Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Facile construction of leaf-like WO_3 nanoflakes decorated on g-C_3N_4 towards efficient oxidation of alcohols under mild conditions

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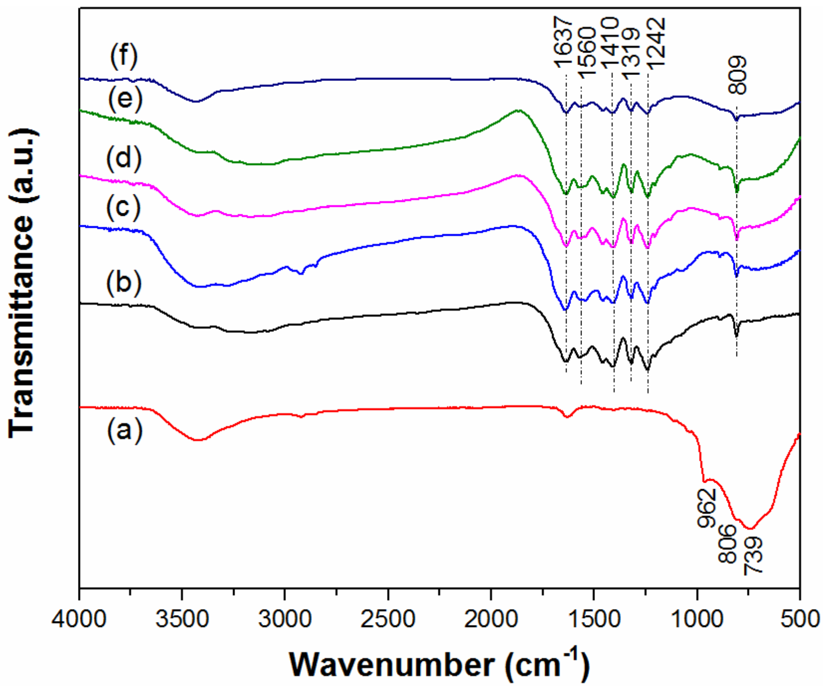

Fig. S1 FT-IR spectra of (a) WO_3, (b) g-C_3N_4, (c) 1WO_3/g-C_3N_4, (d) 2WO_3/g-C_3N_4, (e) 3WO_3/g-C_3N_4 and (f) 4WO_3/g-C_3N_4.

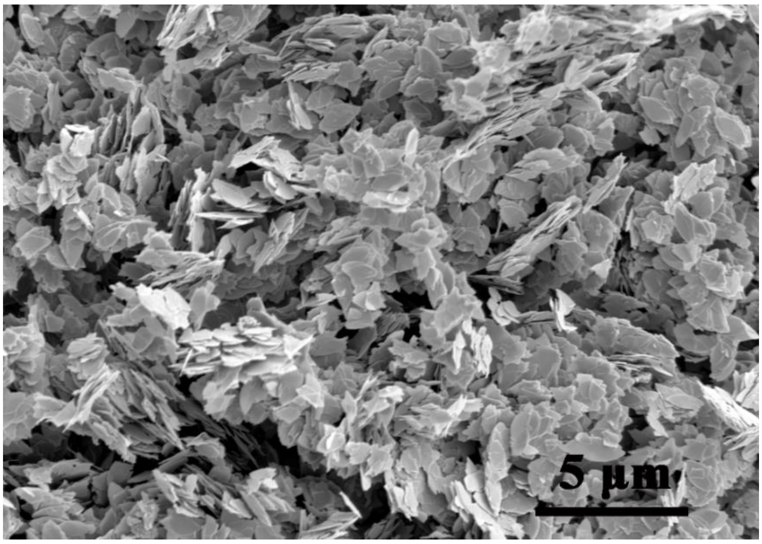

Fig. S2 FESEM image of pure WO_3.

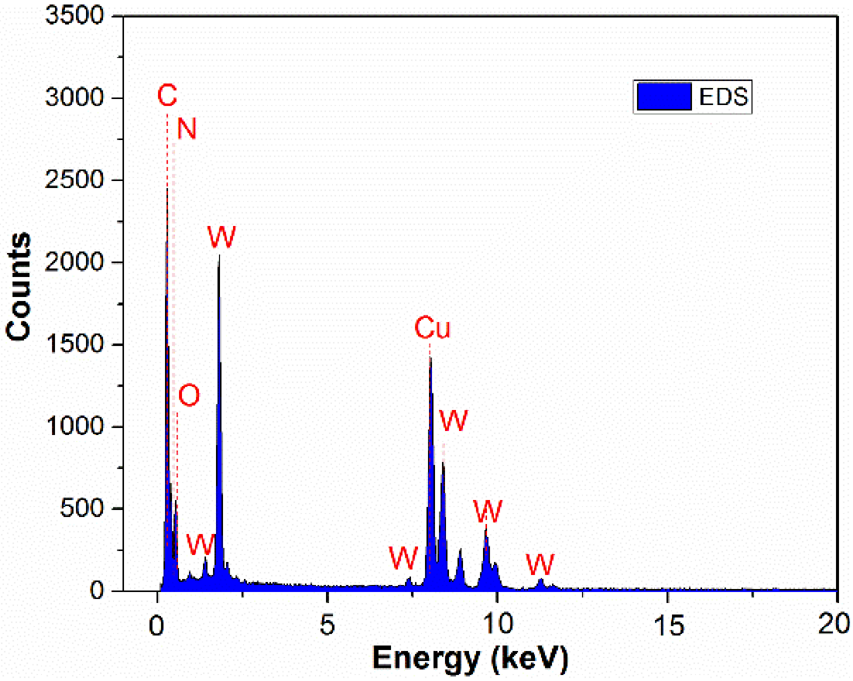

Fig. S3 The corresponding energy dispersive X-ray spectrum (EDS) of $3WO_3/g\text{-}C_3N_4$ form HAADF-STEM mode. The detected Cu signals come from the copper grid that supports the TEM samples.

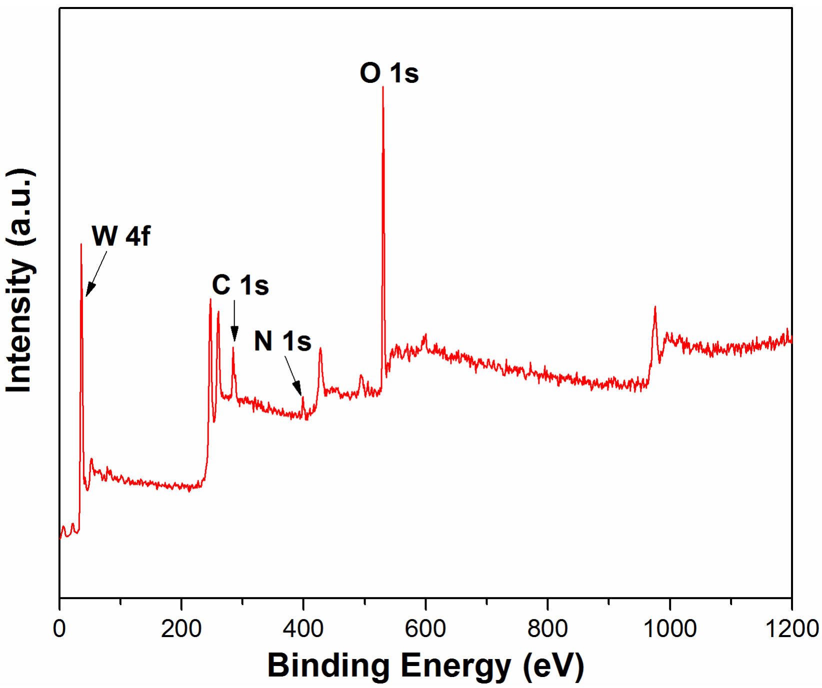

Fig. S4 Wide-range XPS spectrum of $3WO_3/g\text{-}C_3N_4$ sample.

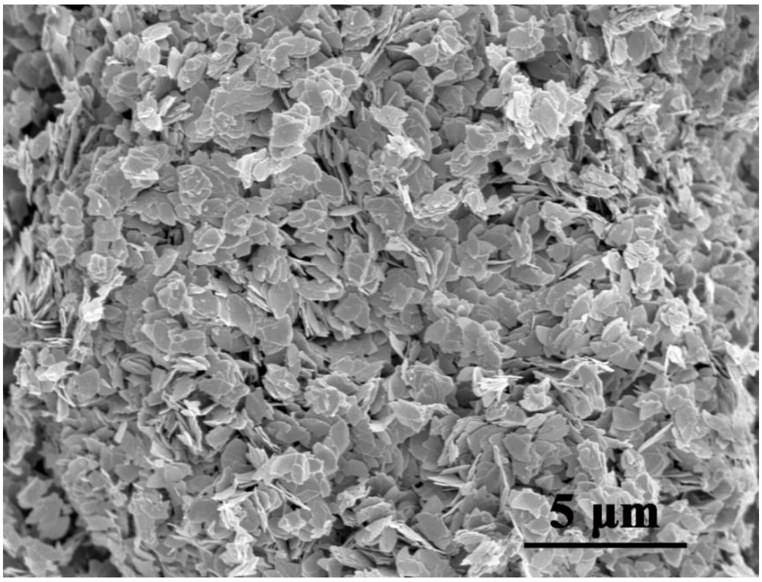

Fig. S5 FESEM image of $4WO_3/g\text{-}C_3N_4$ catalyst.

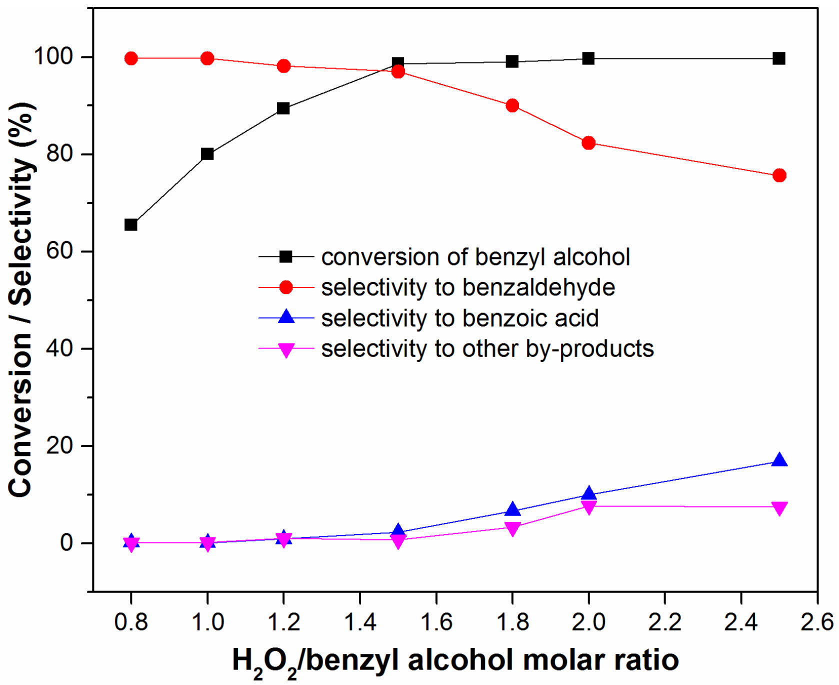

Fig. S6 Effect of H_2O_2 dosage on catalytic performance of $3WO_3$/g-C_3N_4. Reaction conditions: 0.5 mmol benzyl alcohol, 1 ml H_2O, 10 mg catalyst, 80 ℃, 3 h.

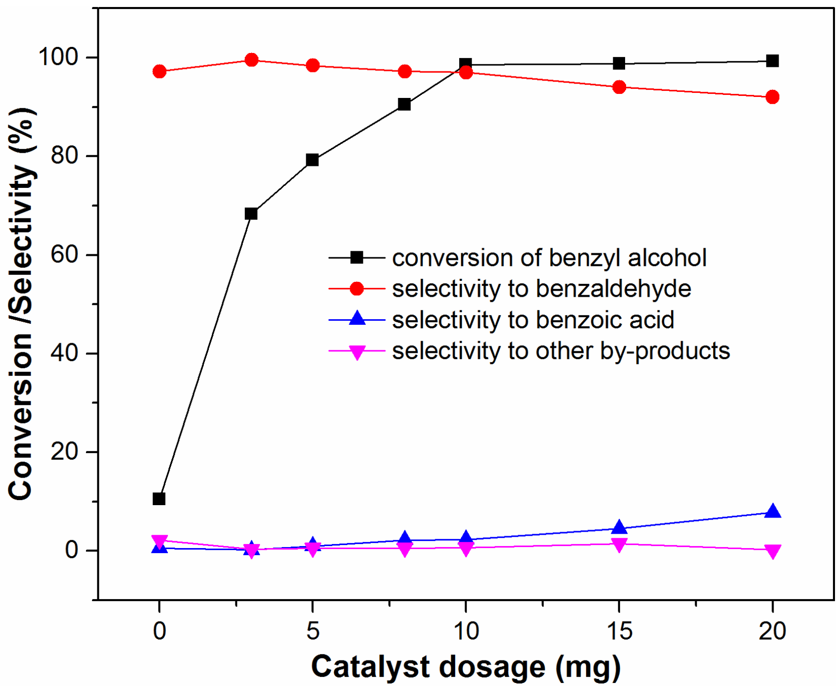

Fig. S7 Effect of catalyst dosage on catalytic performance of $3WO_3$/g-C_3N_4. Reaction conditions: 0.5 mmol benzyl alcohol, 0.75 mmol H_2O_2, 1 ml H_2O, 80 ℃, 3 h.

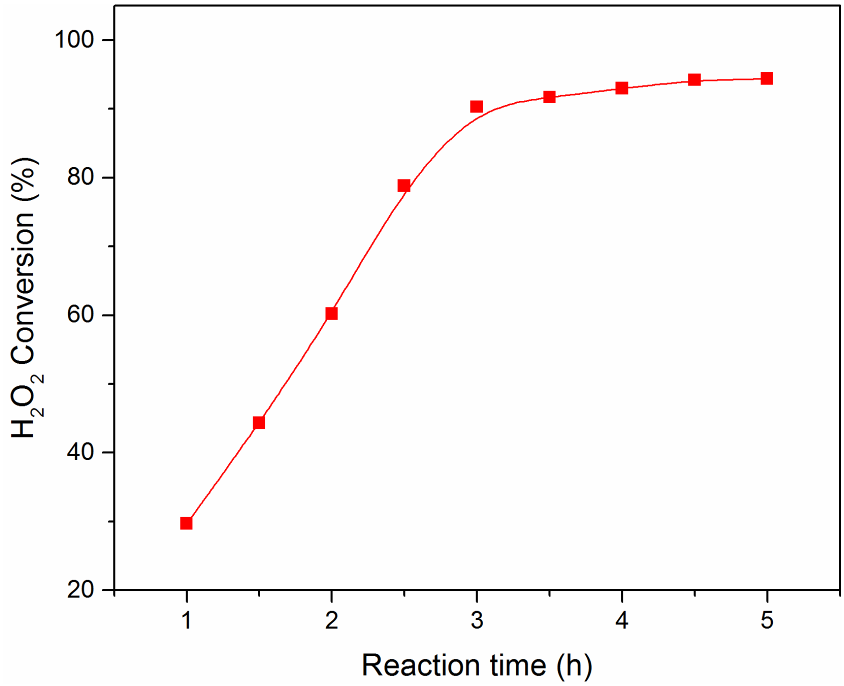

Fig. S8 Changes of the H_2O_2 conversion with the reaction time in the selective oxidation of benzyl alcohol to benzaldehyde over $3WO_3/g\text{-}C_3N_4$ catalyst.

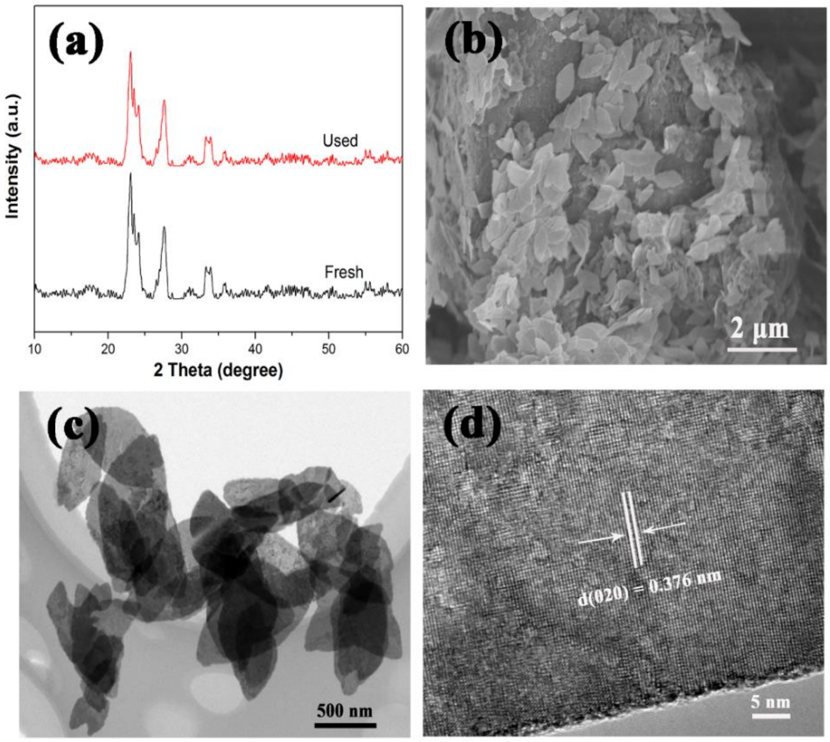

Fig. S9 (a) XRD patterns of the fresh and used $3WO_3/g\text{-}C_3N_4$ catalyst, (b) FESEM image, (c) TEM image and (d) HRTEM image of the used $3WO_3/g\text{-}C_3N_4$ catalyst.

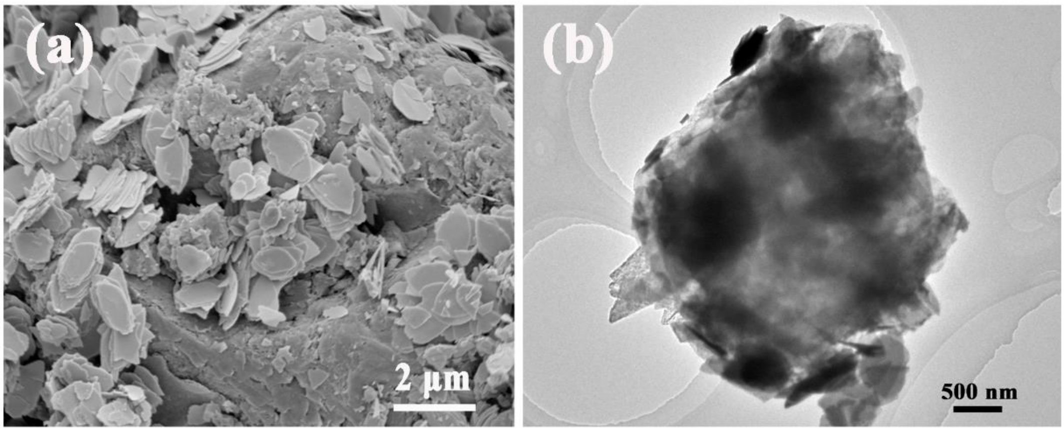

Fig. S10 (a) SEM image and (b) TEM image of the $3WO_3$/g-C_3N_4 catalyst.

Experimental details for GC analysis

Quantitative analysis of the reaction products was used the external standard method with gas chromatography (Agilent 6820, FID detector). Firstly, a series of solutions of standard samples (benzyl alcohol, benzaldehyde and benzoic acid) in ethyl acetate with different concentrations were prepared, respectively. Then, the solutions were analyzed with GC to determine the corresponding working curve and calculate the linear regression equation, respectively. Based on the peak areas of the different substances, we can Fig. out the conversion of reactants and the selectivity to different products. The reactants and reaction products were identified by comparing the retention time with that of the known standard samples.

The GC detecting conditions were as follows: nitrogen as the carrier gas; injection port temperature = 300 ℃; detector (FID) temperature = 300 ℃; column temperature = 50 ℃ (maintained for one min), and then heating up to 200 ℃ at a heating rate of 10 ℃/min (maintained for one min).

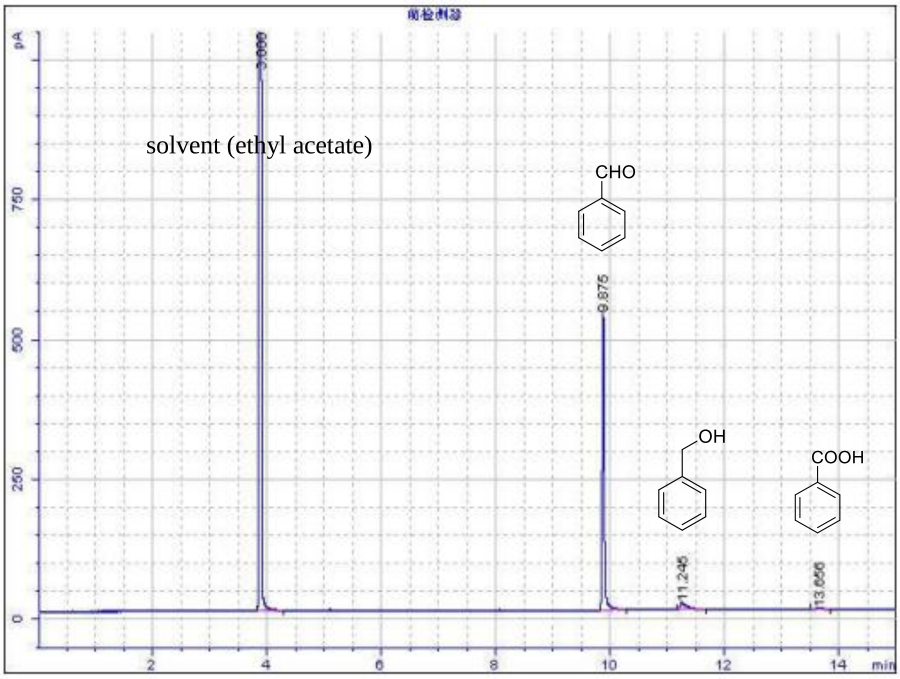

Fig. S11 The typical GC diagram for the selective oxidation of benzyl alcohol. (T = 3.880 min, solvent/ethyl acetate; T = 9.875 min, benzaldehyde; T = 11.245 min, benzyl alcohol; T = 13.656 min, benzoic acid.)

Effect of solvents on the catalytic oxidation reaction

The catalytic oxidation of benzyl alcohol was investigated in different solvents using $3WO_3$/g-C_3N_4 as the catalyst and H_2O_2 as the oxidant, and the results were presented in Table S1. It can be found that both conversion of benzyl alcohol and selectivity to benzaldehyde were very poor when toluene and cyclohexane were used as the solvents (Table S1, entries 6 and 7), which may be associated with the poor miscibility of aqueous H_2O_2 and water-insoluble solvents (toluene and cyclohexane). In addition, with respect to the other organic solvents, such as CH_3CN, THF, DMF, 1,4-dioxane (Table S1 entries 2−5), only moderate catalytic performance were achieved under the optimized reaction conditions. However, when water was used as the solvent (Table S1, entry 1), the most satisfactory catalytic activity with 98.6% conversion and 97.0% selectivity to target product was obtained. It was because that the WO_3/g-C_3N_4 catalyst has a good dispersion in water, which could expose more active sites for the catalytic reaction. On the other hand, WO_3 has an excellent hydrophilic property,[1−3] which could more readily interact with H_2O_2 molecules in aqueous media to more give active oxygen species, and thus leading to the highest catalytic activity among the selected solvents.

Table S1 Effect of different solvents on catalytic oxidation of benzyl alcohol [a]

Entry	Solvent	Conversion (%)	Selectivity (%)	Yield (%)[b]
1	H_2O	98.6	97.0	95.6
2	CH_3CN	66.8	84.9	56.7
3	THF	50.5	85.8	43.3
4	DMF	74.9	88.7	66.4
5	1,4-dioxane	45.7	78.5	35.9
6	Toluene	32.6	67.8	22.1
7	Cyclohexane	44.5	82.7	36.8

[a] Reaction conditions: 0.5 mmol benzyl alcohol, 0.75 mmol H_2O_2, 1 ml solvent, 10 mg $3WO_3$/g-C_3N_4 catalyst, 80 ℃, 3 h. [b] The yields of the reactions were determined by GC analysis with external standard method.

References

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