Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Direct Synthesis of Defective Ultrathin Brookite-Phase TiO_2 Nanosheets Showing Flexible Electronic Band States

Weixin Zhao, Shenqian Ma, Jun Zhou, Guolei Xiang*

State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China.

Email: xianggl@mail.buct.edu.cn

Experimental Section

Chemicals:

Titanium trichloride ($TiCl_3$) aqueous solution (15% dissolved in 3% HCl) was purchased from Alfa Aesar. The solvents, including formamide (FA), N-methylformamide (NMF), N,N-dimethylformamide (DMF), and N,N-dimethylacetamide (DMA), were purchased from Sinopharm Chemical Reagent Co., and used as received without further purification.

Material Syntheses:

Brookite ultrathin nanosheets: $TiCl_3$(aq) (0.50 mL) was dissolved in 30 mL of formamide in a 40-mL Teflon hydrothermal reactor, and then heated at 145 ^oC for 10 h in an electric oven. Then the products were collected via centrifugation at 10,000 rpm, washed with deionized water and ethanol 5 times, and dried using a freezing drier.

Brookite nanorods in formamide: $TiCl_3$(aq) (0.50 mL) was dissolved in 30 mL of formamide in a 40 mL Teflon hydrothermal reactor, and heated at 170 ^oC for 10 h.

Brookite nanorods in DMF: $TiCl_3$(aq) (0.50 mL) was dissolved in 30 mL of DMF in a 40 mL Teflon hydrothermal reactor, and heated at 120 ^oC or 150 ^oC for 10 h in an electric oven.

Anatase and rutile prepared in DMA: $TiCl_3$(aq) (0.50 mL) was dissolved in 30 mL of DMA in a 40 mL Teflon hydrothermal reactor, and heated at 120 ^oC in for 10 h an oven. The product 120 ^oC was anatase, but the phase would evolve into mixed phases of anatase and rutile at 150 ^oC.

Brookite nanoparticles: $TiCl_4$ (0.20 mL) was added dropwise into 7.5 mL of deionized water in a 10 mL Teflon autoclave. After sufficient stirring, 0.625 g of urea was added into this solution with magnetic stirring, then 0.625 mL of sodium lactate (60%) was dropped in the mixed solution during 30 min. Finally the autoclave was sealed and heated in an oven at 200 ^oC for 12 h.

Characterizations:

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) characterizations were carried out on a FEI Tecnai G2 F20 operated at 200 kV. The crystal structures of the samples were analyzed using X-ray powder diffraction (XRD) on Bruker D8 Advance with the energy of 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were conducted on Thermo Scientific ESCALAB 250Xi system using Al $K\alpha$ line as the X-ray source. Ultraviolet and visible light diffuse reflection spectra were collected using Shimadzu UV-3600 spectrophotometer with an integrating sphere.

NEXAFS characterization of Ti-$L_{2,3}$ edge was carried out at the 4B9B beamline of Beijing Synchrotron Radiation Facility (BSRF) with the mode of total electron yield (TEY). The energy resolution power (E/ΔE) of about 1500. The analysis chamber is equipped with a VG Scienta R4000 electron energy analyzer with a pressure of 1×10^{-10} mbar. Ti-L spectra were collected between 455 and 470 eV with a step width of 0.1 eV.

Catalytic oxidation of TMB with H_2O_2

In the reaction 100.0 μL of 10mg/mL catalytic suspension of brookite nanosheets and 100.0 μL of 3% H_2O_2 were mixed with 10.0 mL of ethanol in a 20-mL vial. Then 200.0 μL of TMB (10.0 mg/mL) was added into the mixed solution and kept being stirred for 30 min. The catalytic activity was determined by UV–visible spectroscopy every two minutes.

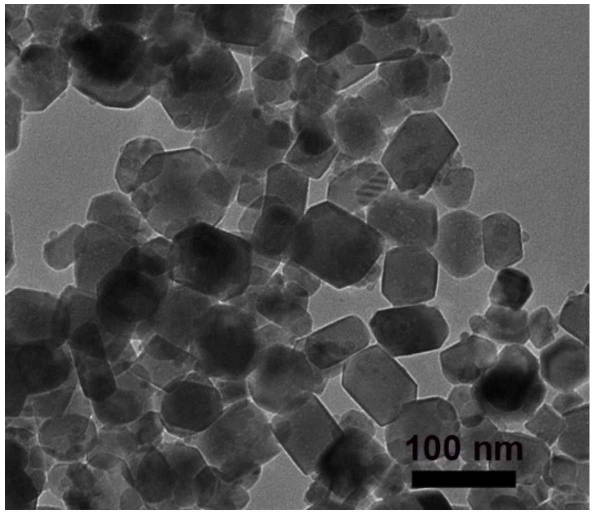

Figure S1. TEM image of brookite nanoparticles.

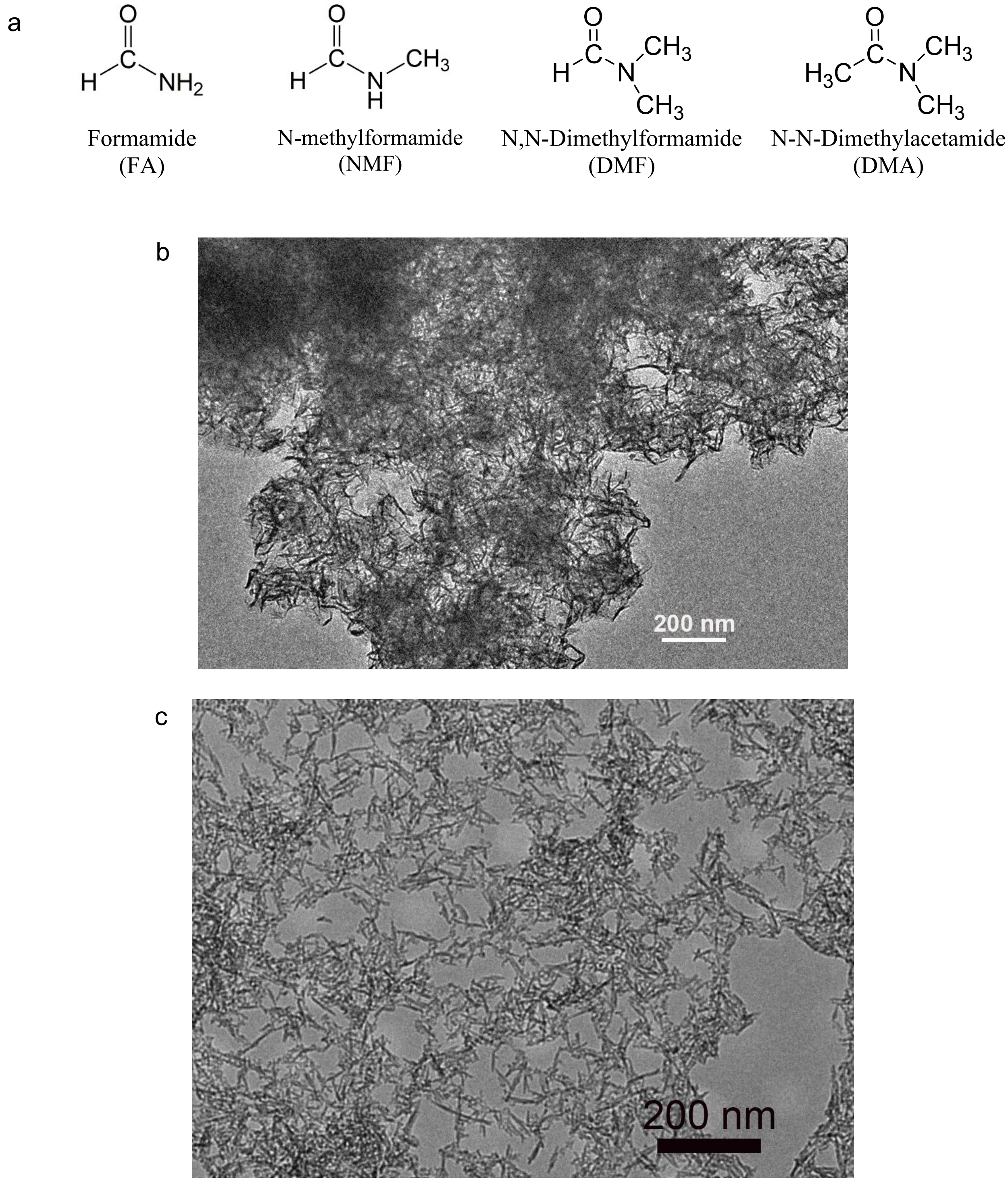

Figure S2. Control synthesis in different solvents. (a) Molecular structures of the four amines used as the solvents to study the effects of functional groups on the synthetic results. (**b**) TEM imge of brookite nanosheets prepared in NMF at 130 ^{o}C. (**c**) TEM image of brookite nanorods prepared in DMF at 120 ^{o}C.

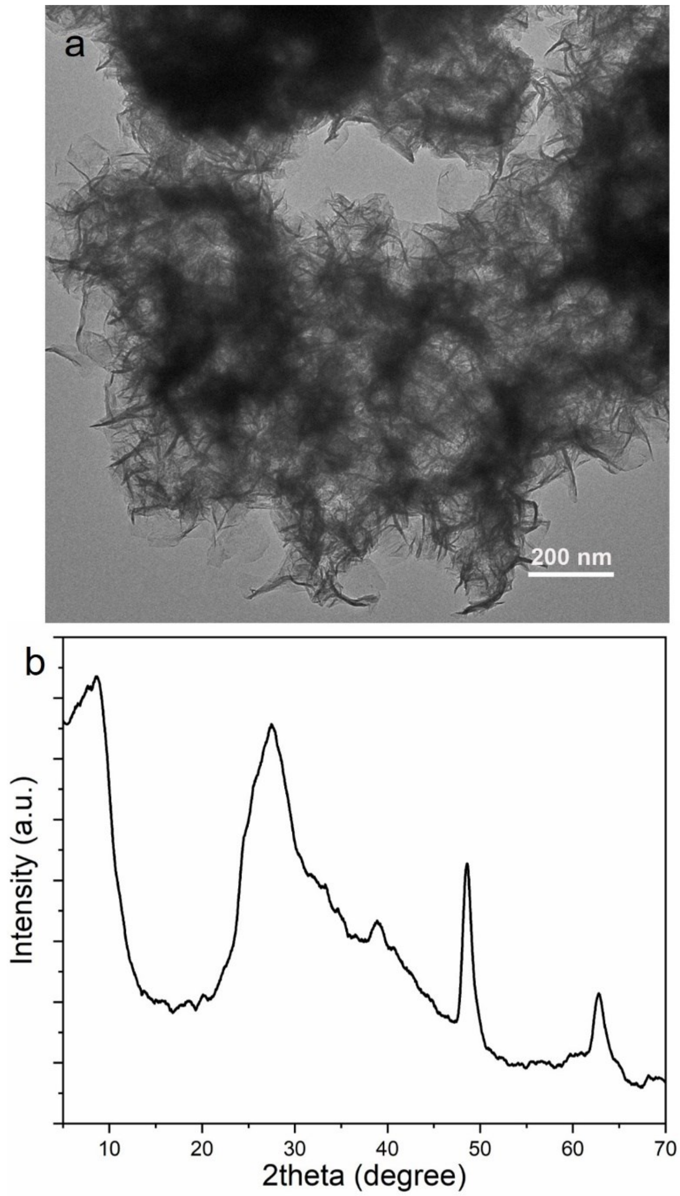

Figure S3. Synthetic results in formamide at 145 ^{o}C for 2 h. (**a**) TEM image showing 2D nanosheet morphology. (**b**) XRD of the precursor.

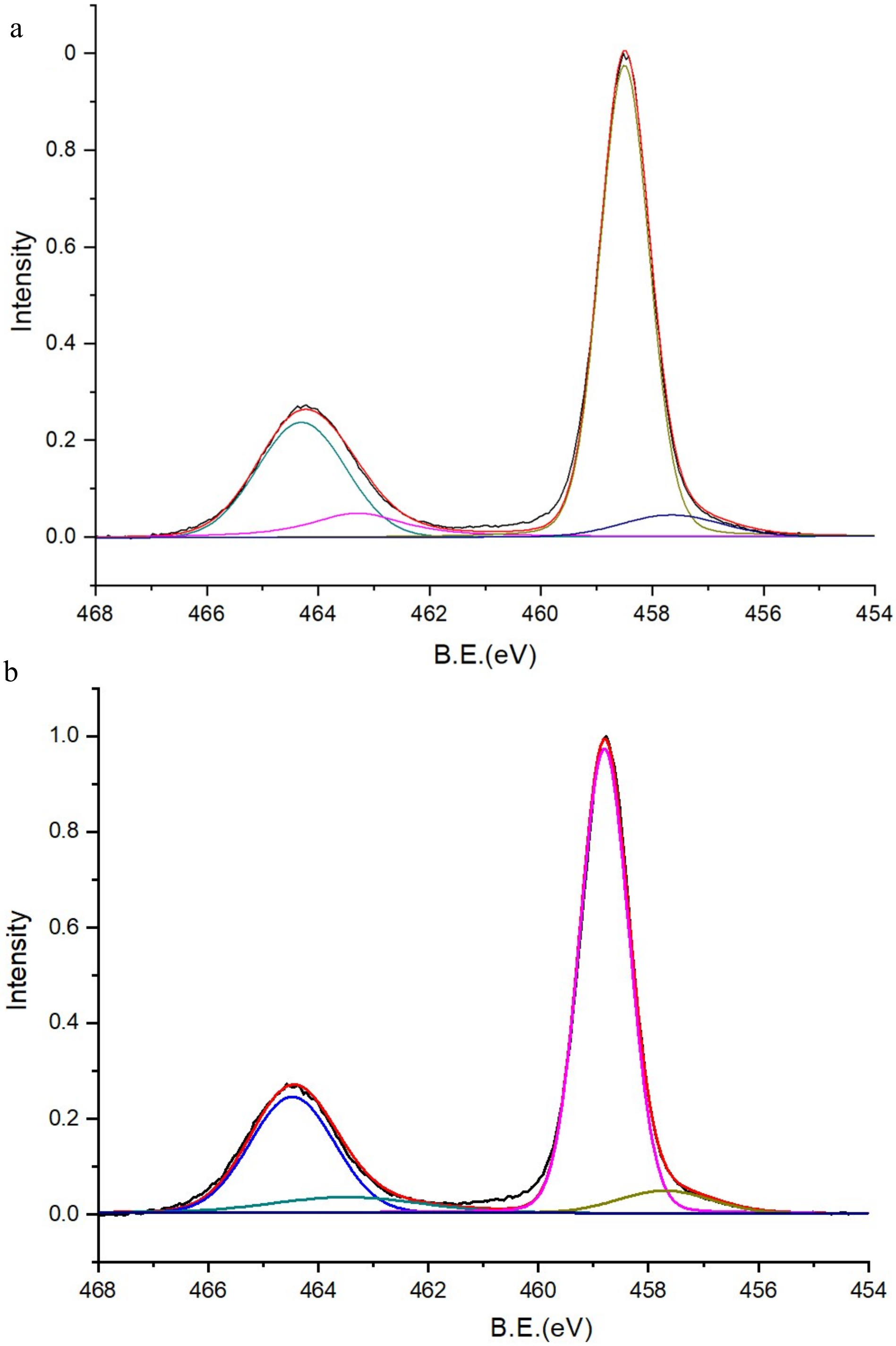

Fig. S4. Fitted Ti_{2p} XPS spectra of brookite nanosheets (a) and nanorods (b).

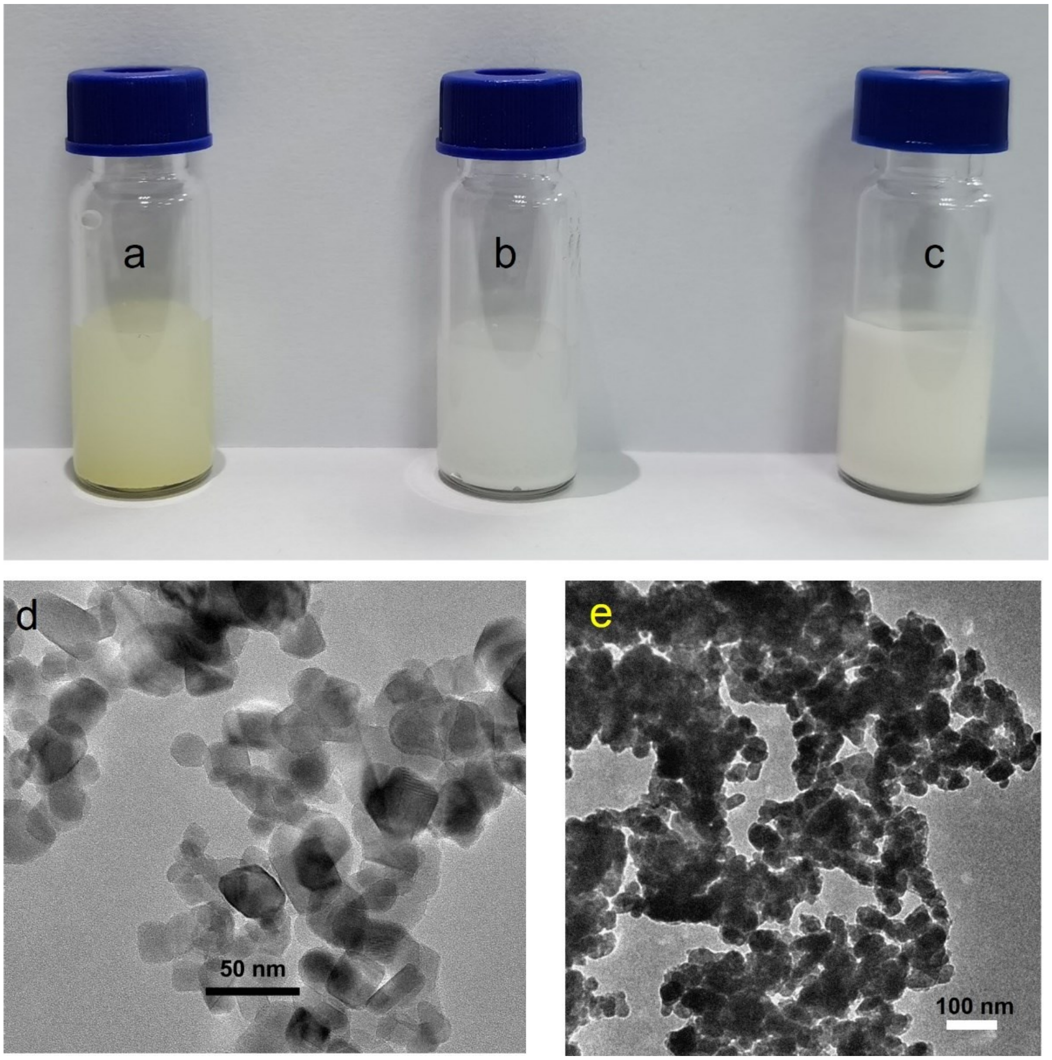

Figure S5. Color changes of (a) brookite nanosheets, (b) P25 TiO_2 nanoparticles, and (c) rutile nanoparticles. (d) TEM image of P25 TiO_2. (e) TEM image rutile nanoparticle.

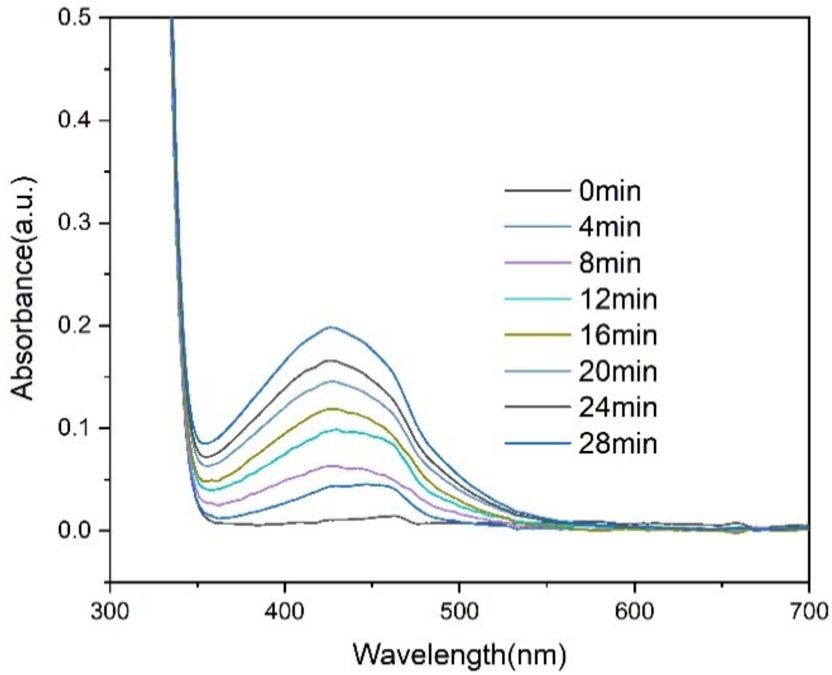

Figure S6. Oxidation results of TMB with H_2O_2 catalyzed by brookite nanosheets in ethanol.