AuPd Nanoparticles Decorated Ultrathin $Bi_2TiO_4F_2$ Sheets for Photocatalytic Methane Oxidation

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Experiment section

1.1. Materials and reagents

Titanium tetrafluoride (TiF_4), Tert.-butyl alcohol ,Bismuth nitrate ($Bi(NO_3)_3●5H_2O$), Trihydrhydrate tetrachlorallic acid ($HAuCl_4•3H_2O$), potassium chloropalladite, palladous chloride, Oleylamine, absolute methanol and Borane-butamine were obtained from Sinopharm Chemical Reagent Co., Ltd,Shanghai, China.

1.2. Preparation

Synthesis of bulk $Bi_2TiO_4F_2$: $Bi_2TiO_4F_2$ bulk crystals were synthesized by hydrothermal method. 7.5 mmol TiF_4 was dissolved in 60 mL tert-butyl alcohol to form a clear solution A. 1.0 mmol $Bi(NO_3)_3·●5H_2O$ was dissolved in 5 mL ethylene glycol to form a clear solution B. Solution A and B were mixed via stirring for 5 min at room temperature, then the suspension was transferred into a 50-mL Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 °C for 18 h. Subsequently, the autoclave was cooled to room temperature naturally, and the resultantsample was centrifuged and washed with deionized water and alcohol several times. The final products were obtained after vacuum drying at 80 °C for 12 h.

Synthesis of $Bi_2TiO_4F_2$ ultrathin nanosheets (BTOF): $Bi_2TiO_4F_2$ ultrathin nanosheets are synthesized by using carbon quantum dots to exfoliate bulk crystals into nanosheets. Disperse 100 g of activated carbon into 50 mL of deionized water, and add 100 mL of concentrated nitric acid to the mixture with stirring. Reflux and condense at 130 °C for 2 days. The obtained carbon quantum dots are extracted, filtered, distilled under reduced pressure, and dried for later use. 180°C-$Bi_2TiO_4F_2$ and carbon quantum dots were dissolved in deionized water with a mass ratio of 1:1, ultrasonicate the cell pulverizer for 6 hours, then centrifuge, wash, and dry to obtain BTOF nanosheets.

Synthesis of Au/BTOF nanosheets: Au/BTOF NSs were prepared via light deposition method. BTOF was dispersed in 40 mL deionized water, add a certain amount of $HAuCl_4•3H_2O$ aqueous solution, stir well at room temperature, and irradiate it with a xenon lamp for 30 min. The color of the solution gradually changed from grayish yellow to faint purple-red. Then the resultantsample was centrifuged and washed with deionized water several times. The products were collected by centrifugation and washed several times with deionized wate, and finally dried at 80 °C under vacuum for 12h. The dried sample was calcined in a tube furnace for 2 h under an argon atmosphere

at 300 °C. By changing the amount of HAuCl4•3H2O aqueous solution to change the amount of Au loading, the resulting sample is expressed as x-Au/BTOF NSs, where x represents the mass percentage of Au.

The process for synthesizing Pd/BTOF nanosheets is similar to that for synthesizing Au/BTOF nanosheets.

Synthesis of Au_1Pd_2 alloy: The Au_1Pd_2 alloy was obtained via the following steps: Dissolve $HAuCl_4•3H_2O$ (4.1 mL, 0.1 mmol) and K_2PdCl_4 (65.2 mg, 0.2 mmol) in 20 mL oleylamine and heated to 60 °C in an oil bath. When the solution turned black, borane-tert-butylamine (400mg , 4.6 mmol) and 4 mL oleylamine mixed solution was added in it quickly. Then heated to 90 °C, and kept for 30 minutes, subsequently naturally cooled to room temperature. Wash and centrifuge the obtained product with ethanol several times, finally dispersed in n-hexane.

Synthesis of Au_1Pd_2/BTOF nanosheets: Disperse the prepared BTOF nanosheets in n-hexane, add a certain amount of Au1Pd2 alloy, and stir at room temperature for 24 hours. It was observed that the solution changed from black to colorless, and the color of the sample changed significantly. The resulting sample was centrifugation and washed with deionized water, and then dried under vacuum at 80°C for 12 hours. After that, Au1Pd2/BTOF nanosheets were obtained by calcining the dried sample in a tube furnace for 2 h under an argon atmosphere at 300 °C. The obtained sample is expressed as x-Au_1Pd_2/BTOF NSs, where x represents the mass percentage of Au_1Pd_2 alloy content.

1.3 Characterization of samples

The crystal structure of the synthesized powder was determined by using a powder X-ray diffractometer (XRD, ESCALA 250 Thermo Fisher Scientific) with Cu-Kα (λ = 1.5416 Å) radiation, and the scanning rate is 8°/min with a step size of 0.02°. Scanning electron microscopy (SEM, F200S Thermo Scientific FEI), transmission electron microscopy (TEM, SU8000 Hitachi, Japan), and high-resolution transmission electron microscopy (HRTEM, SU8000 Hitachi, Japan) were used to characterize the morphology and microstructure of the prepared samples. Ultraviolet-visible (UV-vis) spectrophotometry (Cary-500 Varian, America) was performed to monitor the diffuse reflectance spectra. X-ray photoelectron spectroscopy (XPS) analyses were performed using an ESCALAB 250 system (Thermo Scientific) with Al-Kα (hν=1486.6 eV), and the size of X-ray

electron beam spot is 300 μm× 700 μm. Electron paramagnetic resonance instrument (EPR, ESP300E, Brucker) detect defects and free radicals at room temperature.

1.4 Photoelectrochemical measurement

The photoelectrodes were fabricated was the same as electrochemical preparation method. An Ag/AgCl electrode, and a platinum electrode were used reference electrode, and counter electrode, respectively. The photoelectrochemical tests were performed on CHI-600E electrochemical system with a 0.2 mol/L Na2SO4 electrolyte solution. The light source was the same as that used for photocatalytic methane activation. The photocurrent responses of the samples to were measured at 0.3V with a switching lamp.

1.5 Photocatalytic activity measurement

The photocatalytic methane activation performance were executed on GC online analysis system (Agilent, America) with a 150 mL quartz reactor. PLSSXE 300UV Xe lamp (320–800 nm) was used as the light source. And the light source is about 8 cm away from the sample. 5 mg sample was dispersed in 1 ml of deionized water and then dropped in a quartz wafer container (1.5cm in diameter) to dry, after that put into the reactor for reaction. The reaction was carried out for 2 h and is tested every half an hour. The generated CH_3OH and CO was detected by gas chromatography (Agilent 7890A and 7890B, respectively) with Ar as the carrier gas, and the detector is flame ionization detector (FID).

Supporting figures

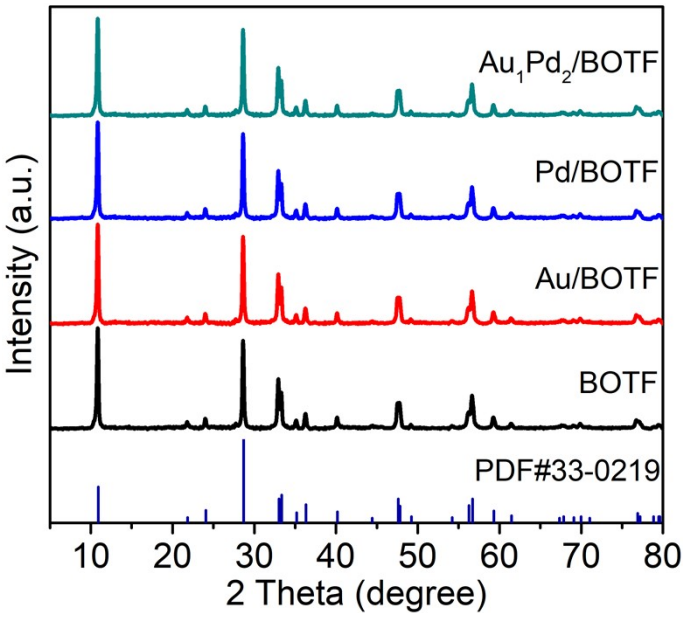

Fig. S1 The Powder X-ray diffraction (PXRD) of the BTOF, Au/BTOF, Pd/BTOF, and AuPd/BTOF

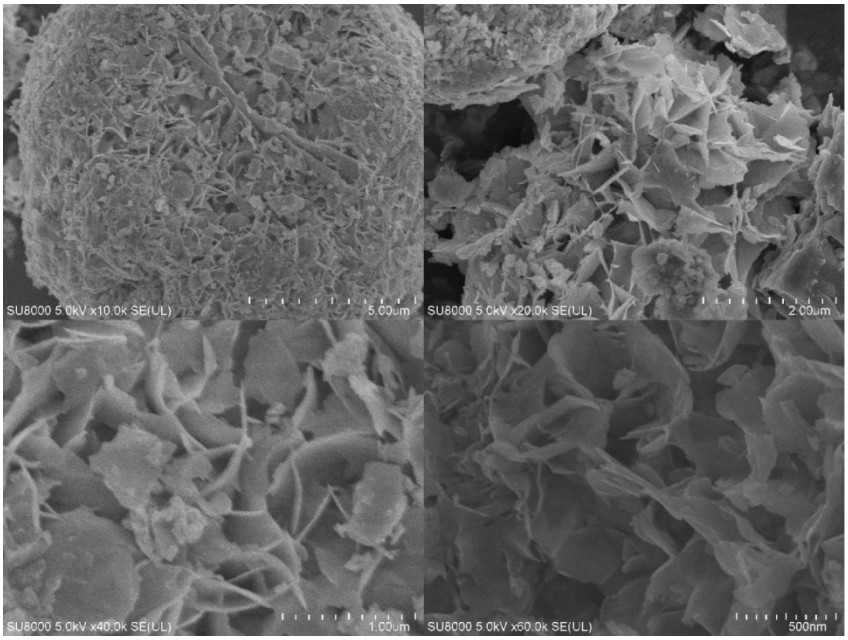

Fig. S2 SEM images of AuPd/BTOF sample at different scales

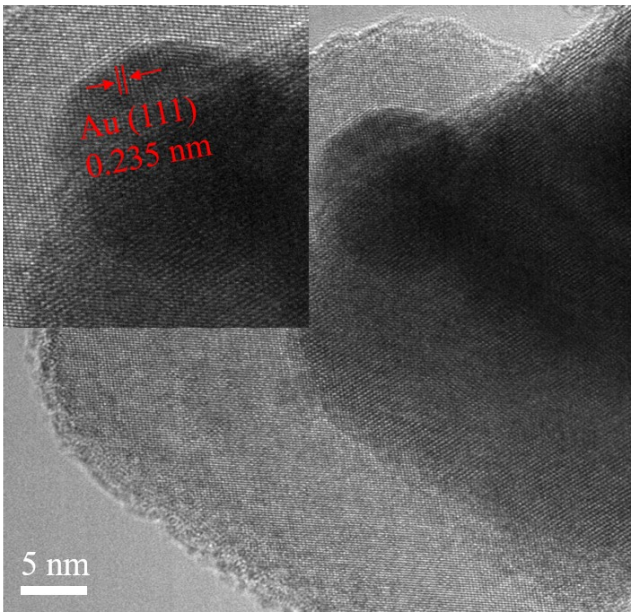

Fig. S3 TEM images of Au/BTOF sample

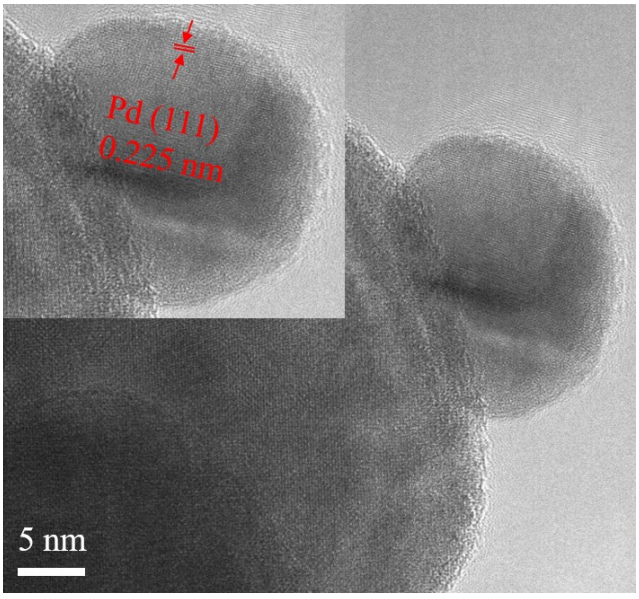

Fig. S4 TEM images of Pd/BTOF sample

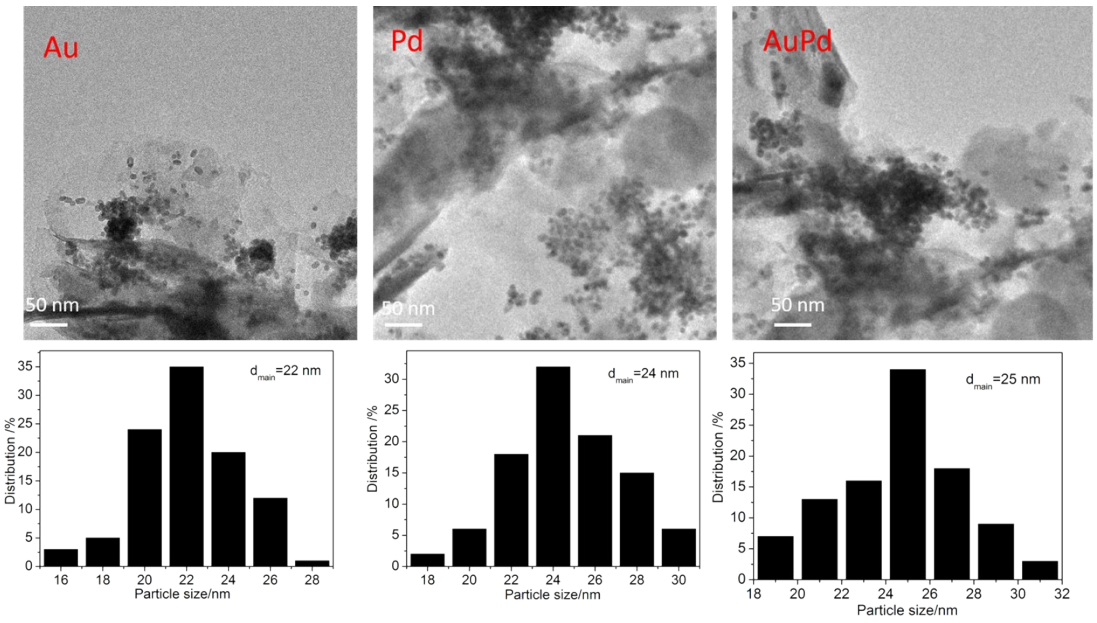

Fig. S5 TEM images (top) and Size distributions (bottom) of Au, Pd and AuPd nanoparticles.

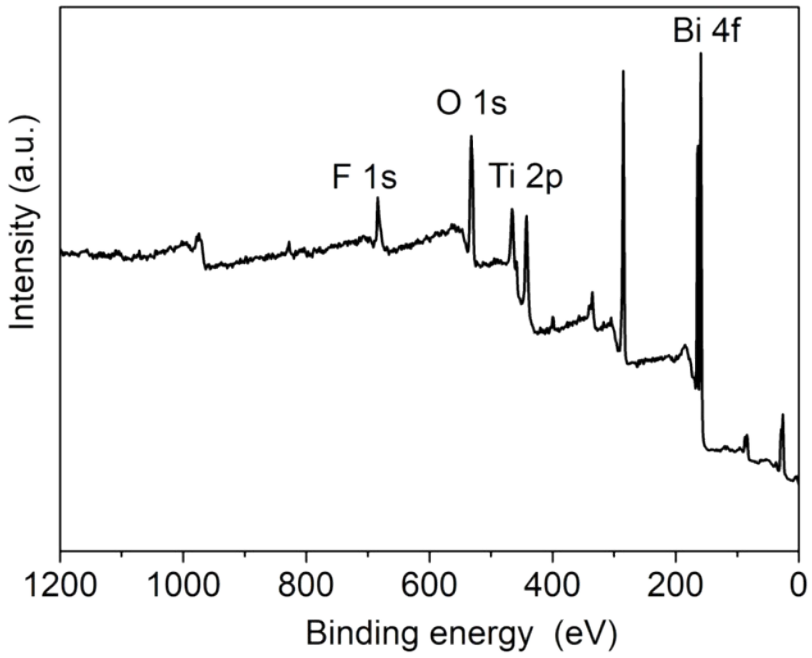

Fig. S6 XPS wide scan spectrum of AuPd/BTOF

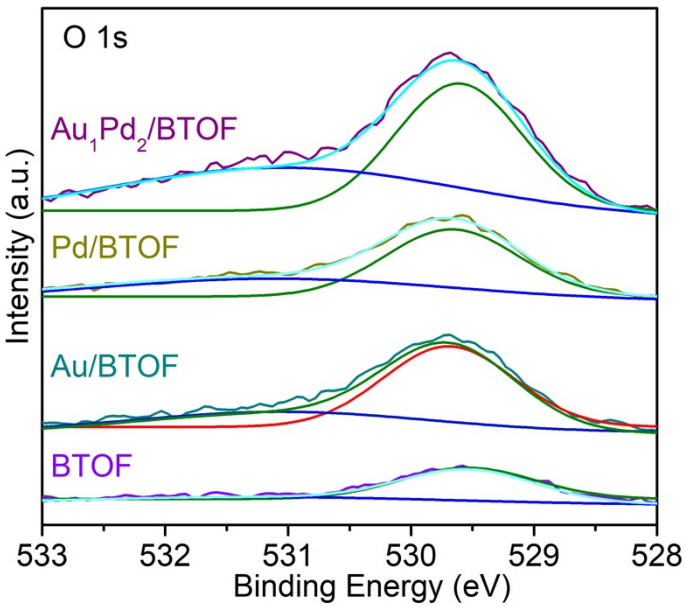

Fig. S7 XPS analysis of the as-prepared photocatalysts: O 1s

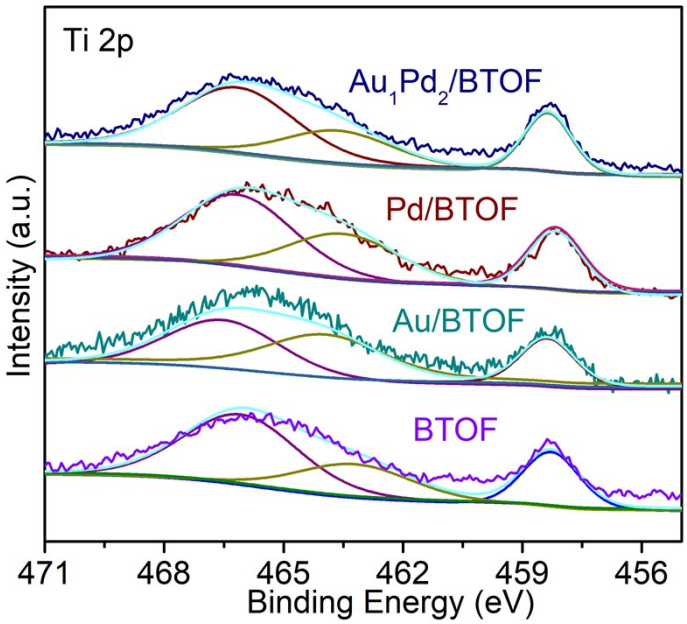

Fig. S8 XPS analysis of the as-prepared photocatalysts: Ti 2p

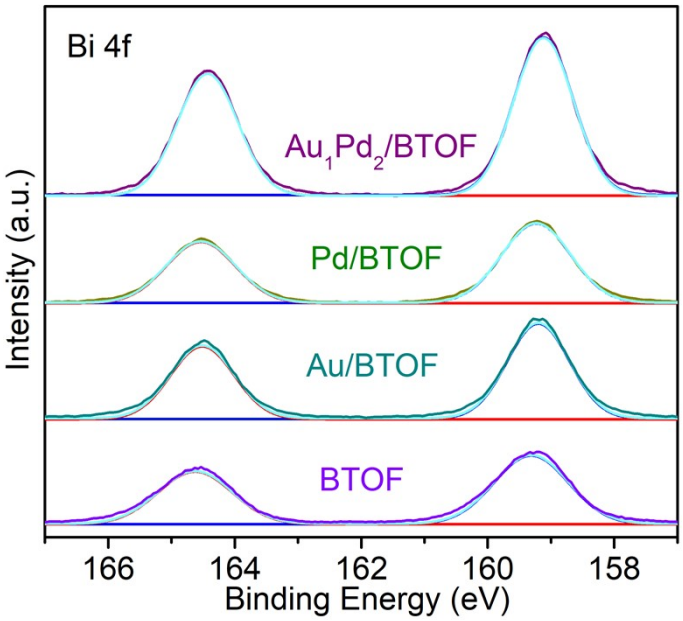

Fig. S9 XPS analysis of the as-prepared photocatalysts: Bi 4f

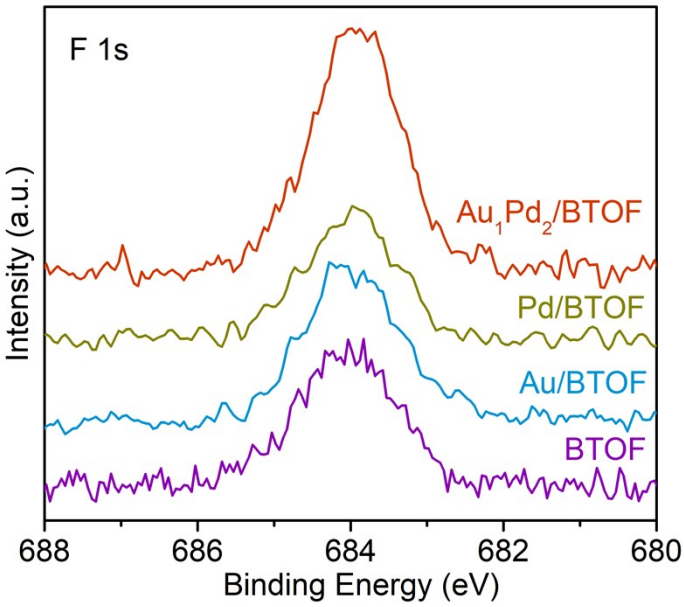

Fig. S10 XPS analysis of the as-prepared photocatalysts: F 1s

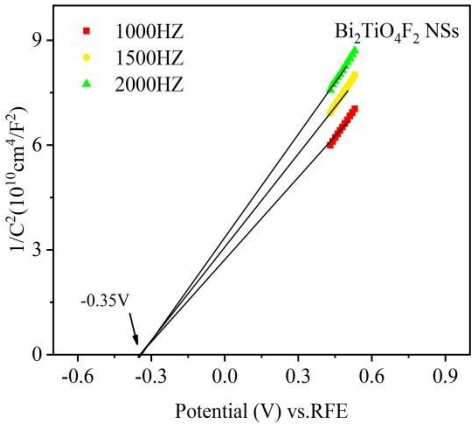

Fig. S11 Mott-Schottky plots of BTOF.

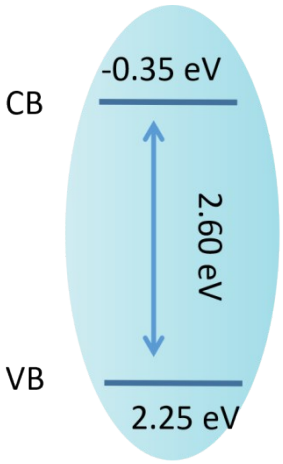

Fig. S12 The band structure of the BTOF.

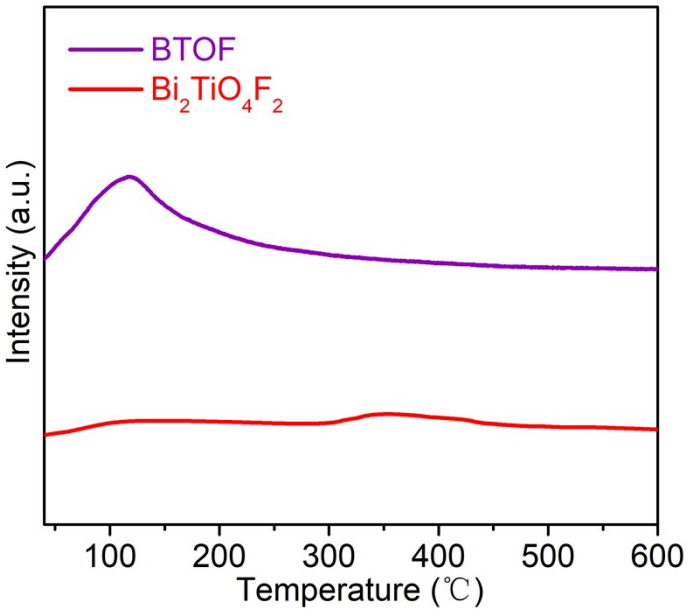

Fig. S13 CH_4-TPD signal of $Bi_2TiO_4F_2$ and BTOF

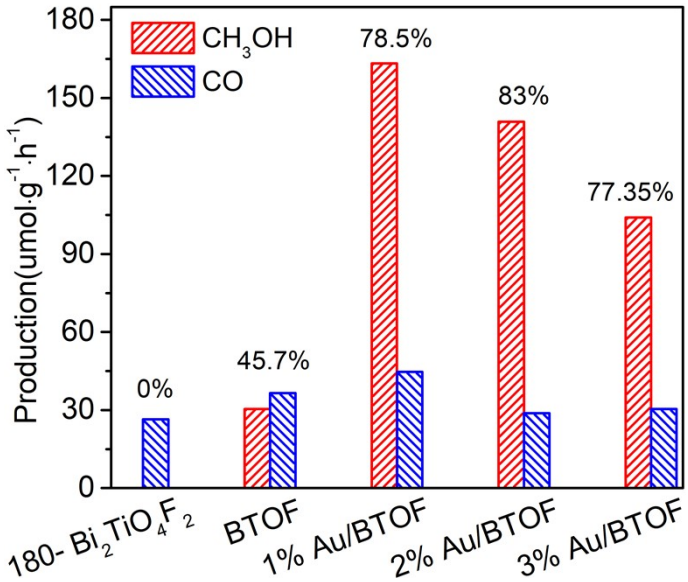

Fig. S14 Comparison of photocatalytic methane oxidation activity on different Au content $Bi_2TiO_4F_2$

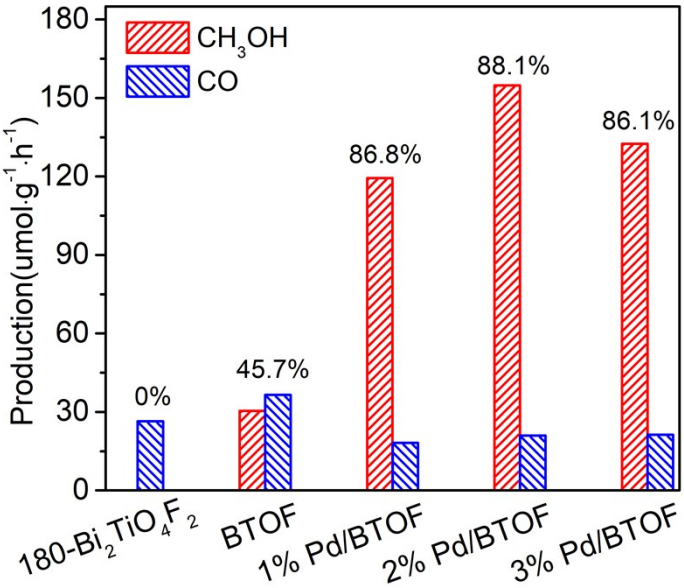

Fig. S15 Comparison of photocatalytic methane oxidation activity on different Pd content $Bi_2TiO_4F_2$

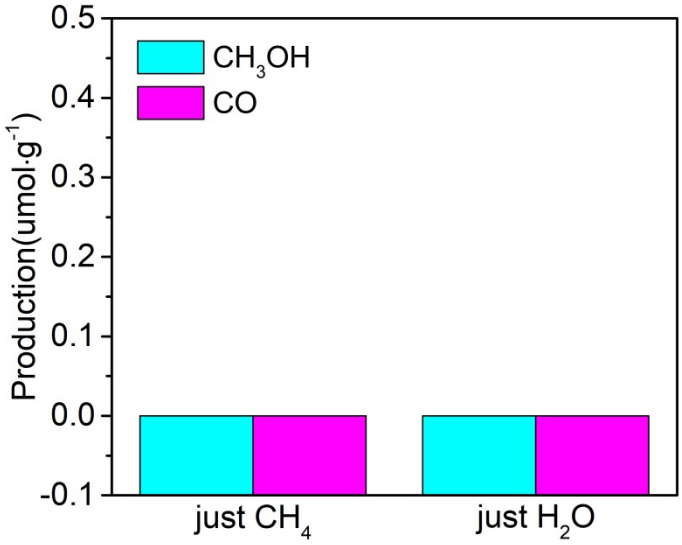

Fig. S16 Photocatalytic activation experimental just using CH_4 or H_2O for BTOF

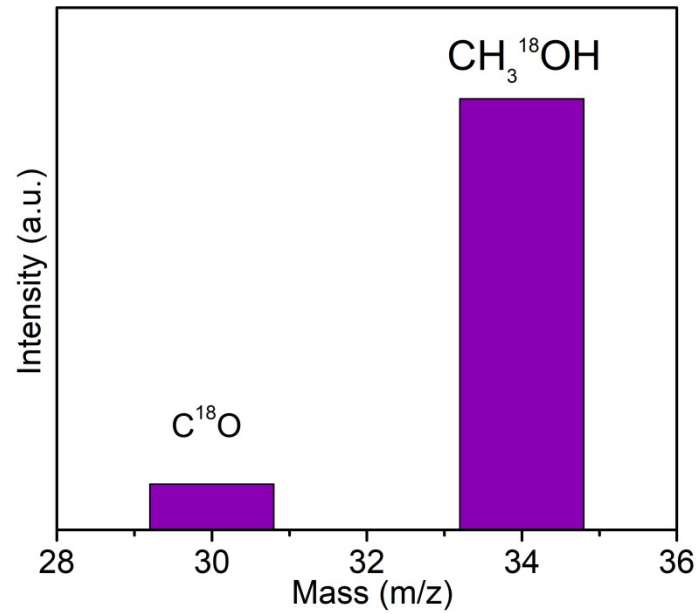

Fig. S17 $C^{18}O$ and $CH_3{}^{18}OH$ signal in AuPd/BTOF sample

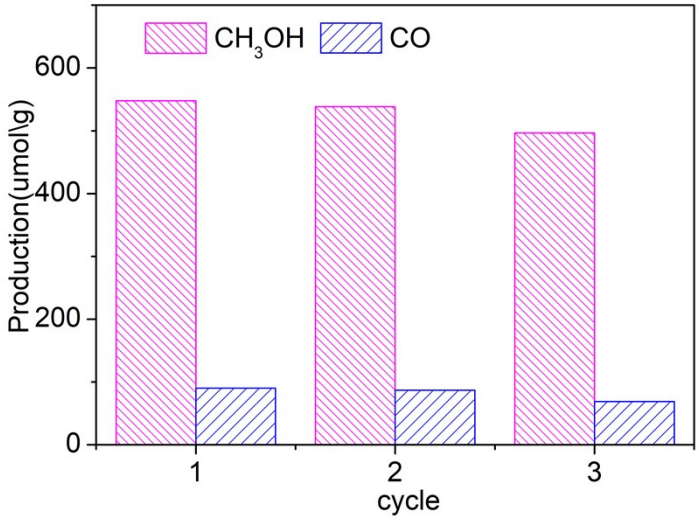

Fig. S18 Cycling measurements for CH_4 photo-oxidation of AuPd/BTOF sample.

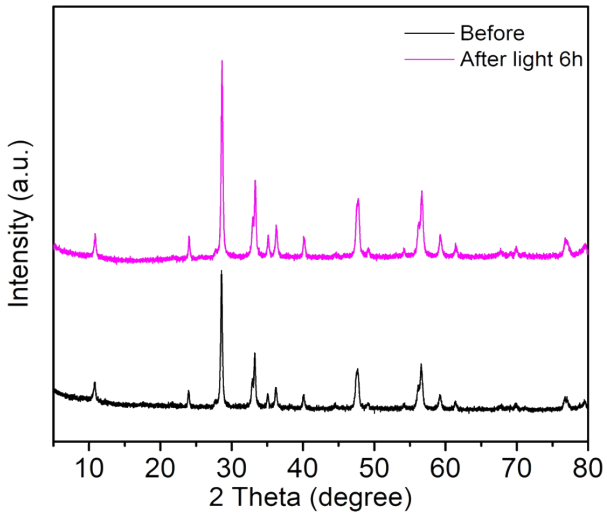

Fig. S19 XRD measurements on AuPd/BTOF before and after photocatalytic recycle reactions.