Supplementary Information (SI) for Materials Advances.

Supplementary Materials

Tandem NiO-Ni(OH)$_2$/VS$_2$ Nanosheets: A Robust Photocatalyst for Hydrogen Evolution

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S1. Optimization study of Synthesis Parameters for VS_2 [1]

To optimize the synthesis of VS_2, the parameters of temperature, reaction time, and precursor molar ratio were systematically varied. The synthesis conditions were adjusted according to the following formula:

$$Yield\ or\ property = f\ (T_s, t_s, R)$$

where f represents a function. This function depends on the variables $(T_s, t_s, and\ R)$. T_s denotes the synthesis temperature in °C, t_s represents the synthesis time in hours, and R signifies the precursor molar ratio. The exact form of (f) would be determined through experimental data that maximizes the desired material property being investigated, such as achieving a small crystallite size with a fully layered hexagonal crystal structure of VS_2. Detailed experimental conditions are discussed in **Fig. S1**.

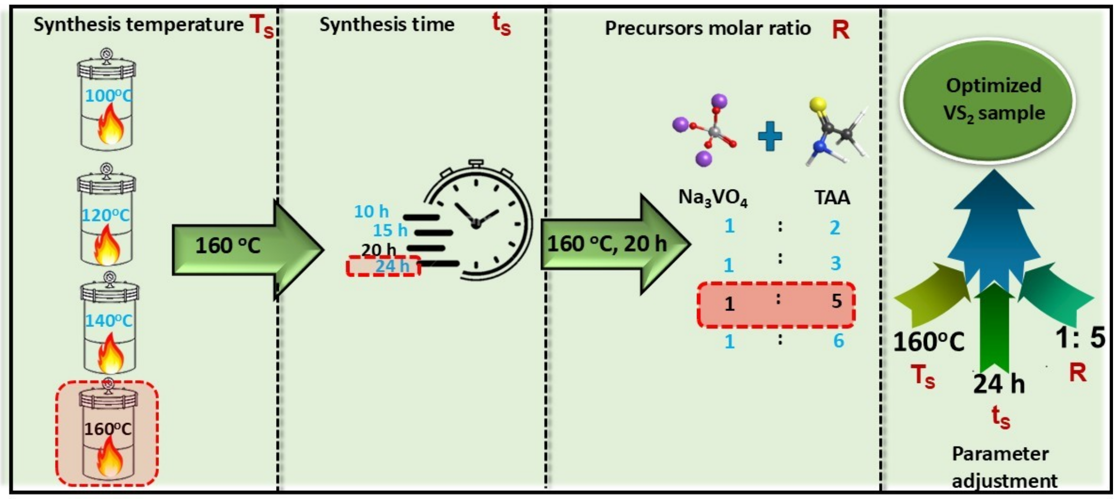

Fig. S1 Schematic procedures for optimal VS_2 synthesis.

S1.1 The impact of synthesis conditions on the particle size of VS_2

a) Optimization concerning reaction temperature

The XRD patterns in **Fig. S2a** illustrate the impact of temperature on the samples categorized by temperature group. Temperature is crucial in determining particle size, as summarized in **Table S2**. It influences both particle growth and crystallization. **Figure S2a** shows that the XRD patterns of samples treated at reactive temperatures of 100, 120, and 140 °C were predominantly amorphous in the range of $2\theta = 20^{\circ}$ to 80°. Notably, a distinct peak at $2\theta = 15.6^{\circ}$ is visible in these samples, corresponding to the (0 0 1) lattice plane of VS_2 nanosheets. Upon increasing the hydrothermal temperature to 160 °C, the XRD peak intensities for VS_2 became stronger, and the XRD diffraction peaks became slightly narrower, indicating the formation of larger and more crystalline VS_2 particles and an enhancement in crystallization. This observation suggested that hydrothermal treatment promotes the phase transition of VS_2 from amorphous to crystalline. The optimal XRD results are obtained at 160 °C.

b) Optimization concerning reaction time

Figure S2b displays the XRD patterns of Time-group samples of VS_2 synthesized at 160 °C. Time significantly impacts particle size, as evidenced by **Table S2**. The results demonstrated that extending hydrothermal treatment results in enhanced peak intensities and a more defined (0 1 1) plane diffraction peak of VS_2 at $2\theta = 35.6^{\circ}$. This pattern signified an increase in the average crystalline sizes and the overall crystallinity of VS_2 with longer treatment times, which was attributed to the facilitation of Ostwald ripening [2]. The optimal XRD results were observed with a reaction time of 24 hours.

c) Optimization concerning molar ratio of precursors

The results from the Ratio-group samples of VS_2 are illustrated in **Fig. S2c**, with the particle size variation detailed in **Table S2**. At a molar ratio of 1: 3, only one peak appeared at $2\theta = 15.6^{\circ}$ corresponding to the (0 0 1) lattice plane of VS_2 NSs. Increasing the molar ratio to 1: 4 revealed the presence of a peak for the (0 1 1) plane, indicating VS_2 NSs growth. Subsequent increases to molar ratios of 1: 5 and 1: 6 resulted in sharper and more intense peaks, with additional peaks at $2\theta = 57.1^{\circ}$, 69.4°, and 69.2° corresponding to complete hexagonal layered VS_2 NSs. It is reasonable that higher V^{4+}: S^{2-} molar ratios lead to smaller particle sizes, attributed to a reduction in reactive velocity due to decreased effective precursor concentrations [3]. Although the 1: 6 molar ratio resulted in a larger particle size than 1: 5, it might be attributed to excessive nucleation, leading to less uniform aggregated particles, reducing the available surface area and overall efficiency [4].

So, the optimal VS_2 sample was achieved through a hydrothermal reaction involving Na_3VO_4 and TAA at 160 °C for 20 hours, with a molar ratio of 1: 5, resulting in a fully formed VS_2 with a layered hexagonal nanosheet structure.

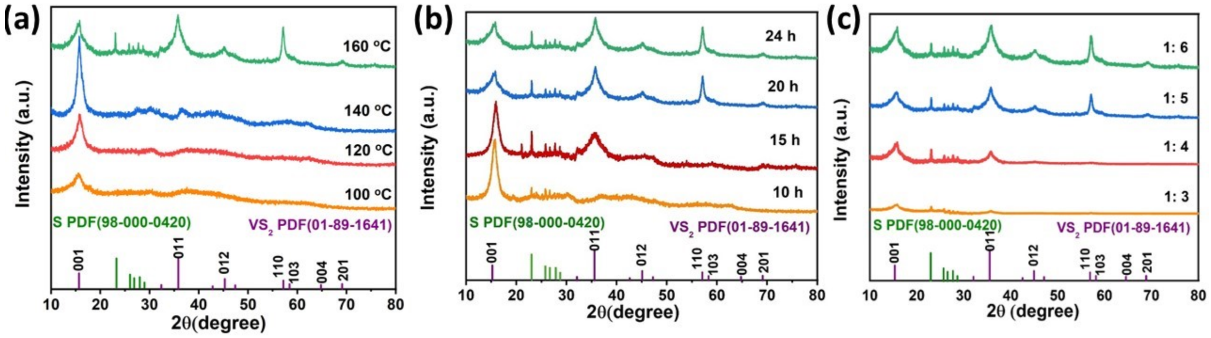

Fig. S2 XRD spectra of VS2 samples (a)Temperature-group, (b) Time-group, and (c) Ratio-group.

Table S1 The average crystallite size (D) of VS_2 samples synthesized at different parameters.

Group	**Parameters**			
Temperature-group samples	100 °C	120 °C	140 °C	160 °C
T_s	**Avg. Crystallite size D (nm)**			
	3.57	3.46	7.19	20.98
Time-group samples	10 h	15 h	20 h	24 h
t_s	**Avg. Crystallite size D (nm)**			
	6.06	11.41	20.73	20.98
Ratio-group samples	1: 3	1: 4	1: 5	1: 6
R	**Avg. Crystallite size D (nm)**			
	7.03	12.7	20.98	24.34

S1-2 The impact of synthesis conditions on the morphological properties of VS_2

To provide a comparison of VS2 morphology, SEM images of one sample from each synthesized group are shown in **Fig. S3**. These images reveal that the nanosheet structure of VS2, particularly arranged in a nanoflower shape, is not evident in the selected non-optimized samples.

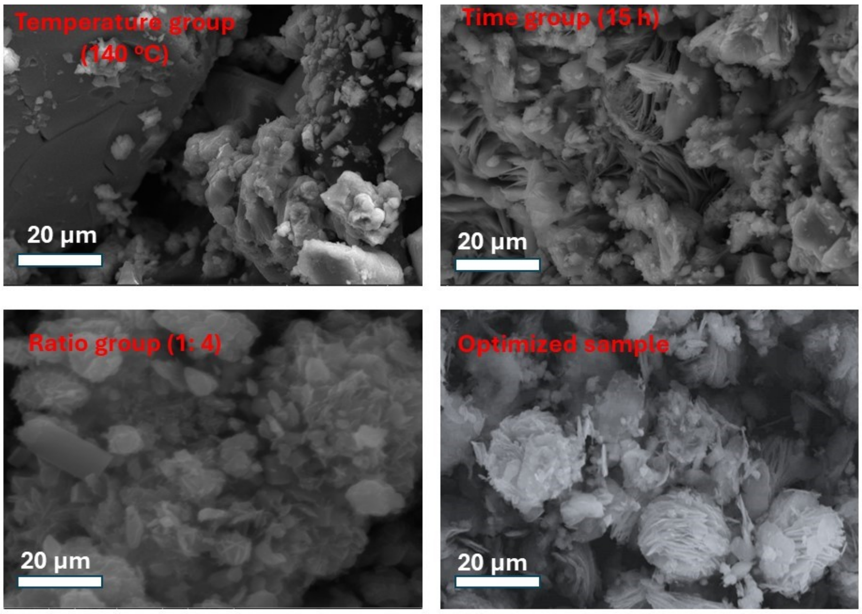

Fig. S3 Comparison of the morphology of selected as-prepared VS_2 samples via SEM analysis.

Table S2 Lattice spacing (hkl) and average crystallite size (D) of pristine and supported VS_2 samples

Lattice planes	**VS_2**	**VN0.2**	**VN0.4**	**VN0.6**	**VN0.8**

	(hkl)						**VN1**
'd' spacing (nm)	001	0.5755	0.581	0.578	0.579	0.581	0.581
	002	0.283	0.283	0.284	0.283	0.281	0.282
	011	0.251	0.251	0.252	0.252	0.252	0.251
	012	0.2003	0.201	0.202	0.201	0.201	0.201
	110	0.1611	0.161	0.161	0.160	0.162	0.161
	004	0.141	0.140	0.140	0.141	0.140	0.141
	103	0.1581	0.159	0.159	0.159	0.159	0.159
	201	0.1356	0.136	0.136	0.136	0.136	0.136
Avg. Crystallite size D (nm)		20.98	20.58	21.42	19.25	17.57	17.6

Table S3 Current densities and peak-to-peak (ΔE_{PP}) potential differences of pristine VS_2 and VN0.8.

Sample	**$I_{d\ anodic}$ (mA.g^{-1})**	**E_{anodic} (V)**	**$E_{cathodic}$ (V)**	**ΔE_{PP} (V)= E_a-E_c**
VS_2	353	0.756	0.726	0.03
VN0.8	466	0.726	0.646	0.08

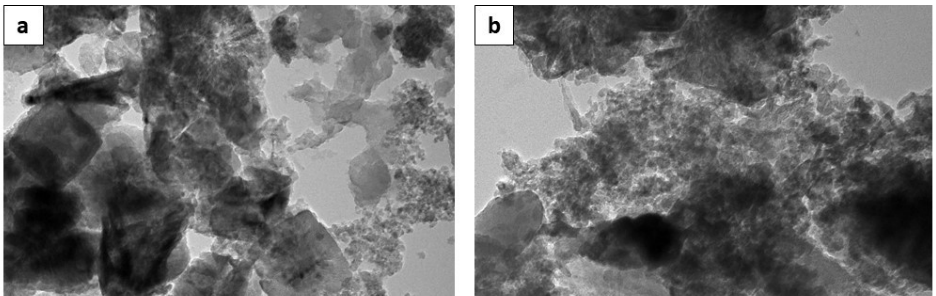

Fig. S4 TEM images for VN0.8 material; (a) before, and (b) after recycling in photocatalytic HER.

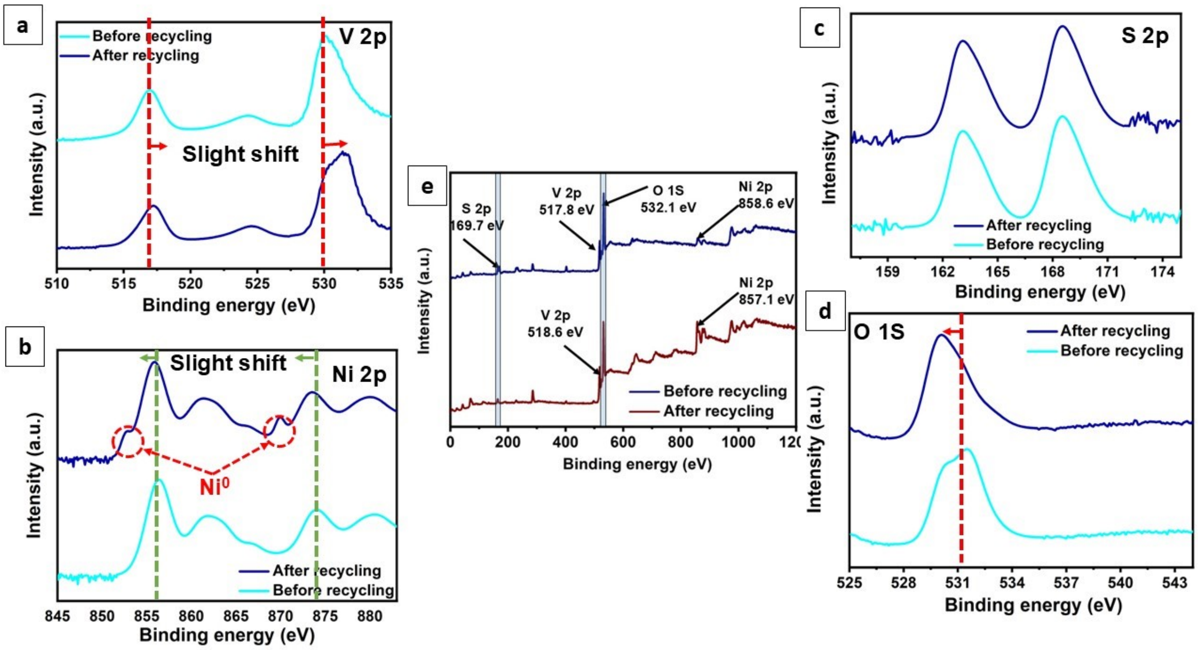

Fig. S5 XPS spectra: (a) V 2p, (b) Ni 2p, (c) S 2p, (d) O 1s, and (e) survey spectrum of VN0.8 before and after recycling in photocatalytic HER.

1. M. S. NourEldien, M. Y. Nassar, I. M. Ibrahim and H. M. Aly, *Benha j. appl. sci.* , 2024, **9**, 1-7.

2. J. D. Ng, B. Lorber, J. Witz, A. Théobald-Dietrich, D. Kern and R. Giegé, *J. Cryst. Growth*, 1996, **168**, 50-62.
3. H. Li, H.-z. Wu and G.-x. Xiao, *Powder Technol.*, 2010, **198**, 157-166.
4. S.-J. Lee, H. Lee, K.-J. Jeon, H. Park, Y.-K. Park and S.-C. Jung, *Nanoscale Res. Lett.*, 2016, **11**, 1-8.