Supplementary information

Microwave-assisted growth of $WO_3 \cdot 0.33H_2O$ micro/nanostructures with enhanced visible light photocatalytic properties

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The $\log K_1$, $\log K_2$ and σ_n were calculated by referring to Saison et al[1]. According to their report, the multi site complexation model (MUSIC model) was used to calculate the effective bond charge (q_0) of different surface groups. Firstly, the effective bond valence (s) is calculated. This valence is defined as $\mathbf{s=e^{(R-R_0)/b}}$, in which R is the metal oxygen distance, R_0 is an element specific distance (R_0=0.1917 nm for tungsten), and b is a constant (b = 0.037 nm). Afterwards, the "q_0" was defined as: $\mathbf{q_0 = \Sigma sj+ms_H+n(1-s_H)+V}$, where $\sum s_j$ is the sum of effective bond valences of metal cations bonded to oxygen, m is the number of donating hydrogen bonds, n is the number of accepting hydrogen bonds, s_H is the bond valence for an adsorbed proton (s_H=0.8), and V is the valence of oxygen (V=-2). For singly metal-coordinated oxygen, the total number of hydrogen bonds (m+n) are defined as 2. For doubly and triply coordinated surface oxygen, m+n is defined as 1. Therefore, by employing the metal oxygen distance and referring the specific interactions between surface groups and water molecule, it is possible to calculate the charge of the surface oxygen q_0. Furthermore, this charge q_0 could be used to obtain the intrinsic proton affinity constant log K by employing the linear relationship between these two values: $\mathbf{\log K=-A*q_0}$, in which A is a constant equal to 19.8. Finally, this relationship allows one to calculate the proton affinity constants K_1 (oxo) and K_2 (hydr) of surface groups M_n-O and M_n-OH:

$M_n\text{-}O+H^+ \leftrightarrow M_n\text{-}OH$ $\quad K_1(oxo)$

$M_n\text{-}OH+H^+ \leftrightarrow M_n\text{-}OH_2$ $\quad K_2(hydr)$

The calculated $\log K_1$ and $\log K_2$ were then considered as the reference to know the nature of surface groups (M_n-O, M_n-OH and M_n-OH_2) as a function of pH. Besides, the effective charge (σ_n) of these groups were calculated with their surface density (N_s) to obtain the positive charge of one specific surface, σ+ ($\sigma+=\Sigma\sigma_n*N_s$), to compare the acidity of the different surfaces.

By using this method, the most exposed three faces ((010), (001), and (110)) in our products were calculated to find their surface differences, which are shown in table ST1. Furthermore, the effective charge (σ_n) of the groups in different faces were calculated with their surface density (N_s) to obtain the positive charge of one specific surface, σ+ ($\sigma+=\Sigma\sigma_n*N_s$), to compare the acidity of the different surfaces. The calculated results are shown in table ST2.

Tab.ST1 Proton affinity constants and charge of the surface groups in different faces

surface	group	$logK_1$	$logK_2$[a]	charge σ_0 W_n-O	charge σ_1 W_n-OH	charge σ_2 W_n-OH_2
(010)	W_1-O_a	15.206	3.326	-0.768	-0.168	**0.432**
	W_1-O_b	-10.959		-0.047		
(001)	W_2-O_a	-5.485		0.277		
	W_2-O_b	-1.782		0.09		
(110)	W_1-O_a	-10.959		-0.047		
	W_1-O_b	15.206	3.326	-0.768	-0.168	**0.432**
	W_2-O_c	-4.95		0.25		
	W_2-O_d	-1.782		0.09		

a: The $logK_2$, σ_1, and σ_2 charge values were calculated only when W_n-OH and Wn-OH_2 is possible within the pH value from 2 to 12.

Tab.ST2 Positive charge σ+ value of the different faces of $WO_3 \cdot 0.33H_2O$ particles

faces	(010)	(001)	(110)
σ_n	0.432	0	0.432
N_s[a]	7.06	0	0.89
σ+	3.050	0	0.384

N_s[a]: acidity site density

Tab.ST3 Approximate calculation of different (010) facets ratios[c]

sample[d]	morphologies	surface area (μm^2)[b]	(010) facets area (μm^2)[b]	(010) facets ratio (%)
S1	hexagonal sheets	0.255	0.011	4.23
S2	snowflakes[a] (nanosheets)	0.371	0.150	40.35
S4	urchins[a] (nanostrips)	0.132	0.041	30.35
S5	hexagonal sheets	3.195	0.308	9.64
S6	nanowires	0.031	0.020	64.52

a: The assembled structures were calculated by measuring one of their specific exposed microstructures (shown in brackets).

b: Average results from 30 particles/exposed microstructures shown in Fig.2, Fig.5 and Fig.8.

c: (110) facets were not calculated since their acidity is low and the exposed area is too small to measure.

d: S3 particles were not calculated because their exposed microstructures are unable to be identified with precise crystal growth information.

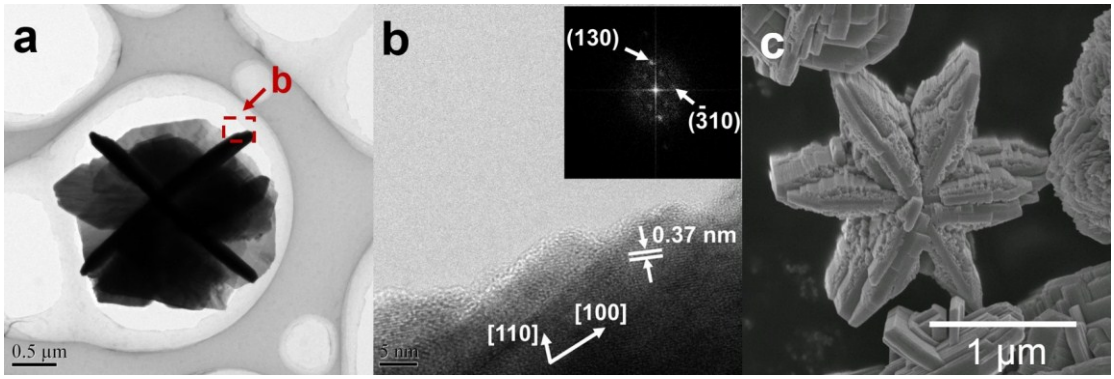

Fig.S1 TEM (a), HRTEM (b) and SEM images (c) of the intermediate products (collected as soon as the reaction temperature reached 180ºC) in the microwave-assisted hydrothermal (MH) process.

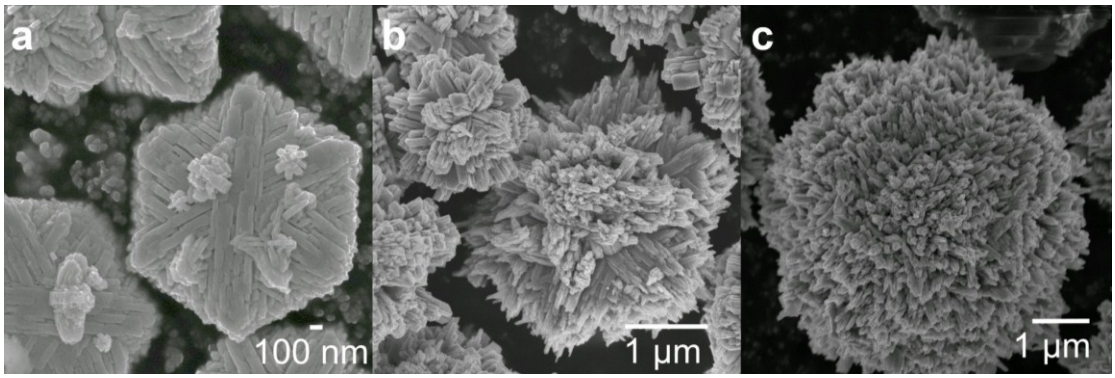

Fig.S2 SEM images of the MH-prepared products with different concentrations of citric acid (a: 0.127 M, b: 0.635M, c: 1.27M)

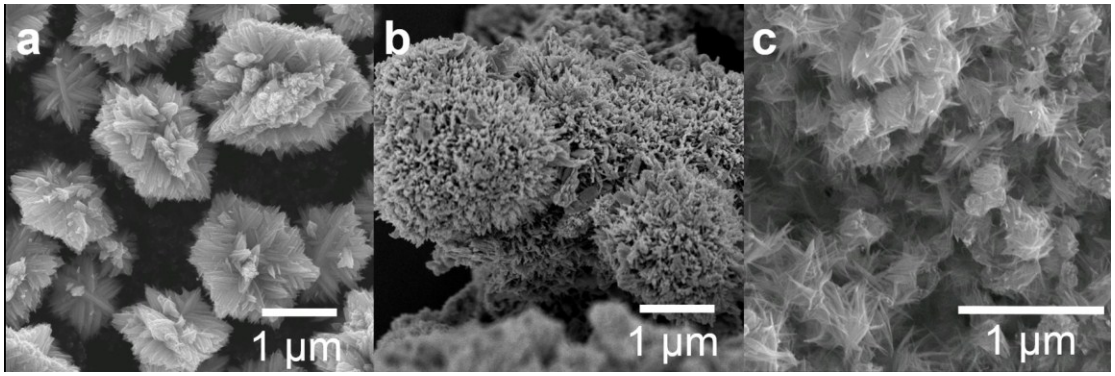

Fig.S3 SEM images of the microwave-assisted products prepared with different amount of isopropyl alcohol in the reaction solvent (a: 10%, b:50%, c:100%)

Reference

Reference

1. T. Saison, N. Chemin, C. Chanéac, O. Durupthy, V. r. Ruaux, L. Mariey, F. o. Maugé, P. Beaunier and J.-P. Jolivet, The Journal of Physical Chemistry C, 2011, 115, 5657-5666.