

Supporting Information

Boosting charge migration in V₂O₅ nanorods by niobium doping for enhanced photocatalytic activity

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Characterization: A Field Electron Scanning Electron Microscope (FESEM-JEOL, Japan) equipped with Energy dispersive X-Ray (EDX) spectroscopy (Oxford, UK) was used to study the surface morphology and elemental composition of the prepared samples. The morphology and crystallographic features were further studied by recording (High resolution Transmission Electron Microscope) HRTEM images in a JEM-2100 HRTEM (JEOL, Japan) microscope having point to point resolution of 0.194 nm and lattice resolution of 0.14 nm. Powder X-ray Diffraction (XRD) patterns of the catalysts were obtained with a PAN analytical diffractometer (model: PW-3050/60, UK), using Cu-K α radiation at 40 kV and 30 mA with 2 θ scanning range from 5° to 70°. A Quantachrome (AUTOSORB1, UK) BET analyzer was used to determine the Brunauer-Emmett-Teller (BET) surface areas of the samples. The isotherms were obtained by adsorption of nitrogen at 77 K after degassing at 573 K for 2 hours under high vacuum. The thermal stability of the developed samples was studied by obtaining thermogravimetric (TGA) profiles from a TGA Q50 instrument operating at a temperature range of 50-750°C and a heating rate of 5°C/min in ambient air atmosphere. The chemical bonds in the samples were studied by obtaining (Fourier Transform Infrared) FTIR spectra from a Perkin Elmer Spectrum 100 instrument. The oxidation states of the constituent elements were studied by obtaining XPS spectra on a ULVACPHI 5000 versaprobe II with K α electrode system. The optical band gap of the developed samples was studied by obtaining their UV Vis spectra from a UV-Vis Spectrophotometer (Lambda 25, Perkin Elmer, India, Model 2600). This spectrophotometer was also used to measure the absorbance of an aqueous solution of caffeine. The electron hole recombination in the developed samples was analyzed by obtaining their Photoluminescence (PL) spectra from a Hamamatsu R928 photomultiplier detector with He-Cd laser as the excitation source at an excitation wavelength of 325 nm and an output power of 50 mW. The active oxidation species during the photodegradation reaction were detected by using Electron Spin Resonance (ESR) technique in a Bruker ELEXSYS 580 X-band electron spin resonance spectrometer with DMPO as a trapping agent for hydroxyl radicals.

Photocatalytic experiment setup: The photocatalytic degradation was carried out on a 20 ppm solution of organic contaminant caffeine. The photocatalytic reactor consisted of a 500 ml cylindrical glass chamber with a centrally pivoted quartz tube equipped with a CFL lamp ($\lambda > 400$ nm, Philips, India with a cutoff filter). The contaminant solution mixed with 0.3 g prepared catalysts was poured in the annular space and agitated with an air supply of 0.5 LPM from a fitted vacuum pump. The reaction was first allowed to take place with the light source turned off for 60 min to achieve adsorption-desorption equilibrium. Then light was turned on and photocatalytic degradation commenced. A 5 ml sample was collected at every interval of 15 minutes followed by separation of the catalysts by centrifuging at 8000 rpm. A UV-vis spectrophotometer was then used to check the absorbance of the samples at a wavelength of 271 nm, which represents the λ_{max} of caffeine. Then the concentrations of the samples were determined from a previously prepared absorbance vs concentration calibration curve.

Radical Trapping experiments : The active radicals during the photodegradation reaction were detected by employing 1 mmol/L of triethanolamine (TEOA), isopropanol (IPA), and p-benzoquinone (BQ) as scavengers of holes (h^+), hydroxyl radicals ($\cdot\text{OH}$), and superoxide radicals ($\cdot\text{O}_2^-$), respectively. The scavengers were added to the solution of caffeine in the photocatalytic reactor as described above, before visible light irradiation.

Photoelectrochemical Measurements: A conventional 3 electrode cell connected to a light source was used for the photoelectrochemical measurements. The cell was connected to a CHI643B workstation with 1.0 M KOH as electrolyte. The working electrodes were prepared by sonicating 30 mg of each sample in a solution of 9 ml ethanol and 1 ml Nafion. Then the solution was deposited on ITO plates with 1 cm² surface area, followed by drying. Ag/AgCl was used as reference electrode and Pt wire was chosen as counter electrode respectively. A 300 W Xe lamp fitted with a cutoff channel ($\lambda > 400$ nm) was used as the light source. Transient photocurrent responses were obtained at a potential of 1.23 V vs RHE by alternatively switching the light on and off at intervals of 50 seconds. The photocurrent generation was further studied by obtaining linear sweep voltammograms at a scan rate of 10 mV/s within a potential window of 0 to 2 V. The impedance to charge migration was studied by obtaining Electrochemical Impedance Spectra (EIS) in a frequency range of 100 kHz to 0.1 Hz at an amplitude of 5 mV. The charge carrier features were further studied by obtaining Mott-Schottky plots in a potential window of 0.6 V to 1.6 V. All measurements have been recorded with respect to Ag/AgCl electrode and were converted and reported with respect to Reversible Hydrogen Electrode (RHE) according to the following equation :

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E_{\text{Ag/AgCl}}^{\text{O}}$$

Where $E_{\text{Ag/AgCl}}$ is the working potential while $E_{\text{Ag/AgCl}}^{\text{O}}$ is the standard potential.

Table S1 Atomic percentages determined by EDAX analysis

Sample	V	O	Nb
VO	27.5	72.5	0
1 Nb-VO	26.92	72.1	0.98
2 Nb-VO	26.36	71.7	1.94
3 Nb-VO	26.24	71.2	2.56

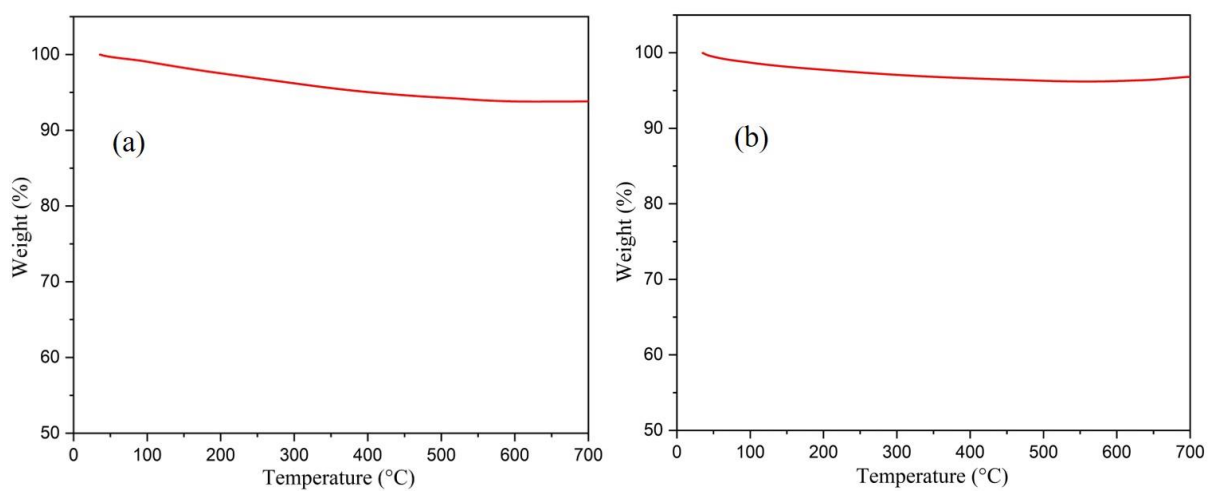


Fig. S1 TGA curves of (a) VO (b) 2 Nb-VO

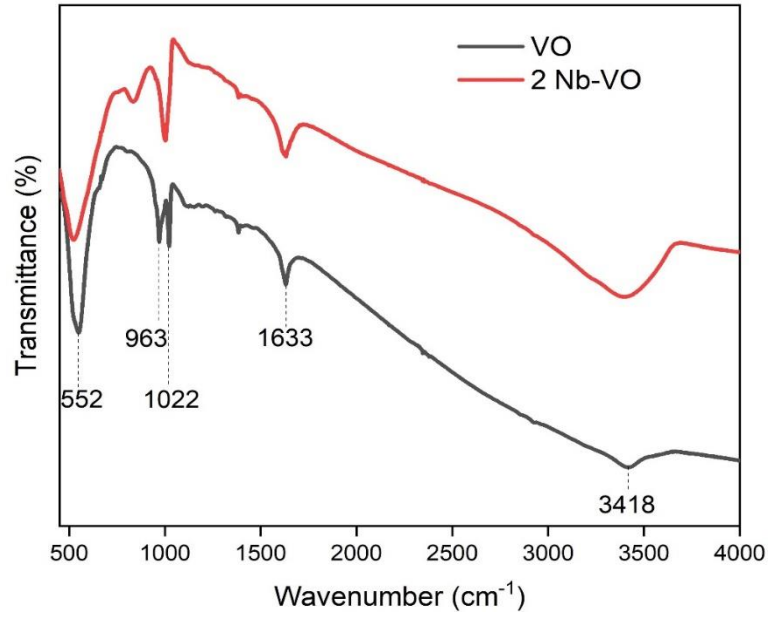


Fig. S2 FTIR Spectrum

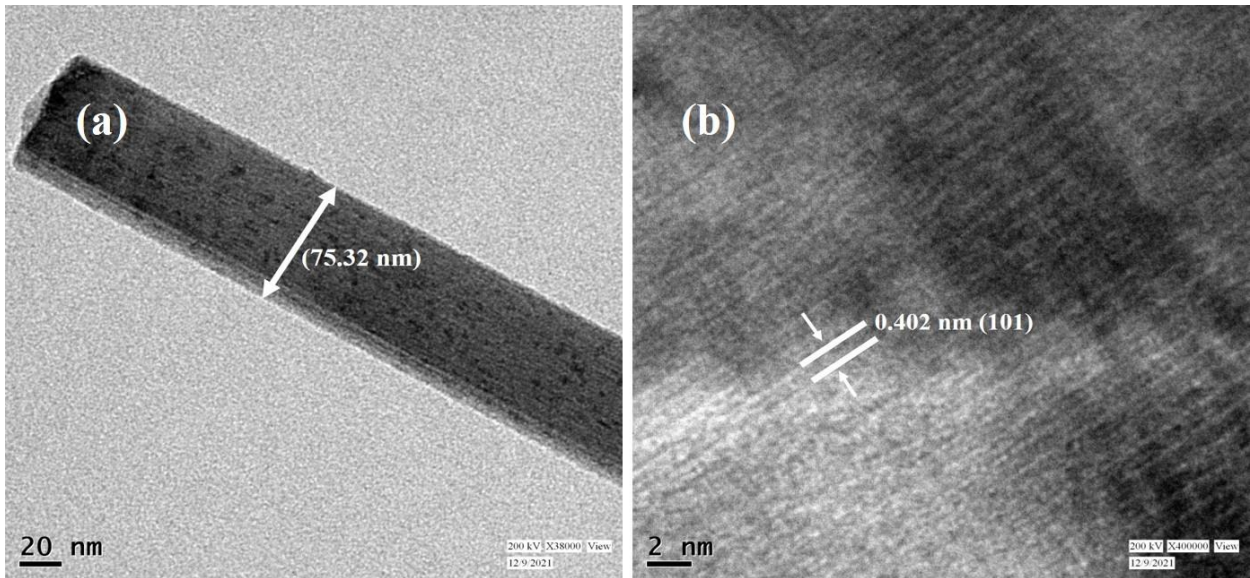


Fig. S3 (a) HRTEM image (b) High Magnification HRTEM image of lattice fringes of VO

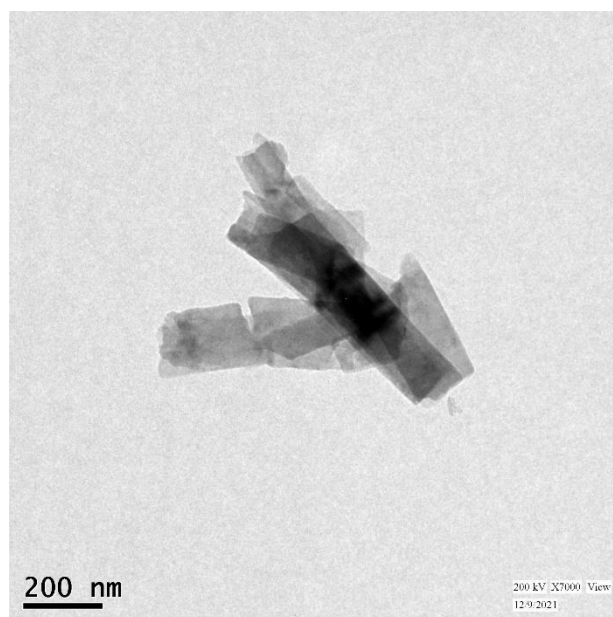


Fig. S4 HRTEM image of 3 Nb-VO

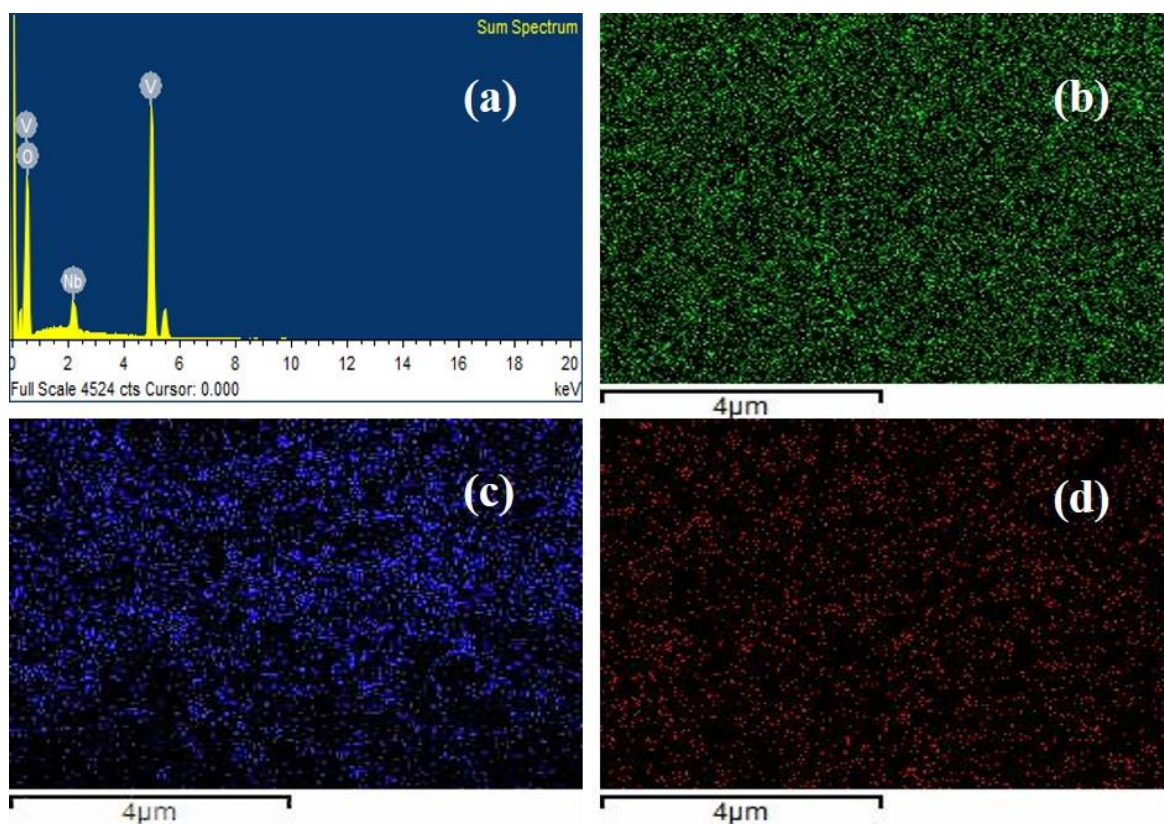


Fig. S5 (a) EDX sum spectrum of 2 Nb-VO (b) Elemental mapping of V (c) O (d) Nb

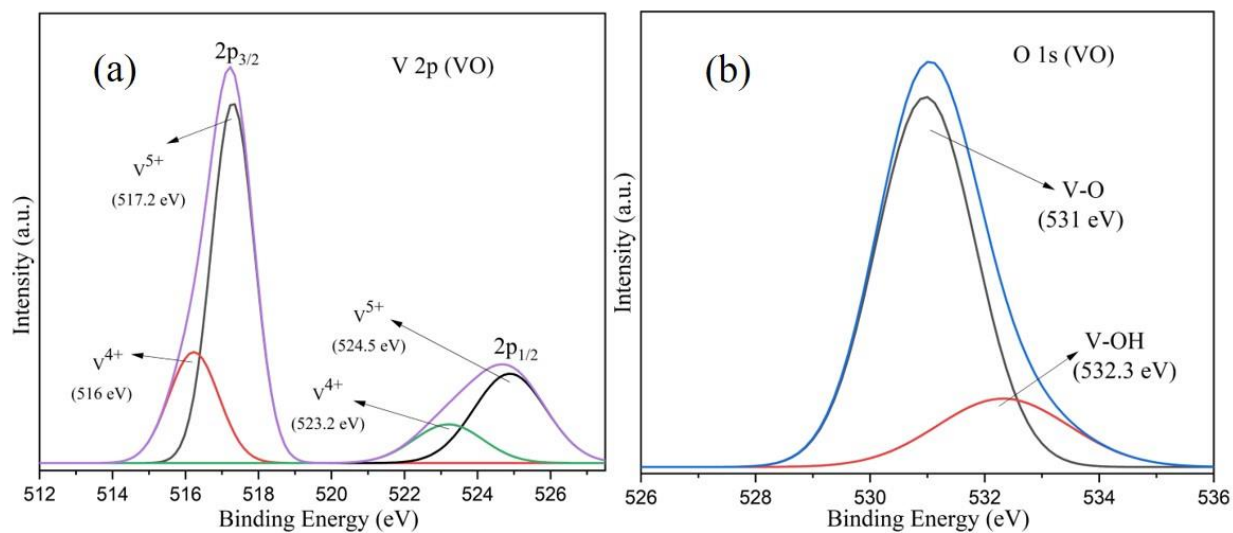


Fig. S6 High resolution spectrum of V 2p and O 1s in VO

Table S2 Calculated CB and VB edge potentials of the synthesized samples

Sample	Band Gap (eV)	CB Edge (eV)	VB Edge (eV)
VO	2.3	0.43	2.75
1 Nb-VO	2.15	0.575	2.67
2 Nb-VO	2.0	0.6	2.6
3 Nb-VO	1.8	0.7	2.5

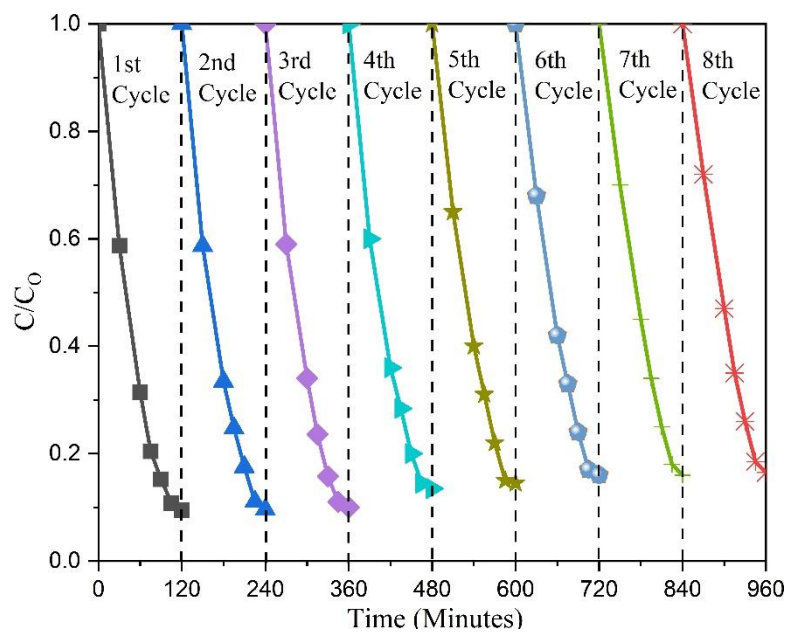


Fig. S7 Photocatalytic Stability of 2 Nb-VO nanorods across 8 cycles

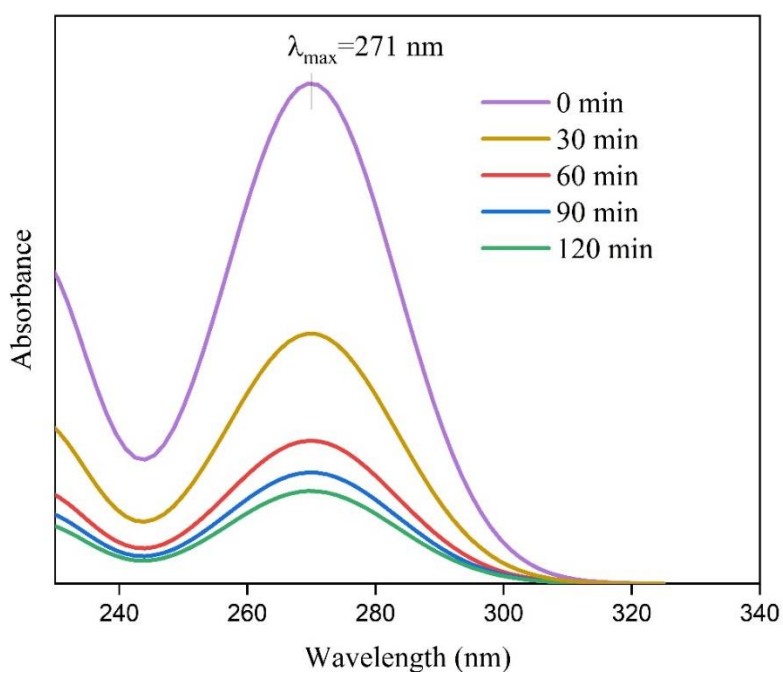


Fig. S8 UV Vis Absorbance spectrum of Caffeine across 120 minutes of photocatalytic degradation