Supporting Information

CuO Nanoparticle-Decorated TiO$_2$-Nanotube Heterojunctions for Direct Synthesis of Methyl Formate via Photo-Oxidation of Methanol

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EXPERIMENTAL METHODS

Chemicals. All the chemicals and reagents were analytical grade and used as received without further purification. P25 oxides were purchased from Beijing Entreprennr Science&Trading Co. Ltd (China). Copper nitrate hydrate (> 99%) and sodium borohydride (> 98%) were purchased from Adamas. Nanopure water (resistivity: 18.2 MΩ·cm) was purified with a Barnstead NANO pure Diwater system. All glassware and reactors were thoroughly cleaned with aqua regia (37% HCl : HNO3 = 3 : 1, v/v) to clear away the metals, and then rinsed with copious amounts of nanopure water, and dried in an oven prior to use.

Characterization. Powder X-ray diffraction (XRD) patterns were recorded with a D/Max-2500/PC diffractometer (Rigaku, Japan) using Cu Ka (λ=0.154 nm) radiation operated at 40 kV and 200 mA. Transmission electron microscopy (TEM) images were recorded using a FEI Tecnai G² Spirit microscope operated at 120 kV, and high resolution TEM (HR-TEM) images were obtained on a FEI Tecnai G² F30S-Twin microscope operated at an accelerating voltage of 300 kV. The specimen was prepared by ultrasonically dispersing the sample in ethanol, and droplets of the suspension were deposited on a carbon-enhanced copper grid and then dried in air. UV-visible diffuse reflectance spectra were recorded in the range of 200–800 nm on a spectrophotometer (PE Lambda850) using BaSO4 as the reference. Photoluminescence (PL) spectra were recorded at room temperature on a HitachiF460. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB MK-II spectrometer (VG Scientific Ltd., UK) with Al Ka
radiation at room temperature. It is worth noting that before the measurements, samples were outgassed in the prechamber of the instrument at room temperature up to a pressure of <10-12 bar. The charging effect was corrected by adjusting the binding energy of C 1s to 284.6 eV. The spectra were deconvoluted using the XPSPEAK program by curve fitting with mixed Gaussian–Lorentzian peaks.