Carbon nanospheres supported visible-light-driven ZnSb_2O_6 : synthesis, characterization and photocatalytic degradation studies

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Abstract

Carbon-based nanocomposites are gaining considerable attention due to their broad range of applicability in various fields, especially as photocatalysts. The present work demonstrates the impact of carbon nanospheres on photocatalytic efficiency of ZnSb_2O_6 (ZSO), a UV active photocatalyst. Carbon nanospheres supported ZnSb_2O_6 (CNSZSO) is synthesized by the hydrothermal method using glucose as a precursor. ZnSb_2O_6 is prepared by metathesis method for the first time. As prepared samples are characterized by XRD, FESEM/EDS, FTIR, XPS, UV–Vis DRS. The samples are crystallized in the primitive tetragonal crystal lattice with space group $P4_2/mnm$ as confirmed by XRD. The optical absorbance profile of CNSZSO showed a clear redshift of absorption edge towards visible region (400–800 nm) and also band gaps obtained from KM plots showed a decrease from 2.96 eV (ZSO) to 1.48 eV (CNSZSO). Further, photocatalytic degradation studies against methyl violet are investigated under visible light irradiation for the first time. The results suggest an enhancement in the degradation percentage by CNSZSO.

Keywords Carbon nanospheres · ZnSb_2O_6 · Powder XRD · Morphology · XPS · Photodegradation

1 Introduction

Water resources have become one of the most vulnerable abiotic components with discharge of two million tons of untreated sewage, industrial and agricultural wastes into it. About 40% of the dyes and pigments used in textile industries are released into water streams without proper treatment leading to water pollution at an alarming rate. It poses harmful effects on both flora and fauna, including humans resulting in ailments like respiratory disorders and skin diseases. Besides being a crucial component in textile industries, dyes are also extensively used in pharmaceutical, food, cosmetic, plastic, photographic, and paper industries. The impacts are not only restricted to fauna but also drenched to flora. It signifies the exigency for developing wastewater treatment technologies.

Photocatalysis, an advanced oxidation process, is one of the most promising methods with a lot of attention being

focused nowadays because of its workability under solar light, which is an amply available continuous resource. It is a convenient process of harnessing solar energy for the degradation of organic substances [1] and water splitting [2]. Comprehensive research is being carried out on the development of efficient photocatalysts as it plays a pivotal role in the process of photocatalysis. Titanium dioxide is the most widely used photocatalyst due to its various favorable properties like long term chemical stability, environmental friendly, economically cheap, high activity. However, its applicability is restricted because of the higher bandgap, i.e., 3.2 eV, which limits its efficiency [3]. Though considerable research is carried out towards the development of an efficient photocatalyst, it is still a great challenge to obtain a photocatalyst which can work even under visible spectra. In such a scenario, extending the applicability of a photocatalyst into the visible region is of great significance.

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In search of an efficient visible-light-driven catalyst, we chose ZnSb_2O_6 as photocatalyst. Careful examination of the literature reveals that considerable research has been carried out on ZnSb_2O_6 due to its various applications like gas sensors [4], electrodes for dye-sensitized solar cells [5] and photocatalyst for dye degradation [6–10]. ZnSb_2O_6 shows good photocatalytic activity under irradiation of UV light. Efforts have been made to enhance the photocatalytic dye degradation efficiency of ZnSb_2O_6 by doping it with Nitrogen [8], Eu^{+3} and Tb^{+3} [9], under UV light irradiation. But attempt to enhance the activity of the compound in the visible region is so far not reported.

Tailoring the optical and surface properties of materials is one of the strategic approaches to enhance the photocatalytic efficiency. It has been established that carbon nanospheres supported oxide materials exhibited excellent photocatalytic activity [11, 12]. However, the impact of carbon nanospheres on the photodegradation efficiency of the ZSO is still not aimed. In the present study, for the first time, we adopted a novel metathesis approach to prepare ZnSb_2O_6 . Owing to the pragmatic impact of carbon-based composites; an attempt is made to enhance the photocatalytic activity of ZnSb_2O_6 by compositing it with carbon nanospheres via hydrothermal method. All-encompassing the present work deals with the synthesis, characterization, and photodegradation of methyl violet dye of ZnSb_2O_6 and carbon nanospheres supported ZnSb_2O_6 .

2 Method of preparation and characterization

2.1 Materials

ZnCl_2 (SDFCL) 97% purity, $\text{KSbC}_4\text{H}_4\text{O}_7$ (SDFCL) 98.5% purity and Glucose (Qualigens Fine Chemicals) are used as precursors for the synthesis of ZnSb_2O_6 and C-nanospheres supported ZnSb_2O_6 .

2.2 Preparation of ZnSb_2O_6 (ZSO) and C-nanospheres supported ZnSb_2O_6 (CNSZSO)

Preparation of inorganic oxide materials by metathetic approach is beneficial in terms of energy, purity, and time. ZSO preparation is as follows. Stoichiometric amounts of potassium antimony tartrate and ZnCl_2 are thoroughly crushed in an agate mortar employing a few mL of acetone. The powder is heated at 773.15 K/6 h in air. The resultant solid is dissolved in water to remove the byproduct KCl.

C-nanospheres supported ZnSb_2O_6 (CNSZSO) composite is prepared through the hydrothermal method [13].

Glucose is used as a source of carbon nanospheres. About 4.449×10^{-4} kg of glucose is dissolved in 0.05 L of deionized water, and ZSO (5×10^{-3} kg) is added to this solution. The resultant mixture is transferred to a Teflon cup, which is carefully sealed inside a steel case (bomb). The bomb is placed inside a hot air oven and heated autogenously at 453.15 K for 12 h. The obtained dark brown solid is washed several times with water, followed by absolute ethanol to remove any remaining traces of organic residue. The solid obtained is dried at 333.15 K and labeled as CNSZSO.

2.3 Characterization

Powder X-ray diffractograms of the prepared samples are recorded using Rigaku Miniflex 600 X-ray diffractometer using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of $10\text{--}80^\circ$ for the phase identification of as-prepared samples. Surface morphology analysis and Energy dispersive of X-rays (EDX) analysis are carried out by field emission scanning electron microscopy (FE-SEM) using a Carl Zeiss model Ultra 55 electron microscope. JASCO V-650 UV-Vis spectrophotometer is used for UV-Vis diffuse reflectance spectra (DRS) measurements in the range 200–900 nm. BaSO_4 is used as the reflectance standard. The X-ray photoelectron spectroscopic (XPS) analysis is performed on AMI-CUS 3400 X-ray photoelectron spectrometer using excitation energy of 1253.6 eV (Mg K α) and pass energy of 40 eV. The XPS experiments are performed at room temperature under ultra-high vacuum (10^{-6} Pa). Infrared spectra are recorded in the form of KBr pellets in the wave number range $4000\text{--}400 \text{ cm}^{-1}$ using JASCO IR-5300 spectrometer.

2.4 Photocatalytic activity

The degradation of methyl violet (MV) dye is investigated in the presence of ZSO and CNSZSO composite under the irradiation of visible light of 300 W tungsten lamp using HEBER visible annular type of photoreactor. About 5×10^{-5} kg of the photocatalyst is dispersed in 0.05 L of methyl violet dye solution of concentration $5 \times 10^{-5} \text{ M}$ and stirred continuously with air bubbling for 1 h in the dark to establish adsorption–desorption equilibrium. The distance between the lamp and solution is fixed to 5 cm during irradiation. Dye solution of $3 \times 10^{-3} \text{ L}$ was collected for every 30 min time interval and sediment to settle the remaining traces of catalyst. The absorbance values of collected samples are recorded at λ_{max} (580 nm for MV) using JASCO V650 UV-Vis spectrophotometer to understand the extent of degradation. The photocatalytic degraded amount (d) of pollutants was calculated using the formula, $d = \frac{(C_{\text{eq}} - C)}{C_{\text{eq}}}$, where C is the concentration of MV solution

at regular interval times in the process of photo-degradation and C_{eq} is the concentration of MV at equilibrium.

2.5 Mechanistic photodegradation pathway studies

Controlled photocatalytic experiments using different radical scavengers are carried out to investigate the role of active species responsible for the removal of dye under similar experimental conditions in the presence of as-prepared catalysts. Ammonium oxalate (AO), benzoquinone (BQ) and isopropanol (IPA) are used as scavengers for photogenerated holes, superoxide radical and hydroxyl radical species, respectively [14, 15]. About 5×10^{-5} kg of CNSZSO composite is dispersed in 0.05 L of methyl violet dye solution containing 3×10^{-3} L of 2 mM Ammonium oxalate, Benzoquinone, and Isopropyl alcohol and placed separately in different tubes inside the photoreactor. Samples are allowed to attain adsorption–desorption equilibrium in the dark for about 60 min and then irradiated with visible light. During irradiation 2×10^{-3} L of sample is collected for every 30 min, and absorbance is recorded.

A supplementary experiment, employing terephthalic acid (TA) as a probe, is also carried out to substantiate the formation of $OH^\bullet$ radicals during photocatalysis under visible light irradiation. The experimental procedure is as follows: typically, 5×10^{-5} kg of the sample is suspended in 0.05 L of a 0.02 M NaOH solution containing 3 mM terephthalic acid (TA). The suspension is stirred in the dark for 60 min followed by visible light (300 W tungsten lamp) illumination. Then, 3×10^{-3} L of the suspension is collected for every 60 min of time intervals, filtered and recorded its fluorescence spectra using JASCO FP-8500 spectrofluorometer. It is well known that the photo-generated $OH^\bullet$ radicals react with TA and form a 2-hydroxyterephthalic acid (TAOH), which shows a characteristic fluorescence signal centered at 426 nm. The increase in the fluorescence intensity is directly proportional to the concentration of photo-generated $OH^\bullet$ radicals. The measurement is carried out at the excitation wavelength of 320 nm.

3 Results and discussion

It is reported that ZSO can be synthesized by the solid-state method [8], sol–gel [9], hydrothermal [6], and the colloidal method [16]. In the present study, the pristine ZSO is prepared by a novel metathesis method. The phase formation of the ZSO is tested by recording powder X-ray diffraction (PXRD) patterns. Figure 1 shows the PXRD patterns of ZSO. The observed d -lines of ZSO are consistent with JCPDS PDF 75-1037. XRD showed characteristic trirutile reflections such as (002), (101) and (112). ZSO is reported to exhibit a typical trirutile

Fig. 1 PXRD patterns of ZSO and CNSZSO

Fig. 2 a Unit cell of ZSO and b crystal structure of ZSO

structure (Fig. 2) with a distorted octahedral arrangement of SbO_6 with three different Sb–O bonds (1.9951 Å, 1.998 Å, 2.011 Å) and the interstices of octahedra are filled with Zn [6]. Further, the Rietveld refinement of ZSO is carried out to study its structural parameters. The Rietveld refined powder pattern of ZSO is showing Fig. 3. It is found that ZSO crystallized in the primitive tetragonal crystal lattice with space group $P4_2/mnm$. The obtained unit cell parameters, $a = 4.669$ Å and $c = 9.266$ Å are in

Fig. 3 The observed and calculated patterns of ZSO

good agreement with the literature data ($a = 4.6719 \text{ \AA}$ and $c = 9.2646 \text{ \AA}$).

CNSZSO composite attained from hydrothermal route also shows a similar pattern without any impurities suggesting that the introduction of carbon nanospheres have no significant impact on the structure of ZSO lattice (Fig. 1). However, slight shifts of d-lines towards lower 2θ values infer the incorporation of a small portion of carbon atoms into the ZSO lattice. The carbon nanospheres on the surface of ZSO is endorsed from FESEM-EDS, FT-IR, XPS and UV-Vis DRS techniques.

The FESEM image of ZSO shows small irregular shaped crystals with more agglomeration. The carbon nanospheres are inserted between the ZSO crystals, as shown in Fig. 4. The element distribution of ZSO and CNSZSO from EDS mapping is shown in Fig. 5, which indicates the uniform distribution of carbon nanospheres in the ZSO sample. FT-IR of the ZSO and CNSZSO are comparable in the range of $400\text{--}1000 \text{ cm}^{-1}$ (Fig. 6). The peak at 505 cm^{-1} represents the symmetric deformation mode of Zn–O bond in ZnO_6 octahedra. The band observed in the $610\text{--}680 \text{ cm}^{-1}$ region corresponds to the stretching mode of Sb–O in SbO_6 octahedra [8]. The additional peaks in the CNSZSO compared to that of ZSO attributed to the surface carbon particles bonding with surface oxygen and hydroxyl groups [17, 18].

XPS analysis is performed to investigate the chemical composition and oxidation state of each element in the CNSZSO and the results are shown in Fig. 7a shows the survey scan spectra of CNSZSO in the range of $0\text{--}1100 \text{ eV}$, which reveal the presence of Zn, Sb, C, and O elements in the CNSZSO catalyst. Further, it is essential to mention that no other elements or impurity peaks are observed in

the CNSZSO sample. The high-resolution XPS of Zn 2p, Sb 3d, O 1s, and C 1s are shown in Fig. 7b–e, respectively. As shown in Fig. 7b, the binding energies of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ appear at 1024.2 and 1045.4 eV, respectively, which indicates the oxidation state of Zn represent in the +2 oxidation state [19, 20]. The binding energy values at around 531.5 and 540.9 eV are ascribed to Sb $3d_{5/2}$ and Sb $3d_{3/2}$, respectively and no peak of Sb^{3+} is observed at 539 eV, which indicates that Sb in both the samples exists only in Sb^{5+} state (Fig. 7c) [19, 21, 22]. As shown in Fig. 7d, the O 1s spectrum of CZSO shows asymmetry and distinctly different peaks. Therefore, the O 1s spectrum is fitted with two kinds of chemical states. Generally, the lower binding energy peak observed at 529.5 eV corresponds to the crystal lattice oxygen (such as O^{2-} species), and the other peak at 531.2 eV is due to the adsorbed oxygen of surface hydroxyl OH groups [19]. As seen in Fig. 7e, the high-resolution XP spectrum of C 1s core level peak for CZSO can be deconvoluted into three peaks at around 286.4, 288.3 and 290.3 eV (designated as α , β , and γ) [17]. The “ α ” peak could be assigned to the surface adventitious carbon. The “ β ” and “ γ ” peaks are characteristic of oxygen bound species, C–O, and C=O, respectively. More importantly, the “ γ ” peak also belongs to the carbonaceous species that form the structure between ZbSb_2O_6 and carbon (such as Zn/Sb–O–C bond species) during the carbon doping process.

Optical absorption profile of ZSO and CNSZSO are shown in Fig. 8. It is noticed that the absorbance of CNSZSO is high in the visible region, and the absorption edge is red-shifted compared to that of parent ZSO. The bandgap energy of these materials is calculated using the Kubelka–Munk (KM) theory. Figure 9 shows the KM plot $(\text{Kh}\nu)^{1/2}$ where $[K = \frac{(1-R)^2}{2R}]$, where R is reflectance (in %)]

ZSO **CNSZSO**

Fig. 4 FESEM images of **a** ZSO and **b** CNSZSO

and $h\nu$ is photon energy vs. Photon energy) of ZSO and CNSZSO. The bandgap energy of the ZSO and CNSZSO is found to be 2.96 and 1.48 eV, respectively. CNSZSO is expected to show high photocatalytic activity under the visible light irradiation compared to that of ZSO due to its lower bandgap energy. It is known that carbon nanospheres assist in improving the photocatalytic activity of the material by providing the high surface area with large adsorptive active sites, photosensitization, bandgap tailoring and decrease in the electron–hole recombination rate

[23]. In the degradation of the organic dyes, carbon nanospheres supported materials increase the dye adsorption on its surface and provide excellent contact between the photocatalyst and the dye.

Photocatalytic degradation studies of ZSO and CNSZSO are conducted on methyl violet (MV) dye. In spite of lethal action of MV, it is used widely in textile and paper industries, and approximately 15% of the dye is escaped into the natural ecosystems without adequate treatment which is of high environmental concern. Hence, MV dye

Fig. 5 EDS mapping of ZSO AND CNSZSO

is taken as a model system for understanding the degradation efficiency of the as-synthesized compounds. The MV dye is irradiated with visible light in the presence and absence of catalysts (ZSO and CNSZSO). Figure 10 shows the temporal change in the concentration of MV dye in the presence/absence of catalysts as a function of irradiation time. As shown in the figure, the percentage degradation of MV in the absence of the catalyst is ~ 3%, indicating negligible photolysis of the dye. The degradation percentage in the presence of ZSO and CNSZSO is about 40 and 93 respectively at the end of 180 min of visible light irradiation. It is observed that about 85% of MV dye is degraded in 60 min of visible light irradiation only. The higher photocatalytic activity of CNSZSO is attributed to its reduced bandgap energy and photosensitization effect

of carbon nanospheres on ZSO. It is reported that carbon nanospheres supported catalyst exhibits higher activity because of the synergistic effect between the catalyst and carbon nanospheres [24].

3.1 Mechanistic degradation pathway and effect of operational parameters on the decomposition efficiency of MV

It is known that upon irradiation of light onto the surface of semiconductor photocatalyst, electrons from valence band get excited to conduction band resulting in the formation of electron-hole pair. This initiates two pathways: (1) a reductive pathway due to excess electron in conduction band reducing O_2 to O_2^- and (2) oxidative pathway

(b) CNSZSO

Fig. 5 (continued)

due to vacant hole in valence band oxidizing H_2O to produce highly reactive $\text{OH}^\cdot$ free radical species which invade the dyes and other organic contaminants present in water converting them ultimately to simple harmless byproducts. The vital factor in photocatalysis is a delay in the recombination time of the electron–hole pair, which will decide the efficiency of the catalyst. It is also reported that carbon-supported materials lower the electron–hole recombination rate by capturing the photogenerated electron during the photoreaction and transport that electron to the surface of the dye due to their high conductive activity [25].

The expected mechanism is as follows: The photoexcited electrons generated on irradiation are transferred into the conduction band of ZSO escalating the production of

$\text{O}_2^{\cdot-}$ by reduction of O_2 . Also, Carbon nanospheres provide an accessible electron reservoir for the valence band electrons of ZSO stimulating rapid electron migration and creating holes which serve as oxidation centers for producing $\text{OH}^\cdot$ free radicals. Besides, the high absorptivity of carbon nanospheres tends to absorb dye and make it available for degradation. Thus the synergetic effect of adsorption and photosensitization results in enormous enhancement of photodegradation. To ascertain the efficiency of charge carrier migration, trapping, and transfer of electron–hole pairs in the present systems, the photoluminescence (PL) spectra of ZSO and CNSZSO are recorded (Fig. 11) [26]. The photoluminescence experiment gives an idea about the lifetime of the electron–hole pair. The PL signal arises due to the recombination of electron and hole. Thus, the intensity

Fig. 6 FT-IR spectra of ZSO AND CNSZSO

of the PL signal is proportional to the rate of electron–hole recombination. Figure 9 shows the PL spectra MV solution in the presence of ZSO and CNSZSO. It is clear from Fig. 9 that the PL signal intensity in the presence of CNSZSO is lower than that of ZSO, indicating lower electron–hole recombination rate in CNSZSO compared to ZSO. A lower electron–hole recombination rate implies the availability of more electrons and holes to attack the dye molecules to initiate a series of dye degradation reactions. Thus, the photocatalytic activity of CNSZSO is much higher (93%) compared to pristine ZSO (40%). In addition to that, the activity of the photocatalyst is directly proportional to the number of active radicals produced during the photoreaction, which in turn is based on the number of photons absorbed. A supportive examination is carried out to establish the mechanism using scavenger test. Scavengers like Benzoquinone (BQ), Ammonium oxalate (AO), and isopropyl alcohol (IPA) trap the $O_2^{\cdot-}$, hole, $OH^{\cdot}$ free radicals respectively thereby inhibiting their activity. Irradiation of light followed by measurement of absorbance values of the CNSZSO samples collected at regular intervals suggested that the degradation of the dye in the presence of scavengers is reduced to a considerable extent. It is

identified to be 22%, 29% and 31% for Ammonium oxalate, isopropyl alcohol, and benzoquinone, respectively supporting the involvement of active species in the photodegradation process (Fig. 12). Further, to support the formation of $OH^{\cdot}$ free radical during the photocatalytic reaction, terephthalic acid (TA) is used as a probe. TA when reacts with $OH^{\cdot}$ will form 2-hydroxyterephthalic acid (TAOH) which shows an intense signal in fluorescence spectroscopy at 426 nm. The regular increase in the fluorescent signal concerning irradiation time indicates the increase in the concentration of $OH^{\cdot}$ during the photoreaction time course (Fig. 13).

4 Conclusion

In summary, carbon nanosphere supported $ZnSb_2O_6$ (CNSZSO) is a novel visible-light-driven photocatalyst synthesized hydrothermally using glucose and ZSO as precursors. ZSO is prepared by metathesis method using potassium antimony tartrate for the first time. These preparation methods are advantageous in terms of cost, energy, purity, and time. As prepared composites are characterized by XRD, FESEM, EDS, FT-IR, XPS, PL for studying their structural and morphological properties. FESEM indicates the presence of carbon nanospheres and further supported by EDS, FTIR, XPS. XRD reflects a slight shift of d-lines, indicating incorporation of a small amount of carbon into the lattice. The optical properties of the composite are investigated using UV–Vis DRS depicts expansion of the absorbance profile of CNSZSO in the visible region. Bandgap energies obtained from KM plots 2.96 and 1.48 eV for ZSO and CNSZSO respectively support the photodegradation percentages recorded against degradation of MV dye. CNSZSO could degrade 85% of the dye within 60 min. Reduction in degradation percentage in the presence of scavengers (BQ, AO and IPA) suggests the role of $O_2^{\cdot-}$, hole, $OH^{\cdot}$ free radicals in the abatement of the dye. The increase in activity is attributed to delay in electron–hole pair recombination, which is evident from PL spectra where the intensity of peak is reduced in case of CNSZSO indicating lower electron–hole pair recombination. In conclusion, we have successfully transformed UV light driven ZSO catalyst to visible light active by incorporating carbon nanospheres and observed remarkable enhancement in the photocatalytic activity.

Fig. 7 a Survey scans XPS of CNSZSO. High resolution XPS of b Zn 2p, c Sb 3d, d O 1s, e C 1s

Fig. 8 Absorption spectra of ZSO and CNSZSO

Fig. 10 Temporal changes in the MV concentration in presence and absence of catalyst (ZSO and CNSZSO)

Fig. 9 KM plots of ZSO and CNSZSO

Fig. 11 PL spectra of ZSO and CNSZSO

Fig. 12 Photodegradation of MV in presence of scavengers (IPA, BQ and AO) with CNSZSO

Fig. 13 Fluorescence spectra of visible light irradiated CNSZSO suspensions in 3 mM terephthalic acid ($\lambda_{\text{excitation}} = 320 \text{ nm}$) (arrow indicates the gradual increase of fluorescence signal with respect to irradiation time)

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Ravi G, Vithal M (2019) Ion exchange synthesis of Ag^+ incorporated LiAlO_2 and its application in photodegradation of organic dyes. *SN Appl Sci* 1:164
- Mandawat NK, Chouhan N, Sharma HS (2019) Nanocomposite Ag@AgCl/ZnO for efficient hydrogen generation through water splitting. *SN Appl Sci* 1:571
- Honarmand MM, Mehr ME, Yarahmadi M, Siadati MH (2019) Effects of different surfactants on morphology of TiO_2 and Zr-doped TiO_2 nanoparticles and their applications in MB dye photocatalytic degradation. *SN Appl Sci* 1:505
- Nishiyama S, Hattori T (2000) Electrical conductivity and thermoelectricity of ZnSb_2O_6 and $(\text{Zn}_{1-x}\text{M}_x)\text{Sb}_2\text{O}_6$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$) Ceramic. *J Ceramic Soc Jpn* 108(5):435–438
- Jang J, Kim S-J (2012) Photoelectrochemical properties of nanocrystalline Sb_2O_3 , MgSb_2O_6 , and ZnSb_2O_6 -based electrodes for dye-sensitized solar cells. *Jpn J Appl Phys* 51:10NE23
- Liu W, Lin P, Jin H, Xue H, Zhang Y, Li Z (2000) Nanocrystalline ZnSb_2O_6 : hydrothermal synthesis, electronic structure and photocatalytic activity. *J Mol Catal A Chem* 349:80–85
- Wu S, Li G, Zhang Y, Zhang W (2013) Surface photoelectric and visible light driven photocatalytic properties of zincantimonate-based photocatalysts. *Mater Res Bull* 48:1117–1121
- Arun Kumar N, Vijayaraghavan R (2014) Enhanced photocatalytic activity of nanocrystalline N-doped ZnSb_2O_6 : role of N doping, cation ordering, particle size and crystallinity. *RSC Adv* 4:65223–65231
- Dutta DP, Ballal A, Singh A, Fulekar MH, Tyagi AK (2013) Multifunctionality of rare earth doped nano ZnSb_2O_6 , CdSb_2O_6 and BaSb_2O_6 : photocatalytic properties and white light emission. *Dalton Trans* 42:16887–16897
- Singh J, Bhardwaj N, Uma S (2013) Single step hydrothermal based synthesis of $\text{M(II)Sb}_2\text{O}_6$ ($\text{M} = \text{Cd}$ and Zn) type antimonates and their photocatalytic properties. *Bull Mater Sci* 36:287–291
- Hu Y, Liu Y, Qian H, Li Z, Chen J (2010) Coating colloidal carbon spheres with CdS nanoparticles: microwave-assisted synthesis and enhanced photocatalytic activity. *Langmuir* 26:18570–18575
- Zhao W, Wang Y, Yang Y, Tang J, Yang Y (2012) Carbon spheres supported visible-light-driven CuO-BiVO_4 heterojunction: preparation, characterization, and photocatalytic properties. *Appl Catal B Environ* 115–116:90–99
- Wang G, Yu J (2008) Hydrothermal synthesis and photocatalytic activity of mesoporous titania hollow microspheres. *J Phys Chem Solids* 69:1147–1151
- Hislop KA, Bolton JR (1999) The photochemical generation of hydroxyl radicals in the UV-Vis/ferrioxalate/ H_2O_2 system. *Environ Sci Technol* 33:3119–3126
- Kurra S, Veldurthi NK, Reddy JR, Reddy CS, Vithal M (2016) A series of novel double perovskite oxides NaMTi_2O_6 ($\text{M} = \text{Eu}, \text{Sm}, \text{and Gd}$): preparation, characterization and photocatalytic studies under visible and solar light irradiation. *J Mater Sci Mater Electron* 27:4194–4200
- Michel CR, Contreras NLL, Lopez-Alvarez MA, Martinez-Preciado AH (2012) Gas selectivity of nanostructured ZnSb_2O_6 synthesized by a colloidal method. *Sens Actuators B* 171–172:686–690
- Wang W, Xu D, Cheng B, Yu J, Jiang C (2017) Hybrid carbon@ TiO_2 hollow spheres with enhanced photocatalytic CO_2 reduction activity. *J Mater Chem A* 5:5020–5029

18. Tang S, Tang Y, Vongehr S, Zhao X, Meng X (2009) Nanoporous carbon spheres and their application in dispersing silver nanoparticles. *Appl Surf Sci* 255:6011–6016
19. Li J, Du K, Lai Y, Chen Y, Zhang Z (2017) ZnSb_2O_6 : an advanced anode material for Li-ion batteries. *J Mater Chem A* 5:10843–10848
20. Wu W, Liang S, Ding Z, Zheng H, Wu L (2012) Low temperature synthesis of nanosized ZnNb_2O_6 photocatalysts by a citrate complex method. *J Sol Gel Sci Technol* 61:570–576
21. Yang L, Huang J, Shi L, Cao L, Zhou W, Chang K, Meng X, Liu G, Jie Y, Ye J (2017) Efficient hydrogen evolution over Sb doped SnO_2 photocatalyst sensitized by Eosin Y under visible light irradiation. *Nano Energy* 36:331–340
22. Peters K, Zeller P, Stefanic G, Skoromets V, Němec H, Kužel P, Fatkhova-Rohlfing D (2015) Water-dispersible small monodisperse electrically conducting antimony doped tin oxide nanoparticles. *Chem Mater* 27:1090–1099
23. Titirici MM (2013) Sustainable carbon materials from hydrothermal processes. Wiley, New York
24. Han C, Yang M-Q, Weng B, Xu Y-J (2014) Improving the photocatalytic activity and anti-photocorrosion of semiconductor ZnO by coupling with versatile carbon. *Phys Chem Chem Phys* 16:16891–16903
25. Raza W, Haque MM, Muneer M, Bahnmann D (2015) Synthesis of visible light driven TiO_2 coated carbonnanospheres for degradation of dyes. *Arab J Chem* 1:11. <https://doi.org/10.1016/j.arabj.2015.09.002>
26. Mamidi S, Ravi G, Kurra S, Velchuri R, Vithal M (2018) Aurivillius family of layered perovskites, BiREWO_6 (RE = La, Pr, Gd, and Dy): synthesis, characterization and photocatalytic studies. *C R Chim* 30:1–6

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