cu 2p3/2 can be fitted by two peaks at 934.3 and 932.5 eV, which can be assigned to the Cu(II)[3] state and the Cu(I)[4] state, respectively. Similarly, Peak Cu 2p1/2 can be fitted by two peaks at 952.4 and 954.4 eV, which can be assigned to the Cu(II)[3] state and the Cu(I)[4] state, respectively. Similarly, Peak Cu 2p1/2 can be fitted by two peaks at 952.4 and 954.4 eV, which can be assigned to the Cu(II)[3] state and the Cu(I)[4] state, respectively. The shakeup satellite peaks around 940.5 and 944.5 eV suggest the existence of fully oxidized Cu2+.[5] The existence of Cu2+ ions indicate that the surface of Cu2O in 3D TiO2 NTAs was partially oxidized into CuO, but its concentration is very low since no CuO diffraction peak is found in the XRD diagram of CT(400) in Fig.5(A).

## References

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