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Development of $Zn_{1-x-y}Ga_xCo_yO_{1-z}N_z$ as a non-oxide semiconductor material with visible light photoelectrochemical activity

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ABSTRACT

The recognition of photocatalysis as a promising approach for green energy generation and environmental pollution degradation has resulted in the emergence of a large number of semiconductor materials as photocatalyst. Here we introduce a non-oxide compound, $Zn_{1-x-y}Ga_xCo_yO_{1-z}N_z$ oxynitride synthesized by solution combustion technique for application as visible light photocatalyst. The structural, microstructural, spectroscopic and photoelectrochemical studies of the samples are demonstrated. The wurtzite structured sample possessed bandgap of 2.76 eV allowing absorption in visible region of spectra which is explained using Valence Band XPS studies. The photoelectrochemical studies on the samples revealed a photo-anodic behavior with total half-life of trap states significantly reduced compared to some conventional photocatalyst materials.

1. Introduction

Wide band gap metal oxide semiconductors have been recognized as potential candidates for photocatalytic application due to their high catalytic activity, photostability, oxidative capacity and easy availability. Even though majority of the metal oxides possess a bandgap greater than 3 eV limiting their activity in UV- Vis region, it is possible to tune the emission by doping with transition metal (TM) ions like Co, Mn, Ni and Fe and tailor its optical and luminescent properties [1]. Doping can modify the optical absorption of zinc oxide by introducing new defect energy levels which can influence the photocatalytic activity to a large extent [2]. Among various TM dopants, Co has been considered to be one of the most effective species to tailor the electronic and optical properties of zinc oxide, since Co^{2+} ions do not affect the lattice structure of zinc oxide and also provides abundant electronic states [3,4]. Co doping produces a significant red shift in the band gap of zinc oxide and also provides oxygen vacancies which can enable the efficient separation of photogenerated charge carriers there by favoring photocatalytic activity [5]. Even though Co doped ZnO has been successfully used in photocatalytic applications, the risk of defect sites arising with doping which acts as recombination centres for photogenerated charge carriers still prevails. The bandgap narrowing by a modification of the valence band structure is assumed to be more efficient for photocatalytic performance. The highly positive valence band energy of metal oxides hence demands its replacement by non-oxide catalyst. β- Ge_3N_4 emerged as the first non-oxide semiconductor photocatalyst, which has activity under UV region of spectra. Since then the development of non-oxide photocatalysts with visible light activity has gained interest. In the present work we report the synthesis of $Zn_{1-x-y}Ga_xCo_yO_{1-z}N_z$ oxynitride by inexpensive solution combustion method. This oxynitride sample is expected to possess a bandgap less than 3 eV, being active in visible region of spectra. The valence band of the oxynitride is assumed to be composed of N2p-O2p orbitals partially overlapping Zn3d orbitals, hence resulting in p-d repulsion which is attributable to the anticipated reduction in bandgap. A systematic investigation of structural, microstructural and spectroscopic properties of the oxynitride has been carried out. We also demonstrate the photocatalytic performance by photoelectrochemical measurements.

2. Materials and methods

A solution combustion technique has been employed for the synthesis of the oxynitride, which is an easy, cost effective and low temperature technique as compared to traditional nitridation technique used for oxynitride synthesis. While nitridation method involves high temperature (~900 °C), NH_3 as nitrogen fuel and longer reaction time

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(5–15 h), solution combustion offers a simpler route. The reaction temperature is limited to 500 °C and takes place within 15 min. Urea acts as the fuel and nitrogen source and doesn't involve any toxic by-products. Zinc nitrate hexahydrate (99.9%), Gallium Nitrate (99.9%) and Cobalt Nitrate (99.9%) were used as metal precursors with urea as fuel. Urea/oxidizer ratio was fixed as 5. The molar ratio of (Zn + Co)/Ga was fixed to be 20. For sample ZGC1, the precursors used were Zn $(NO_3)_2.6H_2O$ (5.91 g), $Ga(NO_3)_3$ (0.25 g), $Co(NO_3)_2{\cdot}6H_2O$ (0.029 g) and urea (6.305 g). For sample ZGC5, the precursors used were Zn $(NO_3)_2.6H_2O$ (5.79 g), $Ga(NO_3)_3$ (0.25 g), $Co(NO_3)_2$ (0.15 g) and urea (6.305 g). Required amount of precursors were dissolved in 5 mL distilled water and the solution was inserted in a muffle furnace maintained at 500° C [6,7]. An ignition and combustion follows and the reaction is completed in ~15 min, yielding samples in the form of fluffy powder. Structural properties of as prepared samples were determined by powder X Ray Diffraction using PAN analytical X'Pert Powder XRD system. The elemental analysis of the samples were done by Energy dispersive X-ray spectroscopy (EDAX) (Carl Zeiss). Transmission electron microscopy studies were carried out to understand the morphology of samples using Carl Zeiss LIBRA 200HR. The core levels and valence band offset of samples were examined using X-ray photoelectron spectroscopy (Omicron, Germany). Room temperature Photoluminescence spectroscopy was carried out at an excitation wavelength of 325 nm using Jobin Yvon spectrophotometer. Raman spectroscopic studies for a temperature range of 83 K–273 K was recorded on a micro Raman spectrometer (Renishaw make, UK inVia) with a laser excitation of 514 nm. Photoelectrochemical studies were carried out on drop casted thin films of the samples on ITO substrate, immersed in a 0.5 M Na_2SO_4 solution in three necked quartz vessel with Pt as counter electrode and Ag/AgCl as the reference electrode using Metrohm-Autolab model PGSTAT302N under UV-vis irradiation of 10 mW/cm^2 intensity.

3. Results and discussions

3.1. Structural and micro-structural analysis

The structure and phase analysis of as prepared samples showed pronounced diffraction peaks corresponding to the wurtzite structure without any additional phase indicating that the Zn, Ga and Co ions are incorporated in a wurtzite crystal structure without creating any secondary phases corresponding to their oxides. The peaks were indexed by comparing with ZnO peak positions, since ZnO forms the major component of the oxynitride [JCPDS Card No: 01-076-0704]. The mean crystallite size estimated by applying Scherrer formula to all the XRD peaks, ranges between 35 and 63 nm, with an average size of 46 nm and showed no particular trend with the dopant level. The ratio of the unit cell axes (c/a) was found to be ~1.6, a characteristic of hexagonal wurtzite structure with an average cell volume of 47.62 Å^3. The quantitative analysis of samples has been carried out using Energy Dispersive X-ray spectroscopy. The chemical formula for as prepared samples could be expressed as ($Zn_{0.96}Ga_{0.036}Co_{0.004}O_{0.92}N_{0.08}$), and ($Zn_{0.95}Ga_{0.037}Co_{0.013}O_{0.92}N_{0.08}$), which will henceforth be named as ZGC1 and ZGC5 respectively (see Fig. 1).

Microstructural study by HRTEM reveals nanoparticles with diameters ranging from 33 nm to 72 nm and average crystalline size of 45 nm which is corroborated by the values estimated from Scherrer formula. The electron diffraction rings are indexed to prominent diffraction peaks and the (100) plane orientation of the crystal structure is well identified in the image (Fig. 2 a–d).

3.2. Diffuse reflectance spectroscopy and photoluminescence

The bandgap of as prepared samples, estimated using Kubelka – Munk function, is found to be 2.76 eV (ZGC1), as evidenced from Fig. 3a, lower than that of wide band gap of zinc oxide (3.37 eV) and GaN (3.4 eV) [8]. It could be seen that the onset of absorption varies slowly with Co content in the samples. It has been reported that Co doping in ZnO results in the modification of band gap due to sp-d exchange interaction between band electrons and localized Co^{2+} d electrons [9]. It also introduces new levels just below conduction band which results in a downshift of conduction band minimum contributing to the reduction of band gap. However, further lowering of CB, upon increasing the Co content, can adversely affect the photocatalytic activity of the samples as the conduction band minimum should remain at a more negative potential than the reduction potential of H^+/H_2.

Photoluminescence spectra of the samples (Fig. 3b) exhibit near band edge emission (NBE) around 375 nm along with emissions at 404 nm, 432 nm and 460 nm. The violet emission at 404 nm is attributed to the transition from oxygen-vacancy related shallow donor level to valence band. The blue emission at 432 nm is attributed to transitions from Zn_i (Zn interstitial) to the valence band as well as to the transitions from the bottom of the conduction band to the O_i (O interstitial) level [5].

To study the photocatalytic activity of as synthesized samples, organic dye degradation was performed using 5 ppm methylene blue dye under direct sunlight for 3 h. UV absorption spectra of the degraded samples revealed higher photo-degradation of methylene blue by ZGC1(Fig. 3c). This is due to the fact that ZGC1 exhibited a lower band gap along with low cobalt content prompting us to use the sample for further characterization. A schematic representation of the position of energy levels of the sample is expressed in Fig. 3d.

3.3. Raman spectroscopy

Raman spectroscopy studies were performed to detect any lattice disorder in the host site (Fig. 4). The zinc oxide rich oxynitride has a wurtzite structure belonging to space group $P6_3mc$. Theoretical studies predict the existence of optical modes which could be represented as $\Gamma_{opt} = A1 + 2B1 + E1 + 2E2$ where B1 modes are silent [10]. E_2 modes (E_2 high and E_2 low) are Raman active, whereas A1 and E1 polar modes are both Raman and IR active and splits to transverse (TO) and longitudinal (LO) modes due to macroscopic electric fields of LO phonons. The formation of the solid solution considerably reduces the intensity of E_2 high mode appearing at 437 cm^{-1}, which is the characteristic wurtzite vibrational mode of zinc oxide [6]. The E_2 high mode for ZGC1 does not undergo a significant shift as compared to zinc oxide, due to the fact that it originates from the vibration of oxygen species and cationic substitution has no significant affect on it [11]. The vibrational mode at 581 cm^{-1} with a shoulder at 595 cm^{-1}corresponds to a mixed A1LO (574 cm^{-1}) and E1LO (591 cm^{-1}) mode of $ZnO_{(1-x)}N_{(x)}$ [12]. Zn–N related mode appearing at 510 cm^{-1} for solid solution blue shifts to 513 cm^{-1} in the oxynitride sample [12]. For the single phase solid solution, the peak observed at 270 cm^{-1} is blue shifted to 279 cm^{-1} in the sample and is attributed to Ga-O-Zn bond formation [13]. The peak at 643 cm^{-1} is attributed to O-Zn-O bond for ZGC1 sample.

Temperature dependent Raman spectra from room temperature down to liquid nitrogen temperature show a decreasing full width at half maximum (FWHM) of the active modes. No additional modes are observed at low temperatures. The FWHM of Raman lines is proportional to inverse of phonon life time and the temperature dependence of FWHM is governed mainly by the change in phonon occupation numbers and anharmonic force constants. The increasing FWHM with temperature indicates decrease in the phonon life time due to the decay of strongly interacting optical phonons to weakly interacting low energy phonons [14].

3.4. X-ray photoelectron spectroscopy

XPS analysis of sample ZGC1 was carried out to investigate the oxidation state of the components present (Fig. 5). The peaks corresponding to Zn2p level is located at 1022.1 eV and 1045.1 eV for 2p3/2 and 2p1/2 respectively, with energy difference of 23 eV, indicating the