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Synthesis of lamellar porous photocatalytic nano ZnO with the help of anionic surfactant

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ABSTRACT

Lamellar porous ZnO has been synthesized at room temperature with the help of anionic surfactant SDS and characterized by XRD, SEM, TEM, PL, UV-Visible and FTIR spectroscopy. In the present investigation, SDS a peculiar surfactant act like a template and catalyses to the self-assembled growth of lamellar structure. Obtained structure is anisotropic lamellar in form with multiple secondary nucleation flaps growing perpendicular to a central lamina with uniform morphology. Photocatalytic activity of as synthesized ZnO on the degradation of bromophenol blue is also studied. The percentage of decolourization of dye was found 84.2% to 77.4% in first 30 min at 431 nm and 590 nm. Copyright © 2013 VBRI press.

Keywords: SDS; surfactant; lamellar and porous ZnO; bromophenol blue.

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Introduction

Over the past decade there has been a dramatic increase in the inorganic/organic hybrid materials due to fast progress in their synthesis. ZnO (zinc oxide) is popular n-type semiconductor metal oxides (SMOs), with wide band gap (3.37 eV) with a high mechanical stability at room temperature along with a high exciton binding energy of 60 meV. The strong exciton binding energy of ZnO is much larger than that of GaN (25 meV), which can ensure an efficient exciton at room temperature under a low exciton energy [**1**]. Therefore, ZnO of the most valuable materials in the study of crystal control because of its electronic and optical properties which are strongly influenced by the various morphologies, crystal sizes, dimensions and aspect ratios. Much effort has been made in the synthesis of one dimensional (1D) zinc oxide with various morphologies, including nanorods, nanowires, nanobelts, nanotubes, whiskers, nanocrystals, and other superstructures, because of their advantageous chemical and physical properties. The synthetic methods developed for the synthesis of ZnO nanostructures, such as vapor-phase deposition (thermal evaporation) [**2, 3**], thermal decomposition [**4**] microemulsion method [**5**], template-assisted growth [**6**] and electrochemical deposition [**7**] have been used by number of scientists. These materials have wide applicable possibilities in nanoelectronics, gas and piezoelectric sensors, emitters, transparent electrodes in solar cells, and in catalysis nanotechnology [**8-10**] Okazaki et al. [**11**] studied lasing characteristics of ZnO nanosheets. Intelligent Nanomaterials [**12**] covered latest research and developments in nanomaterials.

Porous nanoparticles provide higher adsorption surfaces which could be efficiently used to purify potable water. The treatment of effluents from organic dye industries is of interest due to their toxic and esthetic impact on receiving waters. Organic dyes in waste water can be degraded into simple molecules by irradiation of sunlight. However this natural purification process is normally slow and conventional waste water purification treatment also generates wastes during operation, which requires additional steps and cost. Nanomaterials which could act as oxidant can be used to solve these problems. In recent years, heterogeneous photo catalytic reactions on n-type semiconductors are recognized as a new emerging “Advanced oxidation process” for the treatment of chemicals present in waste water [**13**]. Because of the recalcitrant nature of synthetic dyes and the high salinity of wastewater containing dyes, conventional biological treatment processes are ineffective [**14**], also under anaerobic conditions azo dyes are readily reduced to potentially hazardous aromatic amines [**15,16**]. ZnO may be used for this purpose as a photocatayst for the degradation of persistent organic dyes and producing more biologically degradable less toxic substances [**17, 18**].

In present investigation lamellar porous ZnO was synthesized by coprecipitation method with the help of an anionic surfactant, sodium dodecyl sulphate (SDS) and was characterized. A plausible growth mechanism is proposed with its observed lamellar morphology. It is a simple method to get nanoparticles in large scale and is economically viable too. Moreover, the photo catalytic activity of ZnO on the degradation of a dye, namely bromophenol blue, is also studied with the help of UV-Visible spectrophotometry which provides a simpler mean to sustain green and clean environment .

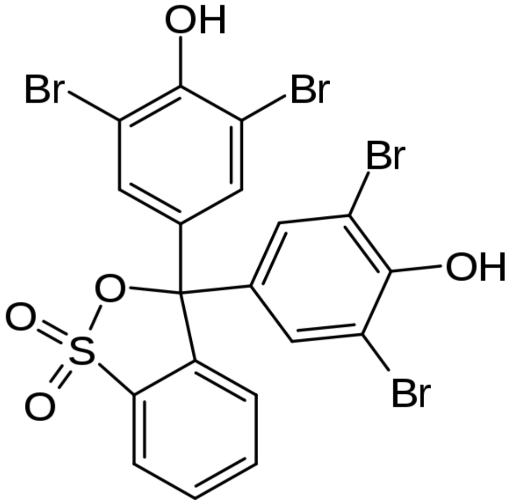
Experimental

Chemicals

The zinc acetate dihydrate ($Zn(CH_3COOH)_2.2H_2O$) (99% purity), Sodium hydroxide (NaOH) (98.5% purity), Sodium dodecyl sulphate (SDS) (98% purity), Ethyl Alcohol (EtOH) (99% purity) and bromophenol blue (98% purity) all reagents were purchased from E. Merck Limited, Mumbai-400018, India. These chemicals were directly used without any special treatment.

Sample preparation

Lamellar ZnO were synthesized by co-precipitation method with the help of SDS. Two sets of solutions of 0.1 M $Zn(CH_3COOH)_2.2H_2O$ and 0.1M NaOH were prepared by dissolving each salt in ethanol and double distilled water in 2:1 ratio. To these solutions $5x10^{-4}$ M SDS solution (by weight) was added slowly drop by drop with constant thorough stirring by placing them on magnetic stirrer at room temperature for 2h. The resulting white turbid products were centrifuged, washed with double distilled water and ethanol. After washing, the products were dried in an oven at 100 °C.



Scheme. 1. Structure of bromophenol blue.

Instrumentation

The crystal structure of lamellar ZnO was characterized by X-ray diffraction (XRD, Rigaku D/MAX- 2200H/PC, Cu Kα radiation). The scanning electron microscopy (SEM) images were taken on a LEO Electron Microscopy Ltd, England. The photoluminescence (PL) study was carried out on Perkin Elmer LS 55 Spectrometer. The photocatalytic activity of ZnO was studied by using UV-Vis spectrophotometry, to observe the degradation of bromopheno blue dye when exposed to UV light.

Photocatalytic study

To observe photo catalytic activity of nano ZnO for the degradation of bromophenol blue dye in presence of UV radiation, the experiment performed in the following way: standard dye stock solution of 50 ppm was prepared by dissolving 50 mg of bromophenol blue dye in 1000 ml of distilled water and the initial absorbance was recorded at 591 nm (λ_{max}). 100 ml of this standard dye stock solution was taken in Borosil® glass beaker and as prepared 0.1g of ZnO composite were directly dispersed in dye solution and the solution was magnetically stirred for one hour. Similarly a blank solution was prepared without ZnO. The pH values of the solutions were adjusted by adding of NaOH (1 M) and HCl (1 M) using an Orion Model 801A pH meter. After one hour the solutions were allowed to equilibrate in dark for 30 minute before the UV lamp was turned on. Then both the solutions were irradiated by UV light for 30 minutes time intervals and their absorbance were recorded and plotted. The percentage of decolorization was calculated by using the following formula.

The percentage of decolorization = $[(A_0 - A_t) \div A_0] \times 100$

where, A_o is the initial absorbance of the dye solution and A_t is the absorbance at time interval 't'.

Results and discussion

The structural characterization of ZnO

Fig. 1 shows the XRD pattern of the ZnO synthesized by the co-precipitation method with SDS. Furthermore, it can be seen that the diffraction peaks are higher and narrower, implying that the ZnO crystallized well. All the diffraction peaks are in good agreement with the JCPDS file for ZnO (JCPDS 36- 1451, a = 3.249 Å, c = 5.206 Å), which can be indexed as the hexagonal wurtzite structure of ZnO. No characteristic peaks of impurities such as SDS or Zn $(OH)_2$ were observed.

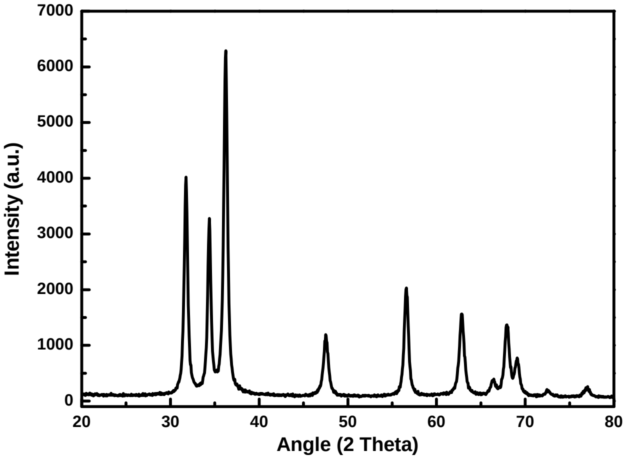


Fig. 1. XRD pattern of ZnO.

Growth mechanism

As observable with naked eyes, the surface morphology of the films clearly differs from that of the pure ZnO films. The as-synthesized SDS coated ZnO exhibit surprisingly large surface areas. The interaction of precursors in the presence of surfactant molecule is totally in different ways. (i)Firstly, there will be electrostatic interaction between surfactant head group [anionic] to cations (Zn^{2+} ions), (ii) Secondly, hydrophobic interaction between alkyl group of solvent and hydrophobic part of surfactant and (iii) lastly hydrophilic interaction between hydrophilic part of surfactant. It is observed that the use of anionic surfactants can reduce the surface energy of specific crystal faces by adsorption of their counter-ions on the negatively charged surfaces [zinc hydrate precursor, Zn $(OH)_4^{2-}$] from the experiment, and it can lead to control the crystals in aqueous solution containing anionic surfactants. The increased binding of the counter-ions to the surfactant depends on the size of cations causes a decrease in the critical micelle concentration (CMC) and an increase in the aggregation number in solution [**19**]. The presence of surface forces at the solid-liquid interfaces, surfactants adhere at the surface most. Therefore, surface micelles can be formed, even when the surfactant concentration is far below cmc. In addition, once the surfactant concentration exceeds the surface micelle concentration, the surface surfactant concentration can be insensitive to the change in the bulk surfactant concentration. The extraction with ethanol is an efficient method to remove SDS contained within the crystals damaging the morphology or decreasing its crystalline nature [**20**]. It is known [**21**] from studies of Zn $(OH)_2$ nanoparticles that SDS molecules can form a layer directly on a particle surface, which helps to limit the particle size to the nanometer range. The negative sulfate groups attach to the positive nanoparticle surface, leaving the hydrocarbon tails unbound in the liquid. Close to and above the cmc, it becomes energetically favorable for the tails from different nanoparticles to intercalate and form lamella, which effectively 'glue' the nanoparticles together in various packed arrangements.

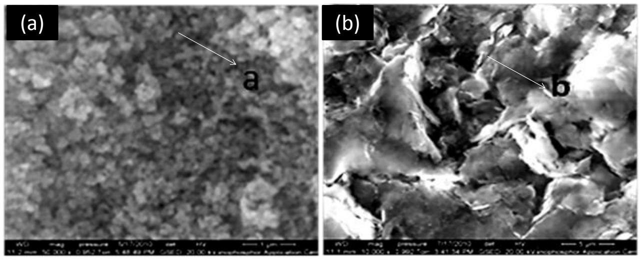


Fig. 2. FE-SEM image of (a) Bare ZnO and (b) ZnO with SDS.

We have obtained more or less ZnO buds in aqueous solution at Zn^{2+} poor condition (lower concentration ratio of Zn^{2+}/OH^-) without any additives. We are newly suggesting that the origin of the leafy-lamellar structured ZnO in an insufficient supplement of Zn^{2+} for ZnO seeds. The negatively-charged SDS ions are assembled and form spherical micelles which encapsulate ZnO seeds. The micelles limit a supplement of Zn^{2+} ions for the encapsulated ZnO seeds, which leads a formation of chemically-activated lattice defects on the surface. These lattice defects will be nucleation sites of new ZnO nanoparticles growing in random directions. Once randomly-oriented sheets are formed, the crystal growth preferentially occurs at the outer edge of the randomly oriented lamellar sheets. The schematic representation of this mechanism is shown in **Fig. 3**. These lamellar sheets exhibit higher photoluminescence intensity of back ground in UV region, which can be interpreted as an effect of a strong light scattering because of the lamellar structure with several μm size. Thus the ZnO nanosheets were suggested to be formed by competitive reactions of the passivation and the micelle formation.

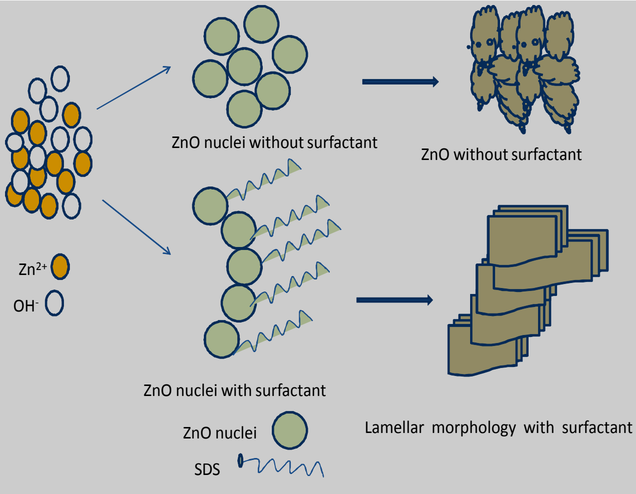


Fig. 3. Schematic representation of growth of lamellar ZnO: as a result of interaction between anionic surfactant head group and tail groups the morphology of ZnO gets affected.

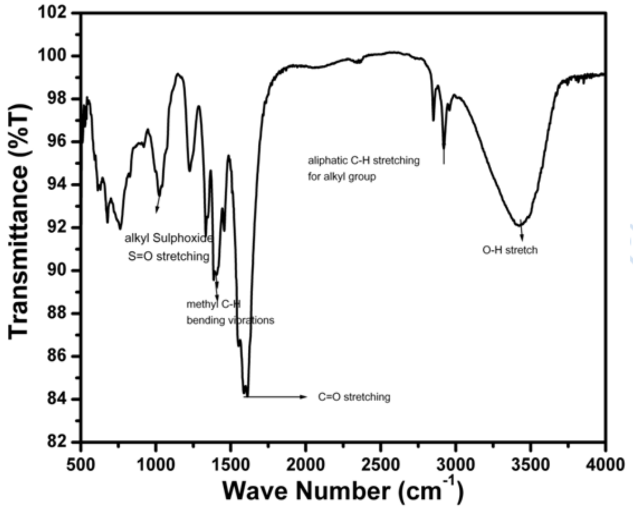


Fig. 4. FTIR spectrum of ZnO synthesized by SDS assisted co-precipitation method.

Fourier transform infra-red (FTIR) clearly indicated (**Fig. 4**) that the surfactant played its vital role in deciding the morphology of the lamellar structure. A sharp S=O stretching peak at 1025 cm^{-1} clearly indicated the presence of alkyl sulphoxide group. A clear peak at 1412 cm^{-1} showed methyl bending vibrations and peak at 2933 cm^{-1} C-H stretch indicated the presence of SDS at the surface. C=O stretch at 1599 cm^{-1} and a broad O-H stretch at 3432cm^{-1} vibrations indicated extensive hydrogen bonding at the composite surface.

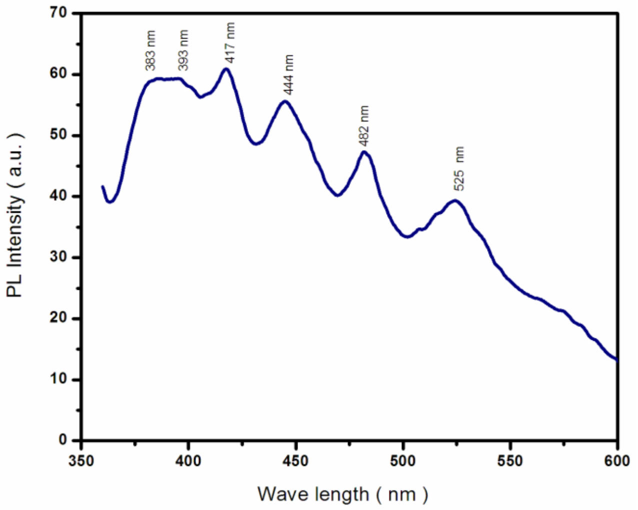


Fig. 5. PL spectrum of ZnO synthesized by SDS assisted co-precipitation method.

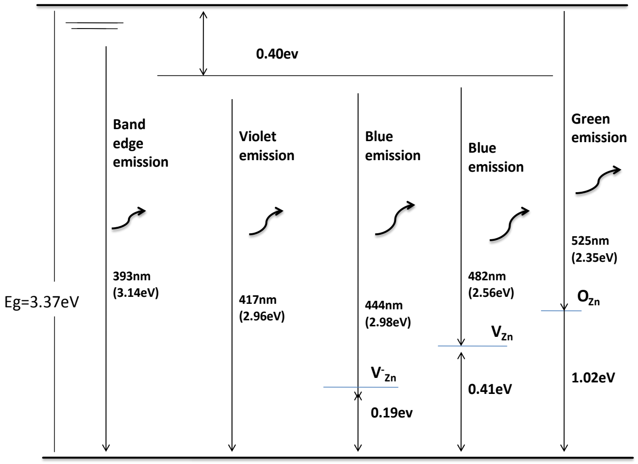


Fig. 6. Schematic representation of emission of nano ZnO synthesized by surfactant assisted coprecipitation method.

Photoluminescence spectral studies

Fig. 5 shows room temperature photoluminescence (PL) spectra of lamellar ZnO nanoparticles synthesized by co-precipitation method with the help of surfactant SDS, at excitation wave length 325 nm. Several emission bands were observed corresponding to – (a) band edge emission , attributed to the recombination of excitons [**22**] and (b) defects related to UV emission . In visible region the emissions are attributed to different intrinsic defects in ZnO nanocrystals. These defects may be due to (i) oxygen vacancies (V_o) (ii)Zn vacancies (V_{Zn}) (iii) oxygen interstitials (O_i) (iv) Zn interstitials (Zn_i) and (v) oxygen antisites (O_{Zn}). A PL peak giving violet emission at 2.96 eV (~497 nm) is attributed to electron transfer from a deep donor level of neutral Zn_i to the HUMO of (top level of) the valence band [**23**] which indicate that the donor level of Zn_i is located at ~ 0.40 eV below conduction band in this case, due to which a violet PL appeared at ~ 2.96 eV. A blue emission peak appeared at 2.56 eV(~482 nm) which is due to a radiative transition of electron from deep donor level of Zn_i to an acceptor level of neutral $V_{Zn]}$ [**24**].

In our work acceptor level of V_{Zn} locates at o.41 eV above the valence band. Another blue emission was observed as reported in literature at around 2.78eV (~444nm). This emission may be due to the surface defects of ZnO nanostructures or may be due to the singly ionized V_{Zn}- located at ~0.19eV above the valence band [**25**] in our case. Green emission here is due to the radiative transition from conduction band to the edge of the acceptor levels of O_{Zn} caused by oxygen antisites [**26,27**] as mentioned above, which is indicated by the peak position at 2.35 eV (525nm) and the acceptor level of oxygen antisites O_{Zn} may be located at ~1.02 eV above the valence shell. All these transitions are schematically represented in **Fig.6**. As said earlier that the anionic surfactants (e.g. SDS) can reduce the surface energy of specific crystal faces by adsorption of their counter ions on the negatively charged surfaces, therefore, green emission might be due to the excess of Zn which comes from the reaction process. Red shift of the band edge emission peak from 379 nm to 393 nm may be attributed to the native defects concentration in the different ZnO nanostructures [**28**].These various defects play very important role on the surface chemistry of ZnO.

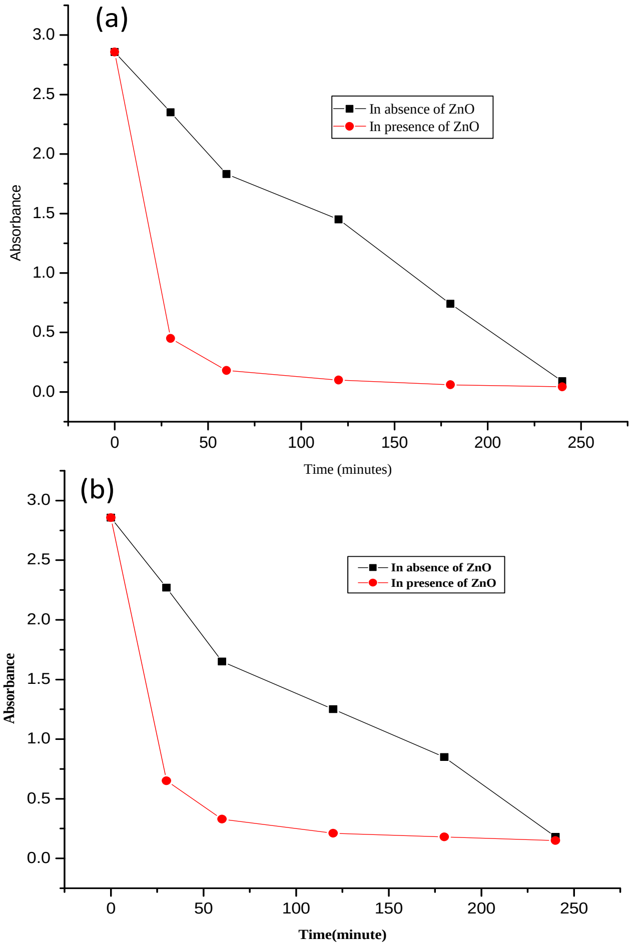


Fig. 7. Absorbance verses Time curve showing degradation of dye (a) at 431 nm and (b) at 590 nm.

Photocatalytic activity

ZnO, a semiconductor material, can be used for photo catalytic applications, due to its environmental stability and low cost when compared to the other nanosized metal oxides. The band gap of ZnO (= 3.37 eV) is in UV range. Therefore, photocatalytic efficiency was found to be high in UV radiation. We have observed the photocatalytic degradation of bromophenol blue dye molecule with ZnO and found to be an efficient photocatalyser (**Fig.7**). The percentage of decolonization of dye was found 84.2% to 77.4% in first 30 minutes with ZnO and 17.8% at 431 nm and 20.9% at 590 nm respectively without ZnO in UV radiation only (**Fig. 7**).

Mechanism of photocatalysation

When stable-solid semiconductors are used as sensitizers, the stimulation of solution- phase reactivity by initial excitation of the solid- phase semiconductor has been termed as photocatalysis, since photosensitive solid can be recovered unchanged after many turnovers of the redox system. This stimulation or photocatalysis is a light induced catalytic process which generates electron-hole(e-,h^+) pairs in a semiconductor which undergoes reaction with adsorbed dye molecule (here bromophenol blue) onto the surface , thereby breaking them into smaller fragments. Two different energy level systems in semiconductor play an important role in achieving charge separation i.e. they are characterized by band structure, a filled valence band separted by an energy gap (Eg) from vacant conduction band. Photo excitation of the semiconductor promotes an electron from the valence band to the conduction band, leaving an electron deficiency or hole in the valence band. When this pair forms in the space charge region of the semiconductor by virtue of absorption of a photon, the electron will move away from the interface to the bulk of the semiconductor as the hole migrates towards the interface where oxidation can occur.

In other words absorption of a photon by the semiconductor effects electron-hole (e-, h^+) pair formation which in turn effects its catalytical reaction process. The most probable reaction mechanism can be represented in the following way.

(i) Photons are used to create e-, h^+ pairs in semiconductor:

$ZnO + h\nu \rightarrow ZnO\ [(e^-) + (h^+)]$ ………. (1) (exciton pair)

(ii) Capture of e^- :

$(e^-) + O_2 \rightarrow O_2^{\bullet-}$ ………. (2)

(iii) Capture of hole (h^+):

$(h+) + OH^- \rightarrow {\bullet}OH$ ………… (3)

(iv) Excitation of dye BPB:

$BPB + h\nu \rightarrow BPB^*$ …………..(4)

(v) Mineralization of dye BPB:

$BPB^* + (O_2^{\bullet-}$ or ${\bullet}OH) \rightarrow$ [Peroxide or hydroxide intermediates] → [Degraded products] ………. (5)

After migration of these charge centers to the surface of the irradiated semiconductor, capture of electron occurs by a reducible adsorbed species and of hole by an oxidizable adsorbed species. The oxidized species then undergoes rapid chemical reaction and subsequent formation of the final products and desorption from the surface completes the usual reaction sequence [**29**]. The positive hole oxidizes either the dye BPB or water to produce hydroxyl radical. Whereas the electron in the conduction band reduces the oxygen adsorbed onto the photo- catalyst ZnO to form active oxygen radicals. These active radicals drive the photo-degradation or mineralization of dye BPB. The trapped holes may be regarded as surface-bound hydroxyl radicals. The bound radicals can also diffuse away from the surface toward the solution bulk and exist transiently as free OH [**30**]. This mechanism suggests that hydroxyl radicals and photogenerated holes (h_{VB}^+) are the primary oxidizing species for the adsorbed or free dye molecules [**31**] while photogenerated electrons (e_{CB}-) are the reducing species, in the UV/ZnO system.

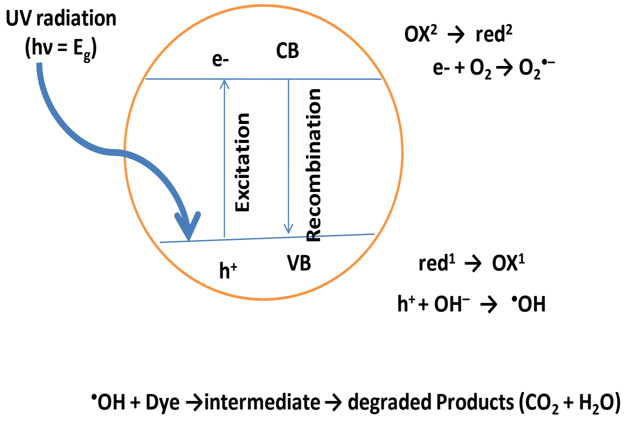


Fig. 8. Simplified figure showing photocatalytic activity of semiconductor.

The presence of oxygen is profoundly important for the effective photo-degradation of dyes. In absence of oxygen, the extent of photo-degradation of dye was found to be negligible [**32**]. Which indicates that dioxygen scavenges the conduction band electron and thus prevents the recombination of e-, h^+ pair. Therefore, it is important for an effective photo-degradation process.The hydroxyl radical attacks dye resulting in the formation of reaction intermediates, which further reacts with OH to produce final degradation products, such as CO_2 and H_2O. In the photocatalytic degradation of pollutants, when the reduction process of oxygen and the oxidation of pollutants do not advance simultaneously, there is an electron accumulation in the CB, thereby causing an increase in the rate of recombination of e- and h^+ pair [**33, 34**].The mechanism is schematically shown in **Fig. 8**. Thus it is of paramount importance to prevent electron accumulation in efficient photo-catalytic oxidation. Surface area and surface defects play an important role in the photocatalytic activity of metal-oxide nanostructures, as the contaminant molecules need to be adsorbed onto the photocatalytic surface for the redox reaction to occur. In our present work defects were introduced by the surfactant SDS, which is clear from the PL studies, thus providing higher effective surface area for the adsorption of target molecules leading to better photocatalytic activity.

Conclusion

We have synthesized lamellar porous ZnO nanoparticles with anionic surfactant, SDS. Several emission bands were observed indicating different types of defects, which reduced the surface energy of specific crystal faces. This surface phenomenon is successfully used to observe its photocatalytic activity for the degradation reaction of a dye bromophenol blue onto the surface of nano ZnO and found ZnO as an efficient photocatalyser.

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