In Situ Synthesis of C-doped $BiVO_4$ with Natural Leaf as Template under Different Calcination Temperature

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Preparation of $BiVO_4$ impregnation solution: The $BiVO_4$ impregnation solution was prepared as follows:[1] (1) 19.4 g $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in a mixture containing 80 mL ethanol and 60 mL glycerol at 70 ℃ with magnetic stirring; (2) 4.68g NH_4VO_3 was dissolved in 20 mL TMAH with gently shaking; (3) these two solutions were mixed together at 70 ℃. After doing this operation, large amounts of yellow deposit appeared, added concentrated nitric acid (65%) timely until the solution became transparent.

Morphology and microstructure analysis. The morphologies of $CNSiBiVO_4$ were observed by FE-SEM (Fig. S1). In Fig. S1, the tubular structure (Fig. S1a and b); surface porous structure (Fig. S1c-f); side section structure (Fig. S1g) and inside section structure (Fig. S1h and i) being consist of crystal particles, can be seen, clearly. These results indicate that $CNSiBiVO_4$ has copied the multi-level structure of natural leaf successfully.

XPS analysis: The XPS patterns of $CNSiBiVO_4$ and $BiVO_4$ were analyzed to identify there elemental composition and chemical state. As shown in Fig. S2A, the XPS survey spectrum confirms the presence of Bi, V, O, Si, N and C elements. In Fig. S2B and C, the peaks with binding energies of 103.5 eV and 405.5 eV in the XPS spectrum of $CNSiBiVO_4$ can be attributed to Si 2p (103.4 eV) and N 1s (405.5 eV),[2] while these peaks are not appear in the spectrum of $BiVO_4$. These results indicate that, parts of the original Si and N element of the leaf were doped in $CNSiBiVO_4$ in the calcination process, and the Si element is present at Si^{4+}.[2] As displayed in Fig. S2D, the peaks with binding energies of 284.4 eV and 286.0 eV can be attributed to C-C bond (comes from carbon tape) and C-V bond (doped into $CNSiBiVO_4$ lattice), which confirms C element doped in $CNSiBiVO_4$, similar to Si and N elements. Fig. S2E shows the XPS spectra of Bi in $BiVO_4$ and $CNSiBiVO_4$. Each spectrum has two major peaks with binding energies at about 159.4 eV or 159.3 eV and 164.6 eV or 164.5 eV which correspond to Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively, demonstrating that the valence state of Bi in the $BiVO_4$ and $CNSiBiVO_4$ are +3.[3, 4, 5] In Fig. S2F, V 2p shows binding energy at 524.4 or 524.3 eV for V $2p_{1/2}$.[6,7] And the other two peaks at around 516.7 or 516.6 and 517.4 or 517.2 eV were attributed to V^{4+} and V^{5+}, respectively.[8,9] It is noteworthy that, for $BiVO_4$, the ratio of V^{4+} to V^{5+} is 1.08, by contrast, in case of $CNSiBiVO_4$, the ratio is 1.63, which probably owing to V^{5+} was replaced by Si^{4+}, because Si^{4+} (0.41 nm) has a close ion radius with V^{5+} (0.59 nm).[2] The decrease of V^{5+} lead to the oxygen vacancy increase,[10] which can inhibit the recombination of photogenerated electrons and holes. Fig. S2G displays the O 1s spectrum of $BiVO_4$ and $CNSiBiVO_4$, which can be divided into two peaks located at 229.9 eV or 229.6 and 231.4 or 231.3 eV, corresponding to lattice oxygen (Olatt) and surface adsorption oxygen (Oabs), respectively.[11,12] For $BiVO_4$, the ratio of Oabs to Olatt is 0.53, by contrast, in case of $CNSiBiVO_4$, the ratio is 1.31. The production of oxygen vacancy is closely related to surface adsorption oxygen. These results indicate that $CNSiBiVO_4$ has more oxygen vacancy compare with $BiVO_4$, which is consistent with the inference of V 2p.

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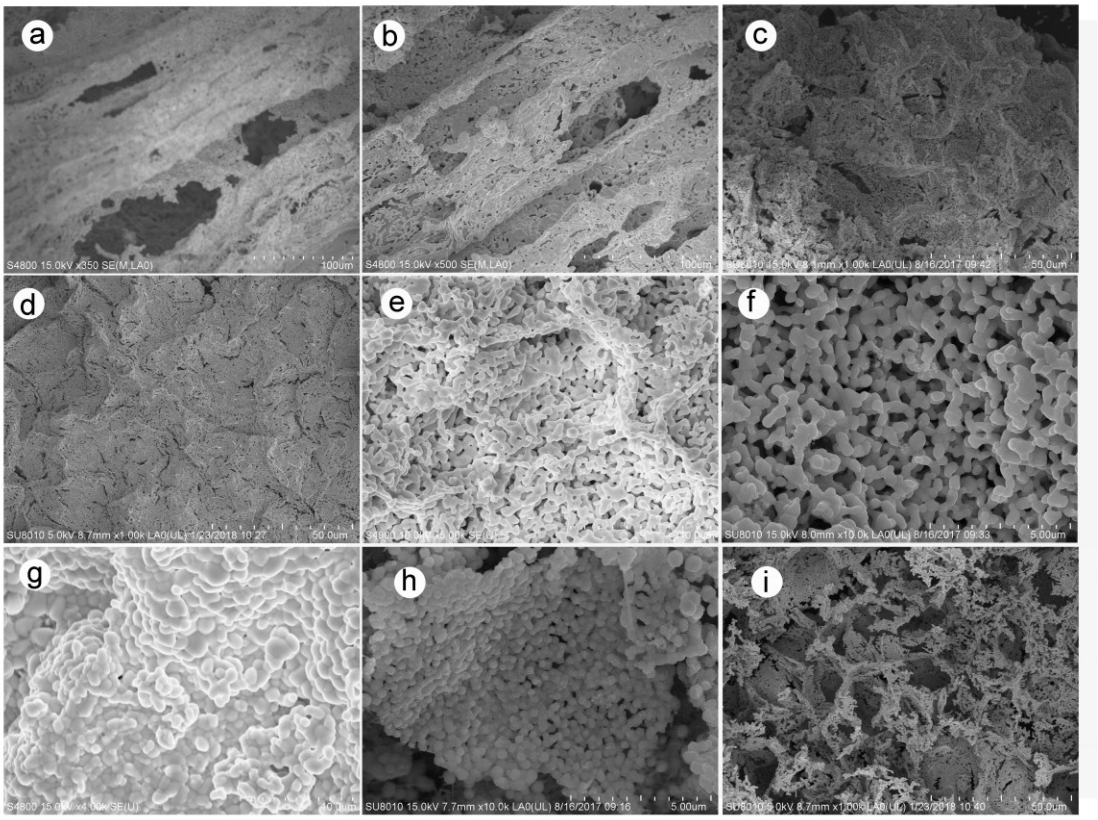


Fig. S1. FE-SEM images of the as-preepared $CNSiBiVO_4$. (a and b) the vein section of $CNSiBiVO_4$; (c-f) the surface section of $CNSiBiVO_4$; (g) the side section of the $CNSiBiVO_4$; (h-i) the inside section of $CNSiBiVO_4$.

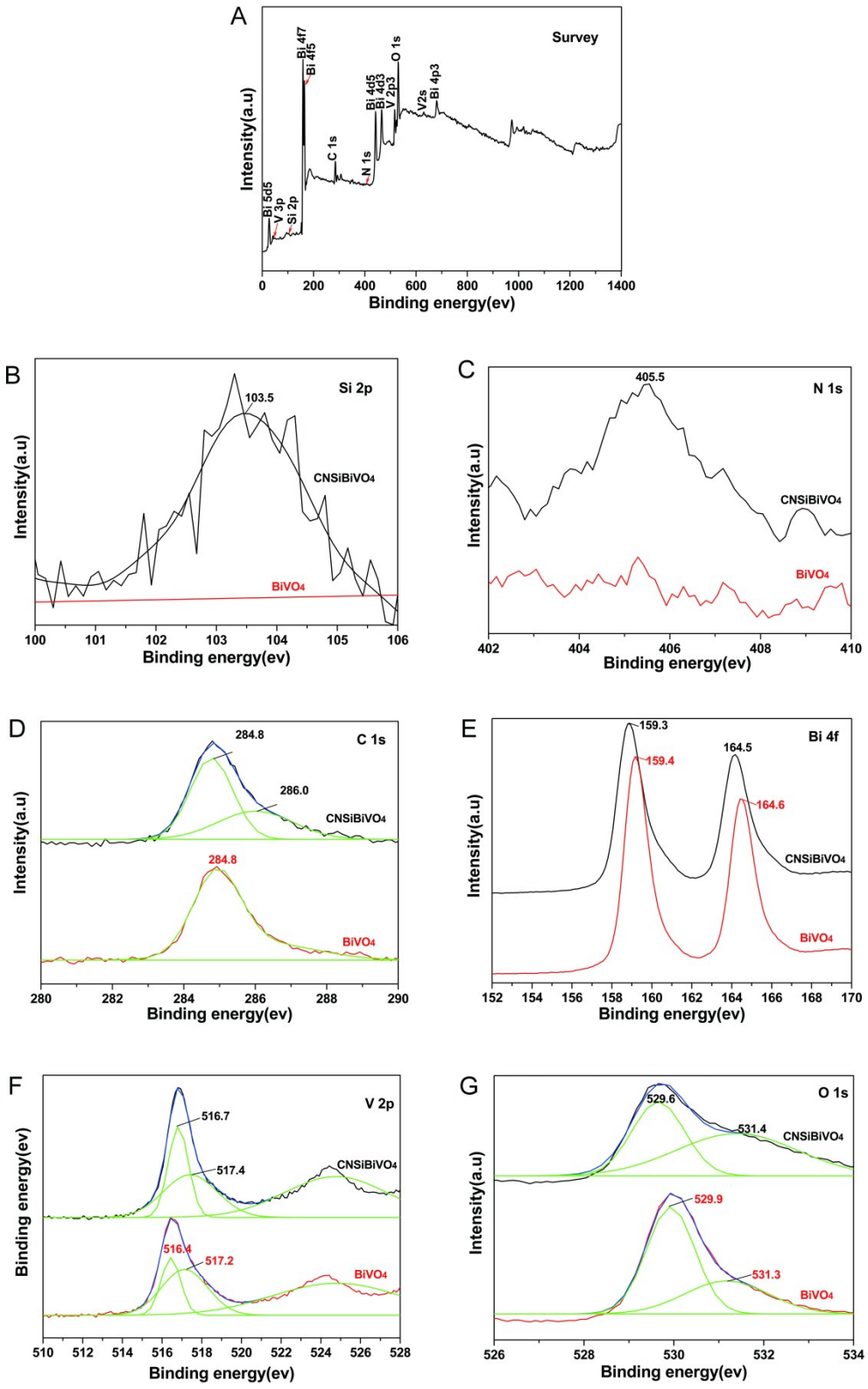
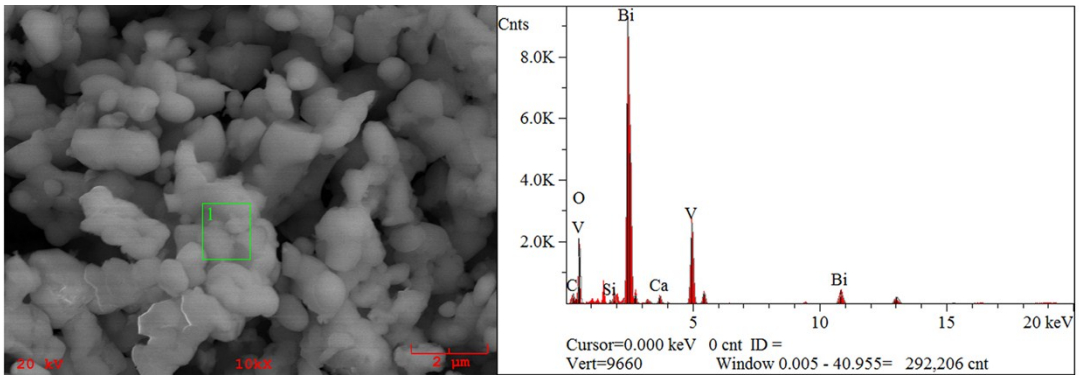


Fig. S2. XPS spectra of the as-prepared $BiVO_4$ and $CNSiBiVO_4$: (A) survey spectrum of $CNSiBiVO_4$; (B) Si 2p; (C) N 1s; (D) C 1s; (E) Bi 4f; (F) V 2p and (G) O2p.



Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units	Error 2-sig	MDL 3-sig	
C	Ka	60.54	9.780	2.577	wt.%	0.142	0.163	
N	Ka	32.91	8.126	2.497	wt.%	0.202	0.246	
O	Ka	328.45	55.512	19.483	wt.%	0.341	0.237	
Si	Ka	21.97	0.358	0.220	wt.%	0.048	0.070	
Ca	Ka	69.60	0.987	0.868	wt.%	0.058	0.077	
V	Ka	757.28	11.925	13.325	wt.%	0.153	0.105	
Bi	La	133.56	13.313	61.029	wt.%	2.008	2.054	
			100.000	100.000	wt.%			Total

Fig. S3. The EDS for $BiVO_4$-600.

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