Materials Research Express

PAPER

Photocatalytic performance of ZnO carbon composites for the degradation of methyl orange dye

Prashant A Borade 1, Jagruti S Suroshe 2, Kashinath Bogale 3, Shivram S Garje 1,4 and Suhas M Jejurikar 1,4

1 National Center for Nanosciences and Nanotechnology, University of Mumbai, Vidyanyagari, Santacruz (East), Mumbai- 400 098, India
2 Department of Chemistry, University of Mumbai, Vidyanyagari, Santacruz (East), Mumbai- 400 098, India
3 School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, India
4 Author to whom correspondence should be addressed.

E-mail: jejusuhas@gmail.com

Keywords: ZnO, carbon spheres, composite materials, AACVD, photoluminescence

Abstract

High yield, low cost, environmentally friendly chemical bath synthesis process is used to produce submicron structures of ZnO and ZnO–carbon composites. Synthesis of ZnO rod structures (submicron sized) were confirmed using SEM images. To synthesis ZnO–carbon composites, well characterized carbon spheres produced using aerosol assisted CVD technique was used. Use of carbon spheres as a seed during synthesis of ZnO is observed to produce multipod structures of ZnO on to the surface of carbon spheres; the growth is explained by proposing suitable model. Room temperature photoluminescence spectra recorded for ZnO and ZnO–carbon composites synthesized show a systematic disappearance of a band-edge emission (sharp peak present at ~380 nm observed for pure ZnO) with increased number of carbon spheres. Competent photo-catalytic activity of synthesized composite is confirmed by studying photo degradation investigation performed using a model dye molecule i.e. methyl orange. The work reveals possibility to use synthesized composites as a nontoxic and biocompatible catalyst for fragmentation of a methyl orange dye molecule. Photo-degradation mechanism of a methyl orange dye is proposed herewith considering the role of carbon spheres and ZnO in presence of UV photon.

1. Introduction

Accessibility of clean and pure water has become a major issue due to the discharge of organic pollutants/ contaminants present into the rivers and the sea [1–3]. One of the major sources of water contamination is the often-uncontrolled growth of industrialization across the globe. Many industries/factories discharge their chemicals directly into the rivers without any due process. Such a discharge of toxic influencers into the water has seriously affected the environment and biodiversity in our river systems [4, 5]. In several countries, about ~17%–20% share of industrial water pollution comes from textile industries. At least 72 toxic chemicals related to textile dyeing have been detected in the river systems out of which ~30 chemicals cannot be treated/removed completely, a serious threat to people dependent upon these river systems [6, 7]. Several efforts have been made to address issue of water contamination caused by the textile industries [8, 9]. Photodegradation of a dye molecule has been attempted as this route is reliable, simple, and the cost effective [10–12]. In this method, the fragmentation of a dye molecule can be achieved using a photocatalysts material which is stimulated/activated mainly by electromagnetic radiation. Researchers have already demonstrated various types of photocatalysts used for dye molecule degradation [13], with the intension that a photocatalyst material synthesized must not be another source of water contamination. In this regard ZnO, a wide band gap (~3.37 eV) compound semiconductor has received special attention [14]. The attention is mainly due to the unique physical and chemical properties associated with ZnO [15]. Despite on many advantages for e.g. non-toxicity, biocompatibility as well as the ability to produce ZnO in bulk, its use as a photocatalyst material is restricted due to its photocatalytic efficiency [16, 17]. In order to increase the photocatalytic efficiency of ZnO researchers have
tried various methodologies which include, doping ZnO with various transition metals [18], forming nanostructures of ZnO with diverse morphology [19, 20] as well as forming its hybrid composites [21–23]. Above all hybrid composites synthesized using various carbon allotropes are marked to be very promising and hence received special attention [24–26]. Apart from various carbon allotropes, carbon spheres (CS) have generated significant interest due to their various applications. They are made up of number of concentric carbon layers, where CS having diameter less than 1000 nm are observed to have similar properties such as graphene and/or fullerene [27]. The CS can be used as a supporting template for synthesizing various composite materials due to its unique properties which mainly include high surface area, high structural stability and many other properties [28]. Hence it is interesting to understand the role of CS while synthesizing various nano composites metal oxides and their related applications in various fields [29].

The aim of this work is thus two fold. First we wanted to demonstrate a cost effective and environmental friendly chemical bath route for photocatalyst materials [30]. In doing so, we wanted to use CS templating for the synthesis of a composite material to act as a potential candidate in order to degrade textile dyes. Second, we wanted to fully characterize the fabricated composite and demonstrate the photocatalytic activity of synthesized composites by recording UV–visible spectra of a mixture of Z–CS and methyl orange dye molecule dispersed in deionized (DI) water exposed to UV light. From observed results the role of CS in Z–CS is claimed to provide/serve as electron scavenging center which can effectively reduce the excitonic recombinations associated with pure ZnO, resulting to improve the photocatalytic activity of composite material synthesized.

2. Materials and methods

In order to synthesize Z–CS composite material, CS were first synthesized using aerosol assisted chemical vapor deposition (AACVD) technique. Toluene was used as a precursor for CS synthesis and the reaction was carried at 1050°C in presence of nitrogen atmosphere using tubular furnace. The detailed experimental procedure synthesis of CS is reported elsewhere [31]. With prior structural and optical characterization CS synthesized were used for producing Z–CS composites by adopting ecofriendly chemical bath route [32]. For Z–CS synthesis, CS (varying weight as 10, 50, 100 and 300 mg respectively) were well dispersed in 50 ml DI water. Well dispersed CS solutions were added into 150 ml of zinc acetate solution prepared in DI water having 0.1 M under constant stirring conditions. The pH value of the mixture was then adjusted to 7.0 by adding appropriate quantity of 2 M NaOH solution. The reaction was allowed to continue for 2 h under constant stirring conditions, where temperature of the chemical bath was maintained at 80 °C. The final product was then rinsed repeatedly using DI water, methanol and finally dried at 100 °C for 2 h. The final product/precipitate was then characterized structurally, morphologically as well as optically using respective techniques which include x-ray Diffraction (Model: Bruker D8 Discover, Cu Kα radiation), Scanning Electron Microscopy (Model: FEI Quanta 250), Transmission Electron Microscopy (Model: FEI Tecnai g2), micro-Raman spectroscopy (Model: Renishaw spectrometer), UV-Visible spectroscopy (Model: Cary 5000 UV-Vis-NIR) and photoluminescence (PL) spectroscopy (Model: PC1 Spectrofluorimeter). In order to investigate the photocatalytic activity of synthesized composites towards dye molecule degradation experiments were planned using methyl orange dye. For this 10 mg of Z–CS (varying CS weight) composite each was added into 50 ml of aqueous solution methyl orange (10 ppm). The mixture was sonicated for 15 min and kept in dark for 30 min under steady stirring conditions to establish adsorption-desorption equilibrium between the photocatalyst and dye used. The mixture was then exposed to UV light (λ = 365 nm, Power 100 W; Light intensity at 104−8.5 mW cm−2) placed at a distance of 10 inch from the source to initiate the fragmentation/degradation of a dye molecule. In order to investigate the percentage of dye molecule degradation, 4–5 ml of specimen was extracted after every 15 min from the parent solution which is under UV exposure. The specimen was then centrifuged to remove photocatalyst and optically investigated using UV-Visible spectrometer to confirm the percentage of dye molecule degradation if any.

3. Results and discussion

Figure 1 present the structural and morphological investigations performed on CS using x-ray diffractogram (XRD) and Transmission electron microscope (TEM).

A strong peak positioned at ~25° observed in figure 1(a) confirms the presence of graphitic carbon [33]. From TEM image it is clear that the graphitic carbon has spherical shape sized in between 500–700 nm. Similarly growth of pure ZnO using chemical bath route was confirmed structurally as well as morphologically. Figure 2 present structural and morphological investigations performed on pure ZnO using XRD and SEM techniques. Peaks positioned at 2θ = 31°, 34°, 36°, 47°, 56°, 62°, 67° and 69° in x-ray diffractogram (figure 2(a)) confirms formation of single phase wurtzite ZnO [34]. From figure 2(b) growth of well isolated ZnO rods having length.
~1–2 μm can be seen. The ZnO rods are observed to have width within the range of ~200–300 nm at one end and ~250–400 nm at the other end. During synthesis (using aqueous solution of Zn(CH₃COO)₂) the OH⁻ ions (source aqueous NaOH) plays an important role to from Zn(OH)₂. Due to the alkaline nature of the solution, Zn(OH)₂ gets dissolve to form a single molecule of ZnO and/or to form growth unit (i.e. (Zn(OH)₄)₂⁻). A single molecule of ZnO formed within the chemical bath then acts as a seed crystal. Due to adsorption of a growth unit on its polar and non-polar faces, the crystal starts growing longer and larger. The growth mechanism responsible to produce ZnO rod type structures has been already discussed with details somewhere else [35].

Figures 3(a)–(d) show x-ray diffractogram recorded for Z-CS composites, where weight of CS was varied while synthesizing Z-CS composites. It is also clear from the diffractogram that formation of wurtzite ZnO is not getting hampered even though excess of CS are used while synthesizing Z-CS. To understand the exact role of CS while synthesizing Z-CS composites microscopic images were recorded using SEM and TEM techniques which are presented as figure 4. From SEM and TEM images multipod growth of ZnO is clear, most likely because of CS present during synthesis. It also reflect from figure 4 that formation of multipode structures of ZnO increases with increasing amount of CS used during Z-CS synthesis.

From figures 4(a)–(h) it is clear that CS is observed to be responsible in producing the multipod shaped Z-CS composite. We believe that CS used during synthesis may act as a seed. Evidences about excess of CS present in Z-CS for composite prepared with higher concentration CS (300 mg) can be seen in figures 4(g) and (h). Since we have proposed that CS play a vital role for the growth of Z-CS composite, herewith we intend to suggest a following model for observed the growth of multipod structures.
It is well accepted that the surface defects as well as nano pores present on any form of a graphitic carbon surface, may acts as a nucleation and/or active sites for subsequent growth [36, 37]. Presence of $-\text{OH}$ and C$=$O groups on the surface of CS make it hydrophilic in nature [38]. Herewith we propose that Zn$_2^+$ produced during synthesis of ZnO using an aqueous solution of Zn(CH$_3$COO)$_2$ can get coupled with such active sites especially where $-\text{OH}$ group is present due to the electrostatic interactions [32, 35, 39–41]. The Zn$^{2+}$ ions coupled at the surface of CS further reacts with the $\text{OH}^-$ ion present in the reaction solution to produce Zn(OH)$_2$ at the CS surface. Since reaction solution is weakly basic in nature: Zn$^{2+}$ produced at the surface of CS start dissolving to harvest a growth unit i.e. [Zn(OH)$_2$]$^{1-}$ and/or single molecule of ZnO (nuclei) at the CS surface. The ZnO nuclei thus formed at the CS surface then acts as a seed crystal to which the growth units incorporate at the polar surface of CS further reacts with the $\text{OH}$ group is present due to the electrostatic interactions [32, 35, 39–41]. The model has been presented as schematic 1.

Optical properties of pure ZnO, CS as well as Z-CS composites were investigated by recording PL and UV–vis spectra at room temperature. Figure 3 presents room temperature PL spectra recorded for each specimen.

Typical characteristic spectra i.e. presence of sharp emission in UV region ($\sim$380 nm) with a broad shoulder towards visible region is observed for pure ZnO synthesized [43]. The observed UV emission can be attributed to band-edge emission, whereas the emissions observed in visible range are due to deep-level defects present in ZnO rods synthesized [44]. PL spectra recorded using CS (figure 5(b)) show presence of a board band centered at $\sim$460 nm. Presence of typical emission observed confirm the presence of defects on the surface of CS as assumed. These surface defect actually acts as energy traps, contributing radiative recombination of excitons [45–47]. The PL spectra recorded for Z-CS composites (figures 5(c)–(f)) varying CS concentration show presence of UV emission (i.e. $\sim$380 nm) along with broad band present in the visible region (i.e. $\sim$460 nm). Visible broad band is observed to increase with increase in concentration of CS in the Z-CS composite. The Z-CS composite with high concentration CS show prominent decrease in the relative intensity ratio of UV and visible peak emission. Considering Z-CS system as heterojunction system, formation of space charge region became obvious phenomenon. Formation of such region are responsible to suppress the recombination rate of photogenerated electron–hole pair, resulting in decrease of intensity ratio of UV and visible peak emission as observed [48].

Figure 3 presents X-ray diffractogram for Z-CS composites where CS composition was varied a.s. (a) 10, (b) 50, (c) 100 and (d) 300 mg.

It is well accepted that the surface defects as well as nano pores present on any form of a graphitic carbon surface, may acts as a nucleation and/or active sites for subsequent growth [36, 37]. Presence of $-\text{OH}$ and C$=$O groups on the surface of CS make it hydrophilic in nature [38]. Herewith we propose that Zn$_2^+$ produced during synthesis of ZnO using an aqueous solution of Zn(CH$_3$COO)$_2$ can get coupled with such active sites especially where $-\text{OH}$ group is present due to the electrostatic interactions [32, 35, 39–41]. The Zn$^{2+}$ ions coupled at the surface of CS further reacts with the $\text{OH}^-$ ion present in the reaction solution to produce Zn(OH)$_2$ at the CS surface. Since reaction solution is weakly basic in nature: Zn$^{2+}$ produced at the surface of CS start dissolving to harvest a growth unit i.e. [Zn(OH)$_2$]$^{1-}$ and/or single molecule of ZnO (nuclei) at the CS surface. The ZnO nuclei thus formed at the CS surface then acts as a seed crystal to which the growth units incorporate at the polar surface of CS further reacts with the $\text{OH}$ group is present due to the electrostatic interactions [32, 35, 39–41]. The model has been presented as schematic 1.

Optical properties of pure ZnO, CS as well as Z-CS composites were investigated by recording PL and UV–vis spectra at room temperature. Figure 3 presents room temperature PL spectra recorded for each specimen.

Typical characteristic spectra i.e. presence of sharp emission in UV region ($\sim$380 nm) with a broad shoulder towards visible region is observed for pure ZnO synthesized [43]. The observed UV emission can be attributed to band-edge emission, whereas the emissions observed in visible range are due to deep-level defects present in ZnO rods synthesized [44]. PL spectra recorded using CS (figure 5(b)) show presence of a board band centered at $\sim$460 nm. Presence of typical emission observed confirm the presence of defects on the surface of CS as assumed. These surface defect actually acts as energy traps, contributing radiative recombination of excitons [45–47]. The PL spectra recorded for Z-CS composites (figures 5(c)–(f)) varying CS concentration show presence of UV emission (i.e. $\sim$380 nm) along with broad band present in the visible region (i.e. $\sim$460 nm). Visible broad band is observed to increase with increase in concentration of CS in the Z-CS composite. The Z-CS composite with high concentration CS show prominent decrease in the relative intensity ratio of UV and visible peak emission. Considering Z-CS system as heterojunction system, formation of space charge region became obvious phenomenon. Formation of such region are responsible to suppress the recombination rate of photogenerated electron–hole pair, resulting in decrease of intensity ratio of UV and visible peak emission as observed [48].

Figure 3 presents X-ray diffractogram for Z-CS composites where CS composition was varied a.s. (a) 10, (b) 50, (c) 100 and (d) 300 mg.
composites the intensity of $E_{2}^{2\text{High}}$ mode is observed to decrease while, the intensity of G band is observed to increase. These result thus support the possible interaction of ZnO with CS forming relevant composite as mentioned earlier.

Photocatalytic activities associated with pristine ZnO and CS using methyl orange dye were investigated by recording UV–vis spectra in absorption mode. For this respective mixtures were exposed to constant UV light

Figure 4. SEM and TEM images (respective SAD patterns are shown as inset) of Z–CS composites synthesized by varying CS amount as (a) and (b) 10, (c and d) 50, (e) and (f) 100 and (g) and (h) 300 mg.
Schematic 1. Model presenting growth of Z-CS composite.

Figure 5. Room temperature PL spectra of (a) ZnO, (b) CS and (c)–(f) for Z-CS composites varying the composition of CS.

Figure 6. Arrhenius plot for ZnO and Z-CS composites.
where changes linked with dye concentration were determined by recording UV–vis spectra at some time intervals (presented as figure 8). From figure 8(a) the photocatalytic activity of pristine ZnO is observed to be \(\sim 56\%\) while, no such activity is observed in the case of pristine CS (figure 8(b)). Figure 8(c) presents blank test performed on 50 ml of aqueous solution of methyl orange (10 ppm), which confirms absence of dye molecule degradation due to UV source used.

Similar investigation (figure 9) were performed using mixture of methyl orange and Z-CS composites in order to investigate the photocatalytic response. As compare with other Z-CS composites, it is observed that the composite synthesized using concentration of CS \(\sim 100\) mg (figure 9(c)) show the highest degradation efficiency.
(i.e. ~87%). Only ~25% degradation efficiency recorded in case of Z-CS composite synthesized using concentration of CS ~300 mg is very surprising. This can be due to high amount of unreacted CS observed in the composite material, which are observed to embed ZnO rods blocking their active faces (i.e. polar surface), giving rise to scattering phenomenon [57].

Figure 10 present the plot of ln (C0/Ct) Vs time extracted from figures 8 and 9 i.e. photocatalytic activity recorded for ZnO and Z-CS composites at different amount. From figure 10 it is clear that the degradation studied follows the pseudo first-order kinetics [58, 59]. The reaction rate concentration extracted from each plots are listed as table 1.

Figure 11 present the graph for Methyl Orange dye degradation using various ZnO based photocatalysts in comparison with our results (especially for Z-CS 100 composite). From the graph it is clear that the result obtained using environment friendly Z-CS composites are promising candidate for dye molecule degradation. The photocatalytic degradation of a dye molecule involves generation of free radicals followed by oxidization of a dye molecule leading towards its fragmentation [60]. Considering the mentioned fact herewith we propose a mechanism which can explain degradation of a dye molecule using Z-CS composite.

The metastable plane (i.e. polar face) of ZnO where, presence of high concentration defects such as $V_{Zn}$, $Zn_{Zn}$ (acting as donors), $V_{O}$, $O_{Zn}$ (acting like acceptors), free electrons as well as surface defects are predominant and are treated to be chemically active [65, 66]. When the dye solution (i.e. methyl orange in DI water) comes in contact with the metastable plane of ZnO, enough energy is provided via quasi-one dimensional dynamics to water molecule to repeatedly associate and dissociate the molecule producing OH$^-$ species [67–69].

Parallel to this under continuous UV expose, ZnO present in the mixture (Z-CS composite + methyl orange + DI water) undergoes photo emission process [70, 71]. As shown in the schematics (figure 12) during excitation and de-excitation process the transfer of electrons from the valance band to conduction band and from there to various defect levels becomes an obvious phenomenon. Further accepting formation of Z-CS composite; it is anticipated that electrons from conduction band of ZnO can migrate to CS to achieve Fermi level ($E_f$) equilibrium. Parallel to this when the mixture is exposed to constant UV radiations, migration of electrons
Figure 10. Plot of degradation rate for ZnO and Z-CS composite.

Table 1. Photocatalyst degradation rate extracted for ZnO and Z-CS composite containing different amount of CS.

| Specimen | Regression Coefficient \((R^2)\) | Rate Constant \((\text{min}^{-1})\) | (%) Efficiency |
|----------|----------------------------------|----------------------------------|---------------|
| ZnO      | 0.90516                          | 0.00424                          | 56            |
| ZCS 10   | 0.92472                          | 0.00511                          | 61            |
| ZCS 50   | 0.94845                          | 0.0053                           | 63            |
| ZCS 100  | 0.98417                          | 0.01012                          | 87            |
| ZCS 300  | 0.97401                          | 0.0015                           | 25            |

Figure 11. Graph indicating methyl orange dye degradation using various ZnO based photocatalysts in comparison with our result [61–64].
from CS to various defect levels of ZnO are also expected. Under these continuous electron migration processes conversion of O$_2^-$ (present at the polar face of ZnO) to superoxide (i.e. O$_2^{*-}$) is proposed. Similarly the holes produced at the valence band of ZnO during the excitation process may react with OH$^-$ species (origin as discussed before) to convert it into super-hydroxyl (OH$^{*-}$) radical. Highly unstable species (i.e. O$_2^{*-}$ and OH$^{*-}$) generated then react with methyl orange dye molecule and are solely responsible for fragmentation of the dye molecule.

4. Conclusion

Simple and environmental friendly chemical bath route is demonstrated for the synthesis ZnO-Carbon (Z-CS) composites. Structural, microscopic and optical properties of synthesized materials were investigated using respective techniques. Photocatalytic activity of said materials were evaluated in order to study dye molecule degradation under constant UV expose. The Z-CS composites synthesized using CS concentration as 100 mg is observed to exhibit higher photocatalytic activity (i.e. 87%) as compare with the other composites synthesized. Generation of highly unstable species i.e. O$_2^{*-}$ and OH$^{*-}$ at the polar face of ZnO due to various migration process of electrons is proposed. The unstable species generated are then suggested to reacts with methyl orange dye molecule leading towards its degradation. This study may explore the synthesis of low cost photocatalyst and understanding their photocatalytic mechanism for effective energy and environmental application.

ORCID iDs

Kashinath Bogale  https://orcid.org/0000-0001-9472-3696
Suhas M Jejurikar  https://orcid.org/0000-0002-5315-7621

References

[1] Wang Y, Tang X, Chen Y, Zhan L, Li Z and Tang Q 2009 J. Hazard. Mater. 172 30
[2] Houas A, Lachheb H, Ksibi M, Elaloui E, Guillard C and Herrmann J M 2001 Appl. Catal. B 31 145
[3] Khraisheha M A M, Al-Ghoutib M A, Allenb S J and Ahmad M N 2005 Water Res. 39 922
[4] Kudo A and Miseki Y 2009 Chem. Soc. Rev. 38 253
[5] Purkait M K, Kumurb V D and Maity D 2009 Chem. Eng. J. 151 275
[6] Kant R 2012 Natural Science. 4 22
[7] Hazardous Substance Research Centers/South and South-West Outreach Program 2005 Environmental hazards of the textile industry Environmental Update # (Washington DC, USA: Business Week) https://cfpub.epa.gov/ncer_abstracts/index.cfm?fuseaction/display.abstractDetail/abstract/5345/report/0 24Environmental Update#
[8] Qiu M, Jian Q, Yu D and Feng K 2010 Desalination and Water Treatment 24 61
[9] Slimani R, Anouzla A, Abrouki Y, Ramli Y, Antri S E, Mamouni R, Lazar S and Haddad M E 2011 J. Mater. Environ. Sci. 2 77 https://www.jmaterenvironsci.com/Document/vol2/10-IMES-58-2011-EP%20Haddad.pdf
[10] Galindo C, Jacques P and Kalt A 2000 J. Photochem. Photobiol., A 130 35
[11] Chen C, Ma W and Zhao J 2010 Chem. Soc. Rev. 39 4206
[12] Ghasabab S, Atai M and Imani M 2017 Mater. Res. Express 4 035010
[13] Min Y, Zhang K, Chena Y and Zhanga Y 2011 Chem. Eng. J. 175 76
[14] Lia C, Hana C, Zhang Y, Zanga Z, Wanga M, Yang X and Dua J 2017 Sol. Energy Mater. Sol. Cells 172 341

Figure 12. (a) Quantitative electronic band structure for ZnO/CS system and (b) schematic presentation of a dye molecule degradation process.
[15] Bagannah D M, Chen Y F, Zhu Z y and Yao T 1998 Appl. Phys. Lett. 73 1038
[16] Fu D, Han G, Chang Y and Dong Y J 2012 Mater. Chem. Phys. 132 673
[17] Liua Y, Hua Y, Zhoua M, Qiana H and Hub X 2012 Appl. Catalysis B 125 425
[18] Schelonka D, Tolasz J and Stengl V 2015 Photochem. Photobiol. 91 1071
[19] Yuan H and Zhang Y 2004 J. Cryst. Growth 263 119
[20] Sheng X and Zhong W L 2011 Nano Res. 4 1013
[21] Worathitianon C, Jangrubol K, Ruengrung P, Donphai W, Chanlek N, Prasitchoke P and Chareonpanich M 2019 Appl. Catalysis B 241 359
[22] Yua W, Zhang J L and Peng T 2016 Appl. Catalysis B 181 220
[23] Danwittayakul S, Saisa M and Dutta J 2015 Appl. Catalysis B 163 1
[24] Su F, Zhao X S, Wang Y, Wang L and Lee S J 2006 J. Mater. Chem. 16 4413
[25] Byrappa K, Subramani A K, Amuda S, Lokanatha Rai K M, Sunita M H, Basavalingu B and Soga K 2006 J. Mater. Sci. 41 1355
[26] Yu H, Zhang H, Huang H, Liu Y, Li H, Ming H and Kang Z 2012 New J. Chem. 36 1031
[27] Li Z, Liu Z, Sun H and Gao C 2015 Chem. Rev. 115 7046
[28] Mao H, Chen X, Huang R, Chen M, Yang R, Lan P, Zhou M, Zhang F, Yang Y and Zhou X 2018 Sci. Rep. 8 9501
[29] Krishnamurthy G, Nair D and Agrawal S 2014 Precedia Materials Science. 5 1056
[30] Lee J, Easteal A, Pal U and Bhattacharyya D 2009 Curr. Appl. Phys. 9 792
[31] Samant K M, Surose I S and Garde S S 2014 Eur. J. Inorg. Chem. 3 499
[32] Borade P, Joshi K U, Gokarna A, Lorondel G and lejurikar S M 2016 Nanotechnology 27 8
[33] JCPDS File No. 75-1621
[34] JCPDS File No. 036-1431.
[35] Borade P, Joshi K U, Gokarna A, Lorondel G, Walke P, Late D and Jejurikar S M 2016 Mater. Chem. Phys. 169 152
[36] Sun X, Yadong L and Angew. L 2004 Chem. Int. Ed. 43 597
[37] Kang Z C and Wuz P L 1997 J. Mol. Catal. A: Chem. 118 213
[38] Hu Y, Liu Y, Qian H, Li J Z and Chen J 2010 Langmuir 26 18570
[39] Han M, Yin X, Ren S, Duan W, Zhang L and Cheng L 2016 RSC Adv. 6 6467
[40] Kim K M, Choi M H, Lee J E, Jeong J, Kim Y R, Kim M K, Pack S M and Oh J M 2014 Int. J. Nanomed. 9 41
[41] Mi Y, Hu W, Dan Y and Liu Y 2008 Mater. Lett. 62 1194
[42] Wander A and Harrison N M 2000 Surf. Sci. 468 851
[43] Janotti A and VandeWalle C G 2009 Rep. Prog. Phys. 72 126501
[44] Willander M, Nur O, Sadaf J R, Qadir M I, Zaman S, Zainelabdin A, Bano N and Hussain I 2010 Materials. 3 2643
[45] Bao L, Zhang Z L, Tian Z Q, Zhang L, Liu C, Lin Y, Qi B and Pang D 2011 Adv. Mater. 23 3801
[46] Minati L, Speranza G, Bernagozzi I, Torrengo S, Toniutti L, Rossi B, Ferrari M and Chiasera A 2010 J. Phys. Chem. C 114 11068
[47] Hu S H, Niu K Y, Sun J, Yang J, Zhaoa N Q and Du X W 2009 J. Mater. Chem. 19 484
[48] Dong S, Li Y, Sun J, Yu C, Li Y and Sun S 2014 Mater. Chem. Phys. 145 357
[49] Arguello C A, Rquisseau D L and Porto S P S 1969 Phys. Rev. B 181 1351
[50] Calleja J M and Cardona M 1977 Phys. Rev. B 16 3753
[51] Damen T C, Portq S P S and TdB B 1966 Phys. Rev. B 142 570
[52] Jeong T S and Youn C J 2006 J. Korean Phys. Soc. 49 1510 https://www.iwps.or.kr/journal/view.html?iuid=80226&vmd=Full
[53] Wei R and Gong H 2009 ECS Trans. 19 129
[54] Serrano I, Manjon F J, Romero A H, Widolte F, Lauk R and Cardona M 2003 Phys. Rev. Lett. 90 055510
[55] Subrahmanyan K S, Vivekchand S R C, Govindaraj A and Rao C N R 2008 J. Mater. Chem. 18 1517
[56] Miyata Y, Mizuno K and Kataura H 2010 J. Nanomater. 2011 786763
[57] Yang H M and Park S J 2017 Mater. Chem. Phys. 186 261
[58] Surose J, Mlowe S, Garje S and Revaprasad N 2018 J. Inorg. Organomet. Polym. Mater. 28 603
[59] Li H, Wang G, Zhang F, Cai Y, Wang Y and Djerd J 2012 RSC Adv. 2 12413
[60] Govender K, Boyle D S, Kenway P B and Brien P O 2004 J. Mater. Chem. 14 2575
[61] Lee K, Lai C, Ngi K and Juan J 2016 Water Res. 88 428
[62] Kumar R, Kumar G and Umar A 2014 Nanoscience and Nanotechnology Letters. 6 631
[63] Mohammad A, Kapoor K and Mobin S 2016 ChemistrySelect. 1 3483
[64] Junseja S, Madhavan A, Ghosal A, Moulick R and Bhattacharyya J 2018 J. Hazard. Mater. 347 378
[65] Wang Z L, Kong X Y and Zuo J M 2003 Phys. Rev. Lett. 91 185502
[66] She G, Zhang X, Shi W, Fan X and Chang J C 2007 Electrochem. Commun. 9 2784
[67] Meyer B, Rababa H and Marx D 2006 Phys. Chem. Chem. Phys. 8 1513
[68] Calzolari A and Catelani A 2009 J. Phys. Chem. C 113 2896
[69] Yan Y and Al-Jassim M M 2005 Physical Review B. 72 235305
[70] Music S, Saric A and Popovic S 2008 J. Alloys Compd. 483 277
[71] Monticone S, Tufeu R and Kanaev K V 1998 J. Phys. Chem. B 102 2854