



Synthesis, characterization and photocatalytic application of type II CdS/Bi₂W₂O₉ heterojunction nanomaterials towards aerobic oxidation of amines to imines

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Abstract: A series of novel type-II CdS/Bi₂W₂O₉ heterojunction nanomaterials were prepared by a two stage process. Initially, phase pure Bi₂W₂O₉ with orthorhombic crystalline structure was prepared by a facile combustion synthesis route. The combustion synthesized Bi₂W₂O₉ was subsequently modified by CdS nanoparticles using a hydrothermal route. The CdS/Bi₂W₂O₉ heterojunctions were characterized using XRD, XPS, FTIR, UV-Vis-DRS, PL, FESEM and HRTEM study. The occurrence of ultrafine CdS nanoparticles with diameter between 8-15 nm well dispersed over BWO plates was inferred from microscopic characterization study. The two crystalline phases exhibited microscopic close contact across grain boundaries facilitating transfer of excitons. The heterojunction materials exhibited improved visible light absorption, enhanced charge carrier separation and suitable band alignment characteristic of a type-II heterojunction. The CdS/Bi₂W₂O₉ heterojunctions were evaluated as visible light active photocatalyst for aerobic oxidation of amines to imines. Structurally and functionally diverse amine molecules were oxidized to the corresponding imines with excellent selectivity in a short span of time.

Introduction

Organic transformations especially oxidation, reduction and coupling reactions are of paramount importance in organic synthesis involving value added and fine chemicals. Many fine chemical synthesis process utilize homogeneous corrosive acid-base catalyst, stoichiometric reagents and harmful chemical oxidants at elevated temperature to achieve high yield of the product. However, processes involving these conventional methods are associated with problems such as catalyst handling, product purification, corrosion and generation of significant quantity of by-products.^[1, 2] The heterogeneous photocatalytic route is a promising alternative to the conventional method of fine chemical synthesis. The photocatalytic route is more sustainable, greener and economic towards fine chemical synthesis, as it makes use of renewable energy source, discourage the use of stoichiometric hazardous reagents, avoid solvent loss and uses atmospheric air as oxidant.^[1-4] The use of H₂O as reaction media is another step to makes the system more eco-friendly.^[3, 5] The generation of reactive 'OH radicals by the photolysis of H₂O over photocatalyst surface may lead the generation of non-selective products in organic synthesis. However, Palmisano and Bahnemann groups successfully conducted the partial oxidation of alcohol to aldehyde with excellent selectivity over TiO_2 and Bi_2WO_6 photocatalyst surface.^[6-8] Recently, many improved heterogeneous photocatalytic routes have been developed for selective oxidation of alcohol, reduction nitro compounds, olefin-imine addition, radical coupling reaction, Suzuki coupling reaction, synthesis of polymer and fine chemicals.^[6-14] The oxidation of amines to imines is one of the important reactions since imines are used as building blocks for many pharmaceuticals and organic dyes molecules.^[15-17] The conventional oxidation of amine involves the use of costly noble metal catalysts at elevated temperature. The adverse environmental impact of oxidants, solvent wastage and unwanted by-product formation is a concern in the conventional amine oxidation processes.^[15, 17] Till date, very few photocatalyst such as TiO₂, Nb₂O₅, WS₂, BiVO₄, BiOX, g-C₃N₄, AgI/AgVO₃, Au-cluster, ZnIn₂S₄, CuWO₄, and organic polymers have been studied for the oxidation of amines.^[15-28] Some of these reported photocatalytic protocols require longer time, employ photocatalyst with poor response to visible light and require molecular O₂ to carry out the oxidation reaction. Keeping in mind the advantages and disadvantages of the reported photocatalytic protocols, there is a lot of scope to develop highly efficient novel photocatalytic system which can accomplish this oxidation reaction in aerobic condition under visible light irradiation.

The Aurivillius oxide $Bi_2W_2O_9$ is yet to be explored as photocatalyst for the oxidation of amines. The $Bi_2W_2O_9$ is the second member of cation deficient Aurivillius family with a

layered structure. Watanabe et al. in the year 1987 first reported the synthesis of orthorhombic Bi₂W₂O₉ using high temperature solid state route.^[29] Cheng et. al. synthesized rare earth substituted Bi₂W₂O₉ by solid state synthesis and studied their optical, electronic properties.^[30 16] Recently, Bi₂W₂O₉ has been synthesized by co-precipitation, Pechini method and a facile combustion synthesis route.^[31-33] The Bi₂W₂O₉ material has been studied as a potential candidate for luminescence, microwave dielectric, gas sensing and photocatalytic applications.^[32-41] However, very few reports are available on the photocatalytic application of Bi₂W₂O₉ primarily due to its UV absorption feature, wide band gap and poor charge carrier separation properties.^[32, 33, 38-41] Due to the high positive valence band potential (3.30 eV), the Bi₂W₂O₉ is an ideal photocatalyst to carry out oxidation reactions.^[33] In order to improve the visible light absorption and charge carriers separation properties of a photocatalyst, formation of heterojunctions with a foreign semiconducting material is an important strategy. The close contact between the two semiconductors minimizes the recombination rate of excitons which results in enhanced photocatalytic efficiency. Among various types of heterojunctions, the type II heterojunction is most efficient towards the separation of photogenerated electron and holes.^[42] With an aim to develop novel and efficient photocatalytic system for selective organic transformation, in this work we have prepared type II CdS/Bi₂W₂O₉ heterojunction photocatalyst and studied their application for selective oxidation of amines to imines. CdS is one of the well explored narrow band gap photocatalyst with band gap energy of 2.42 eV. CdS has been successfully used as visible light active photocatalyst for oxidation of dichloro acetic acid, organic transformations and water splitting reaction.^[9, 11, 43, 44] Because of its narrow band gap, CdS has been coupled with many wide band gap semiconductors such as TiO₂, Bi₂MoO₆, g-C₃N₄, Bi₂PO₄ and SrS to prepare highly efficient visible light active photocatalytic systems.^[45-49] The CdS based coupled semiconductor systems have been evaluated as photocatalyst for H₂ evolution and degradation of organic pollutants under visible light.

Results and discussion

Characterization of CdSBWO heterojunction

The XRD patterns of CdSBWO heterojunction materials together with pure $Bi_2W_2O_9$ and CdS are presented in Figure 1. Pure $Bi_2W_2O_9$ material exhibits intense and sharp diffraction peaks at d-spacing values 3.95, 3.79, 3.45, 3.22, 2.98, 2.96, 2.75, 2.71, 2.42, 1.91, 1.65, 1.61 and 1.55 Å (Figure 1a). These peaks correspond to diffraction from the (006), (111), (113), (114), (115), (008), (116), (020), (120), (220), (134), (228) and (229) crystallographic planes of orthorhombic bismuth tungstate (JCPDS No- 33-0221, space group- Pbn21). No impurity peaks corresponding to any analogous phase could be detected from XRD indicating the high phase purity of the synthesized material.



Figure 1. X-ray diffraction patterns of (a) $Bi_2W_2O_9$; (b) CdS5BWO; (c) CdS10BWO; (d) CdS20BWO; and (e) CdS materials.

For pure CdS material sharp and intense diffraction peaks are observed at d-spacing values of 3.58, 3.35, 3.16, 2.45, 2.07, 1.89, 1.76 and 1.67 Å. These peaks correspond to the diffraction from the (100), (002), (101), (102), (110), (103), (112) and (004) crystallographic planes of hexagonal cadmium sulphide phase (JCPDS No- 41-1049, space group- P63mc) (Figure 1e). The CdS5BWO heterojunction display characteristic diffraction peaks of BWO phase only (Figure 1b). However, for CdS10BWO and CdS20BWO heterojunctions material low intense but distinguishable diffraction peaks for CdS phase was observed along with BWO phase (Figure 1c & 1d). XRD results clearly indicate the presence of both the $Bi_2W_2O_9$ and CdS crystalline phases in the CdSBWO heterojunction materials.

The oxidation state and the chemical environment of the constituent elements in the heterojunction material was probed using XPS study. The XPS spectra of CdS20BWO heterojunction is presented in Figure 2. Figure 2a represents the survey spectrum which confirmed the presence of Bi, W, Cd, O and S along with advantageous carbon in the sample.

In the high resolution spectral region for Bi, a doublet is observed at 158.8 eV and 164 eV, respectively (Figure 2b). These peaks are assigned to photoelectron emission from $Bi4f_{7/2}$ and $Bi4f_{5/2}$ electronic states of Bi in +3 oxidation state.^[33, 38, 50, 51] In this spectral region, a noticeable low intense broad peak at 162.4 eV is assigned to the S2p state.^[43, 48]



Figure 2. XPS spectra of CdS20BWO heterojunction.

Figure 2c presents the fine spectra of W in the 4f region. The binding energy value of 35.2 eV and 37.4 eV with a splitting factor of 2.2 eV can be attributed to W4f_{7/2} and W4f_{5/2} electronic states of W in +6 oxidation state.^[33, 38, 51] A symmetrical doublet observed at binding energy values of 405.1 eV and 411.8 eV with a spin orbit splitting value of 6.7 eV is due to the Cd3d_{5/2} and Cd3d_{3/2} electronic states of Cd in +2 oxidation state (Figure 2d).^[43, 48] Figure 2e represents the high resolution XPS spectra for O in 1s region. A broad asymmetric peak is observed which is fitted to two peaks. These two peaks correspond to the presence of oxygen in two different electronic environments. The peaks at binding energy value of 529.7 eV attribute the oxygen in the $(W_2O_7)^{2^-}$ Perovskite layers while the binding energy value of 531.1 eV is due to the interlayer oxygen associated with the interlayer (Bi₂O₂)²⁺ species.^[33, 38] In the high resolution XPS spectra in the S 2s region, a broad peak with maxima at 525.7 eV is observed (Figure 2f). This broad peak confirmed the presence of sulphide ions (S²⁻).^[33, 50, 51]

The morphology of the BWO and CdSBWO heterojunction materials is studied by FESEM and HRTEM analysis. The FESEM images of BWO and CdSBWO materials are

presented in Figure 3. The BWO material contains micron size plates with L x B x H in the range of 0.40-2.30 μ m, 0.31-1.68 μ m and 0.08-0.42 μ m, respectively (Figure 3a). The CdSBWO heterojunction materials contain uniformly distributed spherical CdS nanoparticles grafted over the BWO plates (Figure 3b-3d). With increase in the CdS content in the heterojunction materials the particle density of anchored CdS species increases. Moreover, local aggregation of the CdS particles is observed at higher content.





Figure 3. FESEM images of (a) $Bi_2W_2O_9$; (b) CdS5BWO; (c) CdS10BWO; and (d) CdS20BWO heterojunction materials.

The size and shape of CdS nanoparticle is further investigated using HRTEM analysis. Figure 4 represents the TEM images of CdS20BWO heterojunction material. The presence of ultrafine near spherical CdS nanoparticles with size in the range of 8-15 nm is noticed for the CdS20BWO material (Figure 4a & 4b). The CdS nanoparticles are in an agglomerated state and are attached to each other through the grain boundary (Figure 4a). The high magnification TEM image of CdS20BWO material revealed the formation of heterojunction between the two phases (Figure 4c). The calculated interplanar distance matches with the (113) crystallographic plane of $Bi_2W_2O_9$ and (002), (101) planes of CdS species (Figure 4c). This observation gives another evidence for the presence of crystalline phases of CdS and $Bi_2W_2O_9$ in the CdSBWO heterojunction sample. The elemental mapping and EDX spectrum of the heterojunction material is presented in Figure 4d-4j. Homogeneous distribution of Bi, W, O, Cd and S elements throughout the specimen sample is observed from the elemental mapping study (Figure 4d-4i). The presence CdS and $Bi_2W_2O_9$ in required stoichiometric quantity is observed from the EDX study of CdSBWO heterojunction material (Figure 4j). The crystallite size of the CdS phase in the CdSBWO heterojunction materials is calculated by Fourier line profile analysis of XRD peaks by Warren and Averbach method using BRAEDTH software.^[52] The Fourier analysis is performed by using (101) and (110) peaks of the CdS phase. The distribution function (PV)~Fourier length (L) and Size coefficient (AS) ~ L plots for pure CdS, CdS10BWO and CdS20BWO materials are presented in Figure S1. The average crystallite size calculated from the initial slope of AS~L plots (Figure S1I) are presented in Table 1. The heterojunction materials display average crystallite size in the range of 7-12 nm. The Fourier analysis data is found to be complimentary to the crystallite size observed from HRTEM study.



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Figure 4. (a-c) TEM images; (d-i) EDS mapping; and (j) EDX spectrum of CdS10BWO heterojunction material.

The optical property of the CdSBWO heterojunction material is studied by UV-Vis DRS and PL techniques. Figure 5I depicts the UV-Vis DRS spectra of Pure BWO and CdS together with CdSBWO heterojunction materials. Pure BWO shows strong absorption in the UV region, which extend up to visible region. Similarly, pure CdS shows optical absorption in the visible region with an absorption edge near 530 nm. The stiff absorption feature observed for both BWO and CdS materials is due to band edge transition rather than the transition from the impurity level. Upon modification with CdS, for all the CdSBWO heterojunction materials the absorption edge shifted to the lower energy region with improved visible light absorption feature. The calculated band gap values for the pure BWO and CdS are 2.95 and 2.36 eV respectively (Figure S2). For the CdS and BWO materials the observed band gap values are consistent with the literature reported values.^[32, 33, 38, 40, 48]

Sl. No	Catalyst	Specific Surface area (m ² /g)	Crystallite size of CdS phase (nm) ^[a]				
1	$Bi_2W_2O_9$	14.3					
2	CdS	32.5	14.5 ± 1.0				
3	CdS5BWO	24.8					
4	CdS10BWO	28.6	8.5 ± 1.5				
5	CdS20BWO	31.7	10.5 ± 1.6				
^[a] Calculated from the Fourier line profile analysis of the XRD peaks							

Table 1. Specific surface area and crystallite size of CdS phase in CdSBWO heterojunction materials.



Figure 5. UV-Vis DRS (Panel I); FTIR (Panel II); and PL spectra (Panel III) of (a) Bi₂W₂O₉; (b) CdS5BWO; (c) CdS10BWO; and (d) CdS20BWO heterojunction materials.

The BWO and CdS materials exhibit a specific surface area of 14.3 and 32.3 m²/g (Table 1). The heterojunction material exhibits surface area in the range of 24-32 m²/g. The FTIR spectra of CdSBWO heterojunction materials along with pure BWO material are presented in Figure 5II. Pure BWO possesses broad IR bands at 437, 561, 745, 851 and 952 cm⁻¹ (Figure 5IIa). The bands at 437, 561 cm⁻¹ corresponds to the Bi-O stretching vibrations whereas the 745, 851, 952 cm⁻¹ bands are assigned to the symmetric and asymmetric W-O stretching vibrations for WO₆ octahedron.^[31, 33] All the CdSBWO heterojunction display new set of IR bands at 635, 1150 and 1215 cm⁻¹ along with the characteristic vibrational features of BWO (Figure 5IIb-d). These bands are due to the characteristic vibration for CdS component in the

CdSBWO heterojunction materials.^[31] The FTIR study reveals the presence of CdS and BWO components in the CdSBWO heterojunction materials. The charge separation property of the CdSBWO heterojunction materials is studied by using PL technique and photocurrent measurement. The PL spectra of CdSBWO heterojunction materials at an excitation wavelength of 320 nm are presented in Figure 5III. Pure BWO material exhibits PL emission bands at 465, 480 and 490 nm respectively (Figure 5IIIa). The emission bands observed at 465 nm is due to the band gap transition whereas the PL bands at 480 and 490 nm are due to presence of defects and vacancies in the BWO material.^[33, 40] The intensities of these PL bands decrease significantly after modification with CdS. This observation indicates efficient charge carrier separation in the CdSBWO heterojunction materials (Figure 5IIIb- 5IIId). The charge carrier separation property is further studied by taking the photocurrent measurement of the BWO and CdS20BWO materials. The charge transport ability of the heterojunction material is investigated by transient photocurrent measurement (Figure 6). The enhancement in photocurrent of CdS20BWO material over BWO material indicates an improvement in the charge carrier separation ability of the heterojunction material (Figure 6I). The current (I) vs voltage (V) measurement for the BWO and CdS20BWO heterojunction material is presented in Fig. 6II. The higher slope observed in I~V plot for CdS20BWO heterojunction material indicate the higher mobility of the photo excited electrons (Figure 6II). The enhanced photocurrent and improved charge transport efficiency of the CdS20BWO material can be ascribed to the formation of heterojunction between the CdS and BWO component which allow the facile migration of charge carriers across the grain boundary. The UV-Vis DRS and PL study along with the calculated band gap values of CdSBWO heterojunction materials indicate that these materials can be used as photocatalyst under visible light.



Figure 6. (I) Transient photocurrent; and (II) current (I) vs voltage (V) measurement; plots for (a) BWO; and (b) CdS20BWO heterojunction materials.

Selective aerobic oxidation of benzylamine catalysed by CdSBWO heterostructure

The photocatalytic activity of the CdSBWO heterojunction materials is evaluated for the selective oxidation of benzylamine under visible light irradiation using air as oxidant (Scheme 1).



Scheme 1. Selective photocatalytic oxidation of benzylamine catalysed by CdSBWO heterostructure photocatalyst

As a model reaction, a reaction mixture containing 1 mmol of benzylamine and 25 mg of CdSBWO catalyst in 5 ml CH₃CN solvent is stirred under dark condition for 30 min to achieve adsorption-desorption equilibrium. The reaction mixture was exposed to visible light under constant stirring. The progress of the reaction is monitored by gas chromatography. In absence of catalyst and under dark condition the formation of N-Benzylidenebenzylamine could not be detected which confirmed the photocatalytic nature of the oxidation reaction. The photocatalytic efficiency of the CdSBWO heterojunction photocatalyst together with CdS and BWO material is presented in Figure 7. Although both pure CdS and BWO

materials are active towards the oxidation reaction, the percentage conversion is quite low (22.5 and 40.2 % for BWO and CdS material, respectively after 12 h).



Figure 7. Photocatalytic efficiency of CdSBWO heterojunction (Panel I) and catalyst weight variation of CdS20BWO heterojunction (Panel II) for the photocatalytic selective oxidation of benzylamine.

In contrast to this observation, all the CdSBWO heterojunction materials exhibited higher photocatalytic efficiency with good % conversion and selectivity towards N-Benzylidenebenzylamine (Figure 7I). Among the heterojunction materials, CdS20BWO exhibited highest photocatalytic efficiency achieving 89.3 % conversion after 8 h of reaction. Since, the surface area of CdSBWO heterojunctions increase with CdS content, the role of surface area on the photocatalytic activity is evaluated by preparing CdS20BWO material by precipitation (P) and reflux (R) methods. The CdS20BWO-P and CdS20BWO-R materials show surface area of 20.5 and 24.3 m²/g, respectively (ESI file). These materials after 8 h of reaction time exhibited 83.5 and 84.7 % conversion of benzyl amine. This observation indicates that the CdS content in the heterojunction is the primary factor responsible for higher photocatalytic activity. The presence of CdS improves the visible light absorption and charge carrier separation properties of BWO which are vital for the photocatalytic activity. Based on the results described in Figure 7I, the CdS20BWO material is chosen for further study.

The catalyst weight is optimized by varying the catalyst amount between 5-35 mg in the reaction mixture. It is observed that, 25 mg of CdS20BWO catalyst is sufficient to carry out the oxidation of 1 mmol of the reactant with excellent conversion and selectivity (Figure 7II). Further increase in catalyst amount does not have any significant impact on amine oxidation. The effect of solvent on benzylamine oxidation is studied by using different media in presence of CdS20BWO photocatalyst (Table 2).

1	CUCN			(%)	(%)
1	CUCN			(/0)	(70)
	CH ₃ CIN	Air	12	92.5	> 99
2	CH ₃ OH	Air	12	88.4	> 99
3	C ₂ H ₅ OH	Air	12	85.8	> 99
4	H_2O	Air	12	26.5	45
5	CHCl ₃	Air	12	84.7	> 99
6	CH_2Cl_2	Air	12	82.4	> 99
7	Hexane	Air	12	56.4	> 99
8	Tolune	Air	12	53.6	> 99
9	DMF	Air	12	81.2	> 99
10	DMSO	Air	12	83.5	> 99
11	CH ₃ CN	N_2	24		
12	CH ₃ CN	O_2	8	93.6	> 99
13	CH ₃ CN	O ₃	6	90.2	> 99
14	CH ₃ CN	H_2O_2	6	94.5	> 99
15	CH ₃ CN	Oxone	6	92.3	> 99
16	CH ₃ CN	NaClO	6	92.7	> 99

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The catalytic activity is significantly higher in polar solvent in comparison to the nonpolar solvent. The higher conversion in polar organic solvent can be ascribed to better solubility of the reactant molecules and their easy accessibility to the catalyst surface. Highest conversion of benzyl amine is obtained using acetonitrile as solvent. Hence further studies are performed using acetonitrile as solvent. In order to study the effect of different oxidant on the oxidation of benzylamine, the oxidation reaction is carryout in presence of 3 molar excess of different oxidant. It is observed that in presence of different oxidants, the oxidation rate is expedited and > 90 % of conversion is achieved within 6 h (Table 2). When the reaction is conducted under N_2 atmosphere no benzylamine conversion is noticed even after 24 h of

reaction. This observation suggests that under aerobic condition the molecular O_2 present in dissolved state acts as oxidant in oxidizing the benzylamine. Although better conversion are achieved using different oxidant within a short span of time, further studies are carried out in presence of atmospheric air as oxidant in order to make the processes sustainable and greener.

After optimizing various reaction parameters, the versatility the CdS20BWO catalyzed oxidation protocol is tested by using different amines (Table 3).

Entry	Reactant	Product	Conversion ^b (%)	Selectivity ^b (%)
1			81.6	> 90
2	N CH3	N CH3	66.4	85
3	NH ₂ N H		86.4	> 90
4	NH ₂		88.6	> 90
5	NH ₂		90.3	> 90
6	NH ₂ +		89.4	85
7	H ₃ C NH ₂	H ₃ C CH ₃	18.5	70
8	H ₃ C NH ₂	H ₃ C CH ₃	14.3	68

Table 3. Selective Oxidation of various amines catalysed by CdS20BWO heterojunction^a

The CdS20BWO photocatalyst is highly active for selective oxidation of both the primary as well as secondary amines to the corresponding imines. However, the oxidation

^[a]Reaction conditions: amine (1 mmol), solvent (5 mL), catalyst 25 mg (CdS20BWO), reaction time 12 h, ^[b]Determined from GC analysis

rate for secondary amines is relatively sluggish along with by-products formation (Table 3, Entry 1 & 2). Excellent conversion is also observed for the oxidation of heterocyclic amines with very good selectivity towards imines (> 90 %) (Table 3, Entry 3, 4 & 5). In case of aliphatic primary amine the conversion is quite low with poor selectivity to corresponding imines (Table 3, Entry 7 & 8). The oxidation protocol is also extended to mixed system by taking 0.5 mmol each of benzylamine and aniline (Table 3, Entry 6). Formation of both N-benzylidene(phenyl)methanamine and N-benzylidenebenzenamine is noticed for this mixed amine system. However, the CdS20BWO catalysed photocatalytic protocol is more selective towards formation of N-benzylidene(phenyl)methanamine (Selectivity 85 %). The results described in Table 3 suggest that the CdS20BWO catalysed photocatalytic protocol is applicable for the oxidation of a variety of amines under visible light irradiation.

In order to understand the mechanism of photocatalytic oxidation of benzylamine, control experiments are performed in presence of equimolar quantity of different radical scavengers (Figure S3). In presence of hole scavenger (ammonium oxalate), superoxide radical scavenger (benzoquinone) and electron scavenger (AgNO₃), the oxidation rate of benzylamine amine decrease drastically. However, presence of hydroxyl radical scavenger (t-BuOH and isopropanol) only marginally affects the oxidation reaction (Figure S3). This observation rules out the active role of hydroxyl radical during the oxidation of benzylamine. Hence from scavenger experiments, the h^+ , e^- and O_2^+ are identified as the primary active species responsible for the selective aerobic oxidation of benzylamine.

Based on the scavenger experiment, a plausible mechanism for the amine oxidation is proposed over the CdSBWO photocatalyst surface (Figure 8). Upon irradiation, the electrons get excited to the conduction band (CB) leaving behind the holes in the valence band (VB). Since the band gap of both the BWO and CdS components are < 3 eV, both the components of the heterojunction is capable to generate excitons under visible light irradiation. The valance band (VB) and conduction band (CB) potentials of the pure CdS and BWO materials are calculated theoretically using the formula in equation 1.^[33, 50, 51]

$$E_{VB} = X + 0.5E_g - E_e \text{ and } E_{CB} = E_{VB} - E_g$$
 (1)

 E_{VB} and E_{CB} correspond to the valence and conduction band edge potential (eV *vs* NHE). X is the electronegativity of the semiconductor. Whereas, E_e and E_g are the energy of free electron (4.5 eV) on hydrogen scale and band gap of the photocatalyst. The X values for CdS and $Bi_2W_2O_9$ photocatalyst are 5.05 and 6.3 eV, respectively.^[33, 46] The CB of pure CdS and BWO occur at -0.62 eV and 0.325 eV respectively, whereas the VB are placed at 1.74 eV and 3.275 eV. Upon material contact between the two semiconductor phases, there is realignment

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in band positions due to Fermi level equilibration. The band realignment facilitates transfer of electrons from the CB of CdS to CB of BWO. The movement of holes takes place in reverse direction in VB resulting in formation of a type II heterojunction. The VB of both CdS and BWO are placed at a sufficiently positive potential to oxidize the benzylamine.^[24] The VB holes oxidise the benzylamine to the radical cationic species I. On the other hand, the trapping of CB electron by O_2 leads to the formation of O_2^{\bullet} radical. The O_2^{\bullet} radical react with the benzylamine radical cation to give benzylideneamine (II) by release of H₂O₂. A second molecule of benzylamine reacts with benzylideneamine to give the final oxidized product N-benzylidene(phenyl)methanamine with the release of H₂O and NH₃. The proposed mechanism is in line with the earlier reports for photocatalytic oxidation of amines.^[16, 20-23] The practical applicability of the CdS20BWO heterojunction photocatalyst has been evaluated by checking its activity for several consecutive cycles. After each photocatalytic cycle, the catalyst particle are collected and washed with ethanol followed by drying at 110 ^oC for 12 h. The CdS20BWO heterojunction material shows excellent photocatalytic efficiency for the selective oxidation of benzylamine without any appreciable loss in activity for five consecutive cycles (Figure S4). This observation suggests that the CdSBWO heterojunction photocatalyst systems are stable and recyclable for the oxidation of amine.



Figure 8. Possible mechanism for the oxidation of benzylamine over CdSBWO heterojunction photocatalyst surface.

Conclusions

In this study, we have developed a novel type-II CdS/Bi₂W₂O₉ heterojunction photocatalytic system for efficient and selective oxidation of amines to imines under aerobic condition and visible light irradiation. Bi₂W₂O₉ with excellent phase purity is synthesized by employing combustion synthesis method in a short period of time. The deposition of CdS nanoparticles over BWO plates leads to formation of heterojunction system with improved visible light absorption and charge carrier separation. The CdS nanoparticles are of 8-15 nm in size and are well dispersed over the BWO plates. The CdS/Bi₂W₂O₉ heterojunction materials display excellent photocatalytic activity towards selective aerobic oxidation of amines to imines. A variety of primary, secondary and heterocyclic amines are oxidized to the corresponding imines using the CdSBWO material as photocatalyst. The photocatalytic protocol developed in this work is advantageous in terms of use of reneawable energy source, preclusion of toxic oxidants, short reaction time, high selectivity and recyclable photocatalyst.

Experimental section

Materials: All the chemicals were of analytical grade and used directly without purification. Bismuth nitrate (Bi(NO₃).5H₂O), cadmium nitrate (Cd(NO₃)₂.4H₂O), ammonium tungstate ((NH₄)₁₀W₁₂O₄₁), urea (N₂H₄CO), thiourea (N₂H₄CS) and amines were procured from Himedia India Ltd and Avra synthesis India Ltd.

Synthesis of $Bi_2W_2O_9$ (BWO): The $Bi_2W_2O_9$ nanomaterial was synthesized by solution combustion method by taking ammonium tungstate, bismuth nitrate as precursor salts and urea as fuel.^[19] The fuel to oxidizer ratio was maintained at 1.^[53] In a typical synthesis, required amount of $Bi(NO_3)_3.3H_2O$, $(NH_4)_{10}W_{12}O_{41}$ and urea were mixed well and made a paste by drop wise addition of distilled water. The mixture was transferred to a furnace preheated at 400 °C. The mixture instantaneously got ignited producing large quantities of gaseous product and a foamy solid. The combustion mixture was maintained at 400 °C for 30 minutes which was subsequently cooled, grinded to fine powder and calcined at 800 °C for 6 h to obtain the $Bi_2W_2O_9$ material.

Synthesis of CdS/Bi₂W₂O₉ heterojunction material (CdSBWO): The CdS/Bi₂W₂O₉ heterojunction materials were synthesis by hydrothermal method by depositing CdS nanoparticles over the BWO surface. For CdS synthesis, Cd(NO₃)₂.4H₂O was taken as salt precursor and thiourea as sulphur source. In a typical synthesis, required amount of cadmium nitrate and thiourea were dissolved in 50 ml H₂O, to which 1 g of BWO powder was added

and stirred for 30 min. The aqueous suspension was then transfer to a Teflon lined autoclave of 100 ml capacity. The hydrothermal treatment was carried at 150 °C for 12 h under autogeneous pressure. After completion of reaction, the reaction mixture was allowed to cool and the solid materials were collected by centrifugation, washed each with water and ethanol. The solid residue was dried at 110°C for 12 h to get the CdSBWO material. Using this procedure, CdS/Bi₂W₂O₉ materials containing 5, 10 and 20 wt % of CdS were prepared. The CdS/Bi₂W₂O₉ heterojunction materials are referred as CdSyBWO in the subsequent text, where 'y' represents the wt % of CdS present in the heterojunction.

Characterization techniques: The XRD patterns of the CdSyBWO materials were recorded using a Rigaku, Ultima-IV multipurpose X-ray diffraction system using Ni filtered CuK α (λ = 1.5418 Å) radiation at a scan rate of 2° per min. The UV-visible diffuse reflectance spectra of the heterojunction materials were recorded using a Jasco V-650 spectrometer fitted with BaSO₄ coated integration sphere. The FTIR spectra (as KBr pellets) were recorded using a Perkin–Elmer infrared spectrometer with a resolution of 1 cm⁻¹. The X-ray photoelectron spectra (XPS) of CdS20BWO material was recorded using SPECS make (Germany) spectrophotometer with 150 mm hemispherical analyzer at band pass energy of 12 eV. Monochromatic Al Ka radiation of 1486.74 eV was used as X-ray source. Due to electrostatic charging, binding energy corrections were made using the C1s peak at 284.6 eV as standard. The FESEM of BWO and CdSyBWO heterostructure were taken using a Nova NanoSEM microscope model FEI operating at an acceleration voltage of 10 kV. HRTEM images of the CdS20BWO material was recorded using Tecnai 300 kV using carbon coated copper grids of 300 mesh size. The photoluminescence (PL) spectra of the heterojunctions were recorded with a Horiba Scientific Fluoromax-4 spectrofluorometer with an excitation wavelength of 320 nm. The specific surface area of the samples was determined by BET method using N₂ adsorption/desorption at 77 K using a Quantachorme AUTOSORB 1 instrument.

Photocatalytic oxidation of amines catalysed by CdSyBWO heterojunction under visible light: The photocatalytic activity of the CdS/BWO heterojunction materials were evaluated for selective aerial oxidation of amines to imines under visible light irradiation. In a typical experiment, 1 mmol of benzylamine in 5 ml of acetonitrile was taken in a round bottom flask, to which 25 mg of CdSyBWO catalyst was added and stirred for 15 min under dark condition. The reaction mixture was then exposed to a 125 W high pressure mercury vapor lamp with $\lambda > 420$ nm. The percentage conversion at different interval of time was analyzed using a Nucon gas chromatograph using an EC-Wax capillary column and FID detector.

After the completion of the reaction, catalyst particle was separated with a membrane filter and the N-benzylidenebenzylamine was recovered from reaction mixture and purified using column chromatography. All the molecules synthesized in this work are known compounds and were identified by comparing its physical and spectral characteristics with the literature reported values.^[54-58]

Supplementary information can be found in a separate document. Tauc's plots, Radical scavenger experiment and Reusability study of the CdSBWO heterojunction photocatalyst.

Acknowledgements

We thank DST-WTI, New Delhi, India for financial support through grant no-DST/TM/WTI/2K15/93.

Keywords: CdS • $Bi_2W_2O_9$ • heterojunction • amine oxidation

References

[1] G. Palmisano, E. Garcia-Lopez, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro, L. Palmisano *Chemical Communications*. **2010**, 46, 7074-7089.

[2] D. Friedmann, A. Hakki, H. Kim, W. Choi, D. Bahnemann *Green Chemistry*. **2016**, 18, 5391-5411.

[3] G. Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano *Chemical Communications*. **2007**, 3425-3437.

[4] V. Augugliaro, M. Bellardita, V. Loddo, G. Palmisano, L. Palmisano, S. Yurdakal *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 2012, 13, 224-245.

[5] D. Kumar, V. B. Reddy, B. G. Mishra, R. K. Rana, M. N. Nadagouda, R. S. Varma *Tetrahedron*. **2007**, 63, 3093-3097.

[6] Sedat Yurdakal, Giovanni Palmisano, Vittorio Loddo, Vincenzo Augugliaro, Leonardo Palmisano *Journal of Ammerican Chemical Society*. **2008**, 130, 1568-1569.

[7] G. Palmisano, M. Addamo, V. Augugliaro, T. Caronna, E. Garcia-Lopez, V. Loddo, L. Palmisano *Chemical Communications*. **2006**, 1012–1014.

[8] M. Qamar, R. B. Elsayed, K. R. Alhooshani, M. I. Ahmed, D. W. Bahnemann ACS *Applied Materials & Interfaces*. **2015**, *7*, 1257-1269.

[9] M. Gartner, J. Ballmann, C. Damm, F. W. Heinemann, H. Kisch *Photochemical & Photobiological Sciences*. **2007**, 6, 159-164.

[10] H. Kisch Accounts of Chemical Research. 2017, 50, 1002-1010.

[11] T. Mitkina, C. Stanglmair, W. Setzer, M. Gruber, H. Kisch, B. Konig *Organic & Biomolecular Chemistry*. **2012**, 10, 3556-3561.

[12] A. Hakki, R. Dillert, D. Bahnemann Catalysis Today. 2009, 144, 154-159.

[13] Z. Jiao, Z. Zhai, X. Guo, X. Y. Guo *The Journal of Physical Chemistry C.* 2015, 119, 3238-3243.

[14] N. Corrigan, S. Shanmugam, J. Xu, C. Boyer *Chemical Society Review*. 2016, 45, 6165-6212

[15] Y. Wu, B. Yuan, M. Li, W. H. Zhang, Y. Liu, C. Li Chemical Science. 2015, 6, 1873-1878.

[16] A. Han, H. Zhang, G. K. Chuah, S. Jaenicke *Applied Catalysis B: Environmental.* **2017**, 219, 269-275.

[17] S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka ACS Catalysis. 2011, 1, 1150-1153.

[18] Z. Wang, X. Lang Applied Catalysis B: Environmental. 2018, 224, 404-409.

[19] X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji, J. Zhao *Chemistry: A European Journal*. **2012**, 18, 2624-2631.

[20] X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao Angewandte Chemie International Edition.2011, 50, 3934-3937.

[21] F. Raza, J. H. Park, H. R. Lee, H. I. Kim, S. J. Jeon, J. H. Kim ACS Catalysis. 2016, 6, 2754-2759.

[22] B. Yuan, R. Chong, B. Zhang, J. Li, Y. Liu, C. Li *Chemical Communications*. **2014**, 50, 15593-15596.

[23] F. Su, S. C. Mathew, L. Mohlmann, M. Antonietti, X. Wang, S. Blechert *Angewandte Chemie International Edition*. **2011**, 50, 657-660.

[24] X. Wang, J. Yang, S. Ma, D. Zhao, J. Dai, D. Zhang *Catalysis Science & Technology* 2016, 6, 243-253.

[25]] H. Chen, C. Liu, M. Wang, C. Zhang, N. Luo, Y. Wang, H. Abroshan, G. Li, F. Wang *ACS Catalysis*. **2017**, *7*, 3632-3638.

[26] L. Ye, Z. Li ChemCatChem. 2014, 6, 2540-2543.

[27] A. D. Proctor, S. Panuganti, B. M. Bartlett *Chemical Communications*. 2018, 54, 1101-1104.

[28] Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang *Advanced Materials*. 2015, 27, 6265-6270.

[29] A. Watanabe, M. Goto Journal of the Less-Common Metals. 1978, 61, 265-272.

[30] Y. Y. Li, W. D. Cheng, H. Zhang, C. S. Lin, W. L. Zhang, L. Geng, G. L. Chai, Z. Z. Luo, Z. Z. He *Dalton Transactions*. 2011, 40, 7357-7364.

[31] M. Maczka, M. Ptak, L. Kepinski, P.E. Tomaszewski, J. Hanuza Vibrational Spectroscopy. **2010**, 53, 199-203.

[32] S. O. Alfaro, A. M. Cruz Applied Catalysis A: General. 2010, 383, 128-133.

[33] Y. P. Bhoi, C. Behera, D. Majhi, Sk. Md. Equeenuddin, B. G. Mishra New Journal of Chemistry. 2018, 42, 281-292.

[34] O. M. Bordun, A. T. Stetskiv, T. M. Yaremchuk *Journal of Applied Spectroscopy*. **2004**, 71, 136-138.

[35] O. M. Bordun, A. T. Stetskiv, T. M. Yaremchuk *Ukrainian Journal of Physics*. **2004**, 49, 991-995.

[36] A. Feteiraw, D. C. Sinclair *Journal of the American Ceramic Society*. **2008**, 91, 1338-1341.

[37] L. Wu, J. Xia, J. Wu, Q. Li Ionics. 2015, 21, 3239-3244.

[38] S. Obregón, M. A. R. Gómez, D. B. H. Uresti *Journal of Colloid and Interface Science*.2017, 506, 111-119.

[39] S. O. Alfaro, A. M. Cruz, L. M. T. Martínez, S. W. Lee *Catalysis Communications*. **2010**, 11, 326-330.

[40] J. Tang, J. Ye Journal of Materials Chemistry. 2005, 15, 4246-4251.

[41] A. M. Cruz, S. O. Alfaro, L. M. T. Martínez, I. J. Ramírez *Journal of Ceramic Processing Research.* **2008**, 9, 490-494.

[42] R. Marschall Advanced Functional Materials. 2014, 24, 2421-2440.

[43] S. Sakthivel, S.U. Geissen, D.W. Bahnemann, V. Murugesan, A. Vogelpohl *Journal of Photochemistry and Photobiology A: Chemistry*. **2002**, 148, 283-293.

[44] S. Naskar, F. Lübkemann, S. Hamid, A. Freytag, A. Wolf, J. Koch, I. Ivanova, H. Pfnür,
D. Dorfs, D. W. Bahnemann, N. C. Bigall *Advanced Functional Materials*. 2017, 27, 1604685.

[45] Y. Huo, X. Yang, J. Zhu, H. Li Applied Catalysis B: Environmental. 2011, 106, 69-75.

[46] Y. Feng, X. Yan, C. Liu, Y. Hong, L. Zhu, M. Zhou, W. Shi *Applied Surface Science*.2015, 353, 87–94.

[47] J. Fu, B. Chang, Y. Tian, F. Xi, X. Dong *Journal of Materials Chemistry A*. 2013, 1, 3083-3090.

- [48] D. Chen, Z. Kuang, Q. Zhu, Y. Du, H. Zhu *Materials Research Bulletin*. 2015, 66, 262-267.
- [49] Z. Khan, T. R. Chetia, M. Qureshi Nanoscale. 2012, 4, 3543-3550.
- [50] Y. P. Bhoi, B. G. Mishra Chemical Engineering Journal. 2017, 316, 70-81.
- [51] Y. P. Bhoi, S. R. Pradhan, C. Behera, B. G. Mishra RSC Advances. 2016, 6, 35589-35601.
- [52] D. Balzar, H. Ledbetter Journal of Applied Crystallography. 1993, 26, 97-103.
- [53] S. R. Jain, K. C. Adiga, V. R. P. Verneker Combustion and Flame. 1981, 40, 71-79.
- [54] B. Chen, S. Shang, L. Wang, Y. Zhang, S. Gao Chemical Communication. 2016, 52, 481-484.
- [55] Y. Zhi, K. Li, H. Xia, M. Xue, Y. Mua, X. Liu *Journal of Materials Chemistry A*. 2017, 5, 8697–8704.
- [56] T. B. Nguyen, L. Ermolenko, A. Al-Mourabit Green Chemistry. 2013, 15, 2713-2717.
- [57] X. Qiu, C. Len, R. Luque, Y Li ChemSusChem. 2014, 7, 1684-1688.
- [58] Y. Zhang, F. Lu, R. Huang, H. Zhang, J. Zhao *Catalysis Communications*. 2016, 81, 10-13.

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A novel $CdS/Bi_2W_2O_9$ heterojunction photocatalyst is highly efficient towards the aerobic oxidation of amines to imines under visible light irradiation. The heterojunction system shows improved photo induced properties, stable photocatalytic activity and excellent selectivity towards imines.