Electronic Supplementary Information

Unrevealing the impact of Pd nanoparticles@BiVO₄/S-CN heterostructure on the photo-physical & opto-electronic properties for enhanced catalytic activity in water splitting and one-pot, three-step tandem reaction

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Materials and methods

All the raw materials were used as received without any further purification. Urea, thiourea, sodium metavanadate, sodium dodecyl sulphate, HNO₃, Na₂SO₄, CH₃OH, NaBH₄, and hydrazine hydrate were procured from Loba. Chemie. India. Pvt. Ltd. Bi(NO₃)₂.4H₂O, Pd(OAC)₂, benzyl alcohol and its derivatives, nitrobenzene and its derivative, benzaldehyde, aniline, Ag(NO₃)₃, and Nafion were supplied by Sigma-Aldrich. Fluorine doped tin oxide (FTO) was procured from Techinstro, Shilpa Enterprise, Nagpur, India. Millipore water was used in the materials synthesis and other related experiments.

Synthesis of S-CN

Graphitic carbon nitride (g-CN) was synthesized by following our earlier report.^{46,47} Briefly, 5 g of urea and 5 g of thiourea were homogeneously grinded in a mortar pestle and then transferred into a alumina crucible closed with a lid. It was then calcined in a programmable muffle furnace at 550 °C at a heating rate of 5 °C/min. Sulphated g-C₃N₄ (S-CN) was prepared by treating 1 g of g-C₃N₄ with concentrated 15 mL of (20%) H₂SO₄ solution containing 3.06 mL conc. H₂SO₄ and 11.94 mL H₂O. The reaction mixture was stirred at 80 °C for 2 h. Then it was added drop-wise to 50 mL of ice cold water under stirring condition. Finally the solution was centrifuged, and the solid was rinsed several times with water, followed by methanol, and dried at 80 °C in an oven for 12-16 h. The washing with methanol was necessary to obtain crystalline power otherwise it produced a sticky gel material.

Synthesis of BiVO₄

BiVO₄ was synthesized according to our earlier method with little modification.⁴⁸ Briefly, 5 mmol of Bi(NO₃)₃ was dissolved in 2 M 100 mL aqueous HNO₃solution in a 250 mL beaker and it was labelled as solution A. In another 250 mL beaker, labelled as solution B, 5 mmol of NH₄VO₃ was dissolved in 2 M 100 mL aqueous HNO₃ solution. Then solution B was added to solution A drop-wise under magnetic stirring. 500 mg of sodium dodecyl sulphate dissolved in 20 ml H₂O was added to it and the resultant mixture was allowed to stir for another 2 h. The pH of the resultant solution was adjusted to 3 with 2 M NH₃ solution. Finally, it was transferred to a Teflon lined autoclave and hydrothermally treated at 180 °C for 24 h. Autoclave was cooled to ambient temperature; solid was centrifuged, washed with excess water, followed by ethanol, and dried in an oven at 80 °C for 12-16 h.

Synthesis of SBVCN-37 nanocomposite

S-C₃N₄:BiVO₄ = 3:7, labelled as S-BVCN 37 was prepared by following our earlier report.⁴⁸ Briefly, 0.9 g of BiVO₄ and 2.1 g of S-C₃N₄ were separately ultra-sonicated in ethanol for 2 h. Then both the solutions were mixed and allowed to sonicate for additional 2 h. Finally, the mixed solution was vigorously stirred using magnetic stirrer and then ethanol was evaporated to dryness. The solid was further grind mechanically and thermally annealed at 350 °C for 4 h.

Synthesis of (Pd Z%) nanoparticles supported SBVCN-37 (Z =1 wt %, 3 wt %, 5 wt %) heterostructure photocatalyst

The details of the synthesis of (Pd3%)/S-BVCN are as follows: 2.0 g of the nanocomposite (SBVCN-37) was taken in a 250 mL conical flask containing 80 mL of toluene and 44 mg of palladium acetate. The reaction mixture was magnetically stirred for 2 h at room temperature. The solution was centrifuged and dried at 80 °C. Solid was then grinded finely and a solution of toluene:ethanol = 20:1 (80 mL) was added to it under magnetic stirring. To this solution, 60 mg of NaBH₄ was added and the resultant solution was immediately turned to black. This solution was allowed to stir overnight. Finally, the reaction mixture was centrifuged, obtained solid was rinsed with water followed by ethanol, and dried in a vacuum oven at 60 °C for further use. Amount of Pd incorporated in the resultant catalyst was determined from ICP analysis (Table S1).

Materials characterization

X-ray diffraction (XRD) patterns were recorded in the 2 θ range of 5° - 80° with a scan rate of 2°/min on a PAN analytical X'PERT PRO diffractometer, Netherland, using Cu K α radiation (λ =0.1542 nm, 40 KV, 45 mA). Nitrogen adsorption-desorption measurements were performed at -200 °C by using Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer, USA. The specific surface area of the material was calculated from the adsorption data points obtained at P/P₀ between 0.05-0.3 using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using the Barret-Joyner-Halenda (BJH) method. Field enhanced scanning electron microscopy (FESEM) measurements were carried out on ZEISS Supra at an accelerating voltage of 10 kV to investigate the morphology of the materials. The nanostructure was investigated using high resolution transmission electron microscope (Technai-FEI) at an accelerating voltage of 300 KV. X-ray photoelectron

spectroscopy (XPS) measurement was carried out on a XPS system PHI 5000 Versa ProbeII (ULVAC-PHI, INC, Japan) with a microfocused (100 µm, 25 W, 15 KV) monochromatic Al-K α source (hv = 1486.6 eV), a hemispherical analyzer and a multichannel detector. NH₃-TPD profile was recorded using CHEMBETTM TPR/TPD, Quntachrome, USA. For the TPD experiment, 100 mg of sample was placed in a U-shaped, flow through, quartz sample tube. Before the TPD experiments, the catalyst was pre-treated in He (30 mL/min) at 450 °C for 1 h. After cooling down to 50 °C, NH₃ (partial pressure 100 Torr) (10% NH₃ in He) was adsorbed on the samples for 1 h. The sample was subsequently flushed with He stream (30 mL/min) at 50 °C for 1 h to remove physisorbedNH₃. The TPD measurements were carried out in the range of 50-400 °C at a heating rate of 10 °C/min. The NH₃concentration in the effluent was monitored by using a gold-plated, filament thermal conductivity detector. FT-IR spectra were recorded using Bruker Ternsor-F27 instrument. Steady state and time resolved photoluminescence measurements were carried out using Hitachi (F-7000) spectrofluorometer and Perkin Elmer LS 55 instrument, respectively. Solid state ultra violet diffuse reflection spectroscopy (DRUV-visible) was analyzed in a UV-2600 instrument. EPR spectra were measured using a BRUKER Xenon EMX-ER073 spectrometer at ambient temperature.

Photocatalytic H₂/O₂ Gas production

The photocatalytic H_2/O_2 gas evolution was performed in a homemade pyrex type glass reactor (Photographs of the reactor setup is provided in Figure S1. Briefly, 60 mg powder catalyst was suspended into a 100 mL (10 volume % triethanolamine) aqueous solution in the reactor. Similarly, for O_2 gas evolution, 60 mg powder catalyst was dispersed in a 100 mL (0.01 M AgNO₃) aqueous solution in the reactor. Prior to light illumination, the reactor was evacuated several times to ensure the removal of any gas present inside. A 300 W xenon arc lamp (Newport, 66499-300Q-R22) at a distance of 5 cm from the reactor was used as a light source. A cut-off filter of (λ >420 nm) was used for reaction. Wave length dependent HER and OER reaction was also carried out by using different cut-off filters (360, 390, 420, 450, 475 nm) (Oriel Instruments, USA). The temperature of the solution was maintained at room temperature by circulating cold water through the outer jacket of the reactor. At regular time intervals, gaseous product was withdrawn using a gas tight syringe (Shimadzu) (1 mL) and injected into a GC. The gaseous products were analyzed using a Shimadzu GC (GC 2010) equipped with a TCD, 5 Å molecular sieve column, and Ar as a carrier gas. The amount of the H_2 gas was calculated based on the calibration curve of the standard H_2 gas. Similarly, the amount of the O_2 gas was calculated based on the calibration curve of the standard O_2 gas. After photocatalytic HER/OER reaction for 24 h, it was separated from the reaction mixture by centrifugation, washed with ethanol, dried for 12 h at 80 °C, and reused in the next cycle.

Procedure of photocatalytic benzyl alcohol oxidation reaction

Photocatalytic oxidation of benzyl alcohol was performed in a 25 ml two necked round bottom flask. 50 µm benzyl alcohol and 6 mL of acetonitrile were added to the flask. Preactivated catalyst (20 mg) was added to it and the resultant reaction mixture was magnetically stirred in O₂ (1 atm in balloon) for 8 h. The temperature of the solution was maintained at 20-25 °C by circulating water through a water circulation pump. A 300 W Xenon ($\lambda > 420$ nm) Arc lamp from a distance of 5 cm was used as the light source for the reaction. The intensity of the light source was measured to be 100 mW/cm² by a TENMARS T7 solar power meter. After the reaction, the reaction mixture was centrifuged and aliquot of the sample was analysed using Shimadzu GC (Shimadzu GCMS-QP 2010 Ultra; Rxi-5Sil MS; 30m × 0.25mm × 0.25) coupled with a FID detector and Shimadzu GC-MS coupled with a FID (Shimadzu GCMS-QP 2010 Ultra; Rxi-5Sil MS; 30m × 0.25µm). The product was confirmed from GC-MS and the product selectivity/yield was calculated form GC.

Reduction of nitrobenzene

In a 25 ml round bottom flask, 50 μ m nitrobenzene, 20 mg pre-activated catalyst and 6 mL acetonitrile were stirred for 8 h. To this solution 0.1 mL N₂H₄ was added slowly. After the end of the reaction, catalyst was separated by centrifugation and analysed with GC/GC-MS to confirm the yield/selectivity of the products. The photocatalytic reaction condition was the same as stated above.

The nitrobenzene reduction reaction was also carried out with H_2 gas (1 atm, H_2 filled balloon) except the addition of 0.1 mL of N_2H_4 to evaluate the influence of reductant. Rest of the reaction condition remained the same as stated above.

Tandem reaction of nitrobenzene and benzyl alcohol

In the one-pot tandem reaction, first nitrobenzene (50 μ m) reduction was performed in the presence of 25 mg catalyst for 8 h using N₂H₄ as a reducing agent. Later, 50 μ m benzyl alcohol was added and the reaction was carried out in O₂ (1 atm, using O₂ filled balloon) for

next 8 h. The total duration of the tandem reaction was 16 h. In one of the control reaction, the same set of reactions were performed in the presence of Ar gas (1 atm, Ar filled balloon), while rest of the reaction condition was remained the same. In another control reaction, the same reaction was performed in the reverse sequence. First benzyl alcohol was oxidised in O₂ (1 atm, O₂ filled balloon) for 8 h. After that nitrobenzene and N₂H₄ were added and the reaction was carried out for next 8 h. In another control reaction, one pot reaction was carried out containing both the reactants. A 25 ml flask containing 12 ml acetonitrile, 25 mg catalyst, 50 µm of nitrobenzene, 50 µm of benzyl alcohol, and 0.1 mL N₂H₄was irradiated with a 300 W Xenon ($\lambda > 420$ nm) arc lamp for 16 hour in O₂ (1 atm, filled in balloon). After performing photocatalytic tandam reaction, catalyst was separated from the reaction mixture by centrifugation, washed several time with acetonitrile and dried at 80 °C for 12 h. After proper drying, the recovered catalyst was used for the next cycle.

Photoelectrochemical (PEC) activity measurements

Linear sweep voltammetry (LSV), transient photocurrent response (i-t), electrochemical impedance spectroscopy (EIS), and Mott-Schotkky (M-S) analysis were carried out in a Pyrex glass reactor containing 0.5 M aqueous sodium sulphate (pH = 6.5) electrolyte equipped with a three-electrode system. The three electrodes system consists of photocatalyst coated FTO as working electrode, Pt wire as a counter electrode, and Ag/AgCl as a reference electrode. The active photocatalyst was coated over the conducting surface by following doctors blend method. Slurry was prepared by dispersing 2 mg catalyst powder in 2 mL ethanol followed by addition of 10 µl, 10 wt% nation solutions. The solution was ultrasonicated for 30 min. Subsequently, the slurry was coated on FTO surface (1 cm²) to produce a thin film by drop casting. It was dried at 80 °C in a vacuum oven. Utmost care was taken to prepare the film as thin as possible. All the photoelectrochemical measurements were carried out with a AUTOLAB-302 PGSTAT instrument electrochemical workstation and a 300 W Xenon arc lamp light source (Newport R22, λ >420 nm cut off filter). The LSV study was performed in the range of 0 to 1 V at a scan rate of 20 mV/s after carefully purging of N₂ gas inside the electrolyte. In order to evaluate the photo activity of catalyst, LSV and transient photocurrent response measurements were executed under dark and light illumination. The EIS study was performed with the same electrode setup and electrolyte using a sinusoidal AC perturbation signal of 5 mV in frequency domain of 1 MHz to 1 Hz. Mott-Schottky analysis was performed with a constant frequency of 1000 Hz under the applied potential of 1 V with the standard three electrode setup.

Detailed explanation for textual property determination using N₂-adsorption isotherm

The textural properties of all the samples were determined by N₂-sorption experiments. Figure1b presents the isotherm of S-CN, SBVCN-37, and (Pd3%)/SBVCN-37. All the three materials exhibit type IV isotherm and H3 hysteresis loop.⁴⁸ During the preparation of SBVCN-37, BiVO₄ is annealed with S-CN and in this process BiVO₄ particles are dispersed on the surface of S-CN by the physical forces and also through chemical interactions. The S-CN is enriched with the surface hydroxyl groups which make contact with BiVO₄ particles resulting in the formation of a strong interface between the two materials with low surface area when compared to pristine S-CN. While the formation of interconnected interface, intercrystalline void space is created between BiVO₄ and S-CN domains, this resulted in a somewhat uniform pore-size distribution in the case of SBVCN-37 in comparison to S-CN. The textural properties of various materials synthesized in this study are provided in Table S1. After the decoration of Pd nanoparticles over the surface of SBVCN-37, a lowering in the surface area is obtained (Table S1).

Detailed explanation for acidity measured using NH₃-TPD

NH₃-TPD of S-CN exhibits the highest acidity as evident from its NH₃-TCD (Fig. S6). The incorporation of $-SO_3H$ groups in the g-C₃N₄ framework after H₂SO₄ treatment is responsible for such high acidity of S-CN. This is also one of the reasons of S-doping with pristine g-C₃N₄. S-CN exhibits three desorption profiles in the temperature range of 75-180 °C, 180-340 °C, and 340-370 °C, respectively (Fig. S5). These temperature regions are related to the weak acid sites, medium strength acidic sites, and strong acidic sites, respectively. BiVO₄ displays the lowest acidity, whereas the heterostructure SBVCN-37 exhibits the higher acidity than pristine BiVO₄ (Fig. S5). Total acidity of BiVO₄, S-CN, and S-BVCN-37 are determined to be 9.66×10⁻⁶, 6.62×10⁻⁵, 3.43×10⁻⁵ mol/g, respectively (Table 1). When different wt% of Pd nanoparticles is embedded over SBVCN-37 catalyst, their acidity is further reduced. The thermal annealing followed by reducing environment/solvent washing during Pd nanoparticles loading is responsible for this reduction in the total acidity.

Detailed explanation for FT-IR measurement for the identification of functional groups

The incorporation of sulphur into the $g-C_3N_4$ matrix and successful formation of the heterostructures were further confirmed by FT-IR spectroscopy (Fig. 5a). Pure BiVO₄ exhibits three peaks at 474 cm⁻¹, 650 cm⁻¹, and 830 cm⁻¹ that can be assigned to symmetric

 VO_4^{3-} tetrahedral units, Bi-O stretching vibrations, and asymmetric vibrations of VO_4^{3-} tetrahedral of BiVO₄, respectively (Fig. 5a).⁴⁸ S-CN displays three peaks at 650, 1150 and 1350 cm⁻¹ which can be assigned to the 'S-O' stretching, asymmetric and symmetric stretching modes of 'S=O' units, respectively (Figure 3a).⁴⁷ Apart from these peaks, S-CN exhibits a characteristics peak at 807 cm⁻¹ corresponding to the bending vibrations of triaizine unit.⁵⁰ FT-IR peaks in the range of 1050-1450 cm⁻¹ are arises from –C-N symmetric/asymmetric stretching vibrations, and –C-NH bending vibrations (Fig. 5a).⁴⁶ The peak at 1637 cm⁻¹ is due to the –C=N stretching vibration of g-C₃N₄.⁴⁷ A broad band around 3200 cm⁻¹ is due to the –OH groups present in the photocatalyst.⁴⁷ SBVCN-37 nanocomposite exhibits FT-IR peaks corresponding to S-CN and BiVO₄. Different contents of Pd NPs supported SBVCN-37 nanocomposites exhibit similar FT-IR spectra to that of SBVCN-37 indicating that Pd NPs loading has not influenced the functional groups present in SBVCN-37 material (Fig. 5a).

Calculation of apparent quantum yield for HER and OER

The apparent quantum yield was measured by using different wavelength filters (Oriel Instrument, USA) coupled with a Newport 300 W Xenon Arc lamp (Newport, 66499-300Q-R22). The incident area was 12.6 cm² and intensity was 80 mW/cm² at a distance of 5 cm (Tensmars TM-207, Solar Power Meter). Apparent quantum yield for HER was calculated based on the amount of H₂ produced at 1 h by using the equation: AQY (%) = (Ne/Np× 100 %) = 2M/Np× 100 %), where Ne represents the amount of reaction electrons, Np represents the number of incident photons, M is the moles of H₂ produced at 1 h by using the equation: AQY (%) = (Ne/Np× 100 %) = (Ne/Np× 100 %) = (Ne/Np× 100 %), where Ne represents the amount of O₂ produced at 1 h by using the equation: AQY (%) = (Ne/Np× 100 %) = 4M/Np× 100 %), where Ne represents the amount of reaction electrons, Np represents the amount of reaction electrons, Np represents the amount of reaction electrons, Np represents the amount of O₂ produced at 1 h by using the equation: AQY (%) = (Ne/Np× 100 %) = 4M/Np× 100 %), where Ne represents the amount of reaction electrons, Np represents the number of incident photons, M is moles of O₂ molecules produced.

Calculation quantum efficiency for nitrobenzene reduction and benzyl alcohol oxidation

<u>Quantum Efficiency of nitrobenzene reduction</u> was calculated by using the equation: Q. E (%) = $6 \times (No. of electrons involved in the reaction/No. of incident photons) \times 100$ <u>Quantum Efficiency of benzyl alcohol oxidation</u> was calculated by using the equation: Q. E (%) = $2 \times (No. of electrons involved in the reaction/No. of incident photons) \times 100$ For nitrobenzene reduction and benzyl alcohol oxidation 6 and 2 electrons are involved, respectively. In both the cases, Q.E (%) is calculated at 420 nm by considering the yield of the product after the reaction (yield: 49 μ mol for aniline and 46 μ mol for benzaldehyde). The illuminating area was 12.56 cm² and the light intensity was 100 mW/cm².

Calculations of band gap energy of various photocatalysts

The band gap energy (E_g) of the photocatalysts are calculated based on the tau plot using the equation: $ahv = k (hv - E_g)^{n/2}$, where E_g is the band gap energy of the semiconductor (eV), 'k' is the Kubelka-Monk constant, 'hv' is the photon energy, and 'n' is the type of the transition associated with the semiconductor (n =1, direct transition; n = 4, indirect transition).^{47,48,51} The best match fit for BiVO₄ and S-CN is '(ahv)² vs. hv' which indicates that these materials involve direct transition of phonons. Mulliken electronegativity theory can be used to determine the conduction band edge potential at the point of zero charge using $E_{CB} = \chi - E^e - 1/2E_g$, (where E_{CB} =conduction band potentials, χ = absolute electronegativity, E_g = band gap, and $E_e \sim 4.5 \text{ eV}$).^{48,51,46} Further from the equation $E_{CB} = E_{VB}-E_g$, the valance band edge potential can be determined.^{48,51}

Calculation of average charge carriers life time using TRPL analysis

A bi-exponential decay fitting response function is employed to investigate the luminescence decay curves. The fitting is employed with the help of the following equation I (t) = $A_1(exp^{-t/\tau_1}) + A_2(exp^{-t/\tau_2}) + A_3(exp^{-t/\tau_3})$.⁵⁵ Further, the average emission life time which implies the overall decay emission behaviour is calculated using the equation, $\tau_A = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$, where, τ_1 , τ_2 , and τ_3 are the emission lifetimes; and A1, A2, and A3 are corresponding amplitude. Here, τ_1 is caused due to free exciton's recombination in the photocatalyst while τ_2 and τ_3 are generated due to the non-radiative recombination at the semiconductor surface.^{56,57}

Details of optimization of oxidation of benzyl alcohols and reduction of nitrobenzene

First, influence of catalysts is investigated in the oxidation of benzyl alcohol. No reaction has taken place in the absence of catalyst. Further, only a negligible amount of benzyl alcohol conversion is observed in the dark condition (Table S3, entry 1). Both, $BiVO_4$ and $g-C_3N_4$ are less active and produce very low yield of benzaldehyde (Table S3, entries 2-3). In addition to benzaldehyde, benzyl benzoate is observed as a side-product during the reaction. Among

various SBVCN catalysts prepared in this study, SBVCN-37 exhibits better activity when compared to their parent counterparts. With increase in the BiVO4 content in the nanocomposite, benzyl alcohol conversion and benzaldehyde selectivity are increased (Table S3, entries 4-7). A marginal decrease in the catalytic activity is obtained with SBVCN-46 when compared to SBVCN-37. Therefore, SBVCN-37 is considered for further investigation. However, using SBVCN-37, complete benzyl alcohol conversion and high benzaldehyde selectivity are not achieved. For the efficient tandem reaction, it is important to achieve the selective production of benzaldehyde in high yields; therefore it is important to further increase the catalytic activity of SBVCN-37 photocatalyst. Different amounts of Pd are loaded on the surface of SBVCN-37. With increase in the Pd loading from 1 to 3%, benzyl alcohol conversion and benzaldehyde selectivity both are increased (Table S3, entries 8-10). Selective production of benzaldehyde with (92 %) yield is obtained using (Pd3%)/SBVCN-37 as a photocatalyst. With further increase in Pd loading (5%), the benzaldehyde yield is slightly reduced. However in this case also selective production of benzaldehyde is observed. Using (Pd3%)/BiVO₄, the benzyl alcohol conversion and benzaldehyde selectivity both are significantly improved when compared to parent BiVO₄ (Table S3, entry 11). Catalytic activity data suggest that loading of Pd has improved the benzyl alcohol conversion and suppress the over-oxidation of benzyl alcohol to benzoic acid leading to formation of side product benzyl benzoate. Influence of other reaction parameters are investigated and based on the results obtained, the optimum reaction parameter is set as shown in the footnote of Table S3. (Pd3%)/SBVCN-37 is successfully applied to a wide range of substituted benzyl alcohols and produced corresponding aldehydes in excellent yields (Table S3). Electron donating group facilitates the oxidation reaction whereas electron withdrawing group retards the oxidation reaction (Table S3, entries 12-15). However, using this photocatalyst in all the cases greater than (85%) benzaldeyde yield is obtained.

Second step of the tandem reaction, i.e. reduction of nitroaromatic is also optimized. First, influence of various photocatalysts is investigated in the reduction of nitrobenzene in the presence of hydrazine hydrate as a reducing agent. No reaction has taken place in the absence of photocatalyst. Further, reaction did not proceed in the dark condition which further ascertains that nitrobenzene reduction is solely light triggered reaction (Table S3, entry 16). Again, both, BiVO₄ and g-C₃N₄ are less reactive and produce very low yield of aniline (Table S3, entries 17-18). In this case, selective production of aniline is observed. The best nanocomposite photocatalyst SBVCN-37 exhibits better yield of aniline than the parent materials (Table S3, entry 19). The yield of aniline is increased when varying content of Pd nanoparticles loaded SBVCN-37 catalysts are used. In this case also, (Pd3%)/SBVCN-37 exhibits the best photocatalytic activity (Table S3, entry 20). Moreover, (Pd3%)/BiVO₄ exhibits better activity than the pristine BiVO₄ (Table S3, entry 21). The quantum yield for nitrobenzene reduction over (Pd3%)/SBVCN-37 photocatalyst is found to be 6.53 % at the light wavelength of 420 nm (Figure 6a). Further, photocatalytic activity data suggest that an appropriate amount of Pd (3 wt%) embedded system has significantly improved the aniline yield. Therefore, (Pd3%)/SBVCN-37 is successfully applied to a wide range of substituted nitrobenzene and produced corresponding aniline in excellent yields (Table S3, entries 22-25). Influence of other reaction parameters are investigated (Table S4) and based on the results obtained, the optimum reaction parameter is set as shown in the footnote of Table S3.

Photocatalyst	Surface area (m ² /g)	Total pore volume (cc/g)	Content of Pd (ICP) (%)	Total acidity (mol/g)	Band Gap (eV)	Flat Band Potential (eV vs. NHE)	Charge Transfer Resistance (Ω)
S-CN	32	0.159	-	6.62×10 ⁻⁵	2.77	-1.3	41.8
BiVO ₄	6	0.026	-	9.66×10 ⁻⁶	2.45	-0.34	34.7
SBVCN-37	19	0.107	-	3.43×10 ⁻⁵	2.48	-	32.6
(Pd1%)/SBVCN- 37	17	0.108	0.94	6.20×10 ⁻⁵	2.42	-	-
(Pd3%)/SBVCN- 37	16	0.110	2.86	4.27×10 ⁻⁵	2.25	-1.09	27.4
(Pd5%)/SBVCN- 37	12	0.112	4.70	3.30×10 ⁻⁵	2.40	-	-

Table S1 Physico-chemical properties of various materials synthesized in this work.

Sample	χ^2	$ au_1$	$ au_2$	τ ₃	α_1	α2	α3	<\alpha > ns	Ke _{inj} ((ns)-1)
S-CN	1.266	0.763	2.632	9.275	22.81	45.70	31.48	7.07	0.29
BiVO ₄	1.033	0.637	2.263	-	83.66	16.63	-	1.31	0.76
SBVCN-37	1.230	0.874	2.557	7.910	20.48	46.07	33.42	6.01	0.17
(Pd3%)/SBVCN-	1.232	0.679	2.272	7.672	20.73	50.59	28.66	5.18	0.19
37									
(Pd5%)/SBVCN-	1.135	0.549	1.932	7.193	26.16	48.22	25.61	6.12	0.16
37									

 Table S2 Life time and carriers dynamics of various photocatalysts.

		ОН	0	
		Catalyst		
		$O_2 hv$	→ []	
Entry No	Substrate	Catalyst	Benzyl alcohol conv. (%)	Benzaldehyde selec. (%)
a1.	Benzyl alcohol	Dark	2.3	62.3
^a 2.	Benzyl alcohol	CN	9.2	50.9
a3.	Benzyl alcohol	BiVO ₄	24.4	52.3
^a 4.	Benzyl alcohol	S-CN	15.9	58.5
^a 5.	Benzyl alcohol	SBVCN-19	31.1	61.3
^a 6.	Benzyl alcohol	SBVCN-28	39.2	65.4
^a 7.	Benzyl alcohol	SBVCN-37	57.3	79.6
^a 8.	Benzyl alcohol	SBVCN-46	55.6	78.8
^a 9.	Benzyl alcohol	(Pd1%)/SBVCN-37	78.9	95.6
^a 10.	Benzyl alcohol	(Pd3%)/SBVCN-37	92.3	100
^a 11.	Benzyl alcohol	(Pd5%)/SBVCN-37	87.3	100
^a 12.	Benzyl alcohol	(Pd3%)/BiVO ₄	56.8	93.6
^a 13.	Benzyl alcohol	(Pd3%)/ S-CN	44.7	94.9
^a 14.	<i>p</i> -Methoxy benzyl alcohol	(Pd3%)/SBVCN-37	98.6	100
^a 15.	<i>p</i> -Methyl benzyl alcohol	(Pd3%)/SBVCN-37	95.5	100
^a 16.	<i>p</i> -Bromo benzyl alcohol	(Pd3%)/SBVCN-37	88.1	98.3
^a 17.	<i>p</i> -Chloro benzyl alcohol	(Pd3%)/SBVCN-37	87.2	98.6
		NO ₂	NH ₂	
		Catalyst N ₂ H ₄ hv	►	
Entry No	Substrate	Catalyst	Nitrobenzene conv. (%)	Aniline selec. (%)
^b 18.	Nitrobenzene	Dark	0	-
^b 19	Nitrobenzene	CN	11.9	100
^b 20.	Nitrobenzene	BiVO ₄	42.3	100
^b 21.	Nitrobenzene	S-CN	24.2	100
^b 22.	Nitrobenzene	SBVCN-37	63.2	100
^b 23.	Nitrobenzene	(Pd1%)/SBVCN-37	82.5	100
^b 24.	Nitrobenzene	(Pd3%)/SBVCN-37	96.3	100
^b 25.	Nitrobenzene	(Pd5%)/SBVCN-37	90.7	100
^b 26.	Nitrobenzene	(Pd3%)/BiVO ₄	54.3	100
^b 27.	Nitrobenzene	(Pd3%)/S-CN	40.6	100
^b 28.	4-methoxy nitrobenzene	(Pd3%)/SBVCN-37	98.1	100
^b 29.	4-bromo	(Pd3%)/SBVCN-37	97.4	100

Table S3 Photocatalytic oxidation of benzyl alcohol and reduction of nitrobenzene over various photocatalysts investigated in this study.

	nitrobenzene			
^b 30.	4-chloro	(Pd3%)/SBVCN-37	97.8	100
	nitrobenzene			
^b 31.	4-hydroxy	(Pd3%)/SBVCN-37	91.4	100
	nitrobenzene			

Reaction condition: ^aOxidation: Substrate (50 μ M), O₂ (1 atm, in balloon), Catalyst (20 mg), Acetonitrile (6 mL), time (8 h), Visible light $\lambda > 420$ nm; ^bReduction: Substrate (50 μ M), N₂H₄ (0.1 mL/2 mmol), Catalyst (20 mg), Acetonitrile solvent (6 mL), Time (8 h), Visible light $\lambda > 420$ nm.

		ОН	0	
		Catalyst		
		O ₂ hv		
Entry	Catalyst	Time (h)	Benzyl alcohol	Benzaldehyde
No	amount (mg)		conv. (%)	selec. (%)
^a 1.	5	8	29.3	100
^a 2.	10	8	54.6	100
^a 3.	15	8	75.9	100
^a 4.	20	8	92.3	100
^a 5.	25	8	95.8	100
^a 6.	20	2	30.1	100
^a 7.	20	4	55.7	100
^a 8.	20	6	81.6	100
^a 9.	20	10	96.2	100
		NO ₂	NH ₂	
		Catalyst N ₂ H ₄		
		hν		
Entry	Catalyst	Time (h)	Nitrobenzene	Aniline selec. (%)
No	amount (mg)		conv. (%)	
^b 10.	5	8	30.5	100
^b 11.	10	8	57.3	100
^b 12.	15	8	76.2	100
^b 13.	20	8	96.3	100
^b 14.	25	8	98.9	100
^b 15.	20	2	32.4	100
^b 16.	20	4	56.3	100
^b 17.	20	6	78.1	100
^b 18.	20	10	99.4	100

Table S4 Optimization of catalyst amount and time period in the photocatalytic oxidation of benzyl alcohol and reduction of nitrobenzene over (Pd3%)/SBVCN-37.

Reaction condition: ^aOxidation: Substrate (50 μ M), O₂ (1 atm, in balloon), Catalyst ((Pd3%)/SBVCN-37), acetonitrile (6 mL), visible light $\lambda > 420$ nm; ^bReduction: Substrate (50 μ M), N₂H₄ (0.1 mL/2 mmol), Catalyst ((Pd3%)/SBVCN-37), acetonitrile solvent (6 mL), time (8 h), visible light $\lambda > 420$ nm.

Table S5 Photocatalytic reaction of aniline and benzyl alcohol over (Pd3%)/SBVCN-37catalyst.



Time (h)	Benzyl alcohol conversion (%)	Imine selectivity (%)	
2	26.3	100	
4	42.6	100	
6	69.3	100	
8	92.7	100	

Reaction condition: Aniline (50 μ M), benzyl alcohol (50 μ M), catalyst (20 mg), acetonitrile solvent (12 mL), O₂ in balloon, Visible light> 420 nm.

Table S6 Photocatalytic reaction of nitrobenzene and benzaldehyde over (Pd3%)/SBVCN-37 catalyst.



Time (h)	Nitrobenzene conversion (%)	Products selectivity (%)
2	28.9	Imine (89.1 %), hydroxyl amine (10.9 %).
4	46.8	Imine (93.8 %), hydroxyl amine (7.2 %).
6	74.7	Imine (97.1 %), hydroxyl amine (2.9 %).
8	96.9	Imine (99.7 %), hydroxyl amine (0.3 %).

Reaction condition: Nitrobenzene (50 μ M), benzaldehyde (50 μ M), catalyst (20 mg), acetonitrile solvent (12 mL), N₂H₄ (0.1 mL/0.48 mmol), Visible light> 420 nm.



Fig. S1 Photographs of the reaction setup used for photocatalytic HER/OER reaction and tandem reaction.



Fig. S2 Powder XRD patterns of S-doped $g-C_3N_4$ (S-CN) and $g-C_3N_4$ synthesized using urea (U) and thiourea (TU) in this study.



Fig. S3 (a-b) TEM images, (c) SAED pattern, (d) HAADF, (e) STEM-HAADF of individual elements, and (f) EDAX of $BiVO_4$.



Fig. S4 NH₃-TPD profiles of various catalysts synthesized in this work.



Fig. S5 Plots of $(\alpha hv)^2$ vs hv and estimated band gap values of (a) S-CN, (b) BiVO₄, (c) SBVCN-37, (d) (Pd1%)/SBVCN-37, (e) (Pd3%)/SBVCN-37, and (f) (Pd5%)/SBVCN-37.



Fig. S6 LSV profiles under dark and light illumination of (a) S-CN and (b) BiVO₄.



Fig. S7 Recyclability of Pd(3%)/SBVCN-37 (a) for 5 cycles in the tandem catalytic reactions, and (b) photocatalytic HER/OER reactions with 24 h time scale (2 cycles).(Analysis errors bar represent n=3 and ± 0.1).



Fig. S8 Wavelength dependent (a) HER, (b) OER over (Pd3%)/SBVCN-37 photocatalyst (Errors bar represent n=3 and ± 0.1).



Fig. S9 Powder XRD patterns of (Pd3%)/SBVCN-37 before and after HER for 24 h (two cycles).



Fig. S10 FESEM image of recovered photocatalyst (Pd3%)/SBVCN-37 after HER for 24 h (two cycles).



Fig. S11 Nyquist plots of (Pd3%)/SBVCN-37 before and after HER for 24 h (2 cycles).