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Cobalt doped antimony oxide nano-particles based chemical sensor and photo-catalyst for environmental pollutants

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ABSTRACT

Cobalt doped antimony oxide nano-particles (NPs) have been synthesized by hydrothermal process and structurally characterized by utilizing X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and Fourier transforms infrared spectrophotometer (FT-IR) which revealed that the synthesized cobalt antimony oxides ($CoSb_2O_6$) are well crystalline nano-particles with an average particles size of 26 ± 10 nm. UV–visible absorption spectra (~286 nm) were used to investigate the optical properties of $CoSb_2O_6$. The chemical sensing of $CoSb_2O_6$ NPs have been primarily investigated by I–V technique, where dichloromethane is used as a model compound. The analytical performance of dichloromethane chemical sensor exhibits high sensitivity ($1.2432\ \mu A\ cm^{-2}\ mM^{-1}$) and a large linear dynamic range ($1.0\ \mu M$–0.01 M) in short response time (10 s). The photo catalytic activity of the synthesized $CoSb_2O_6$ nano-particles was evaluated by degradation of acridine orange (AO), which degraded 58.37% in 200 min. These results indicate that $CoSb_2O_6$ nano-particles can play an excellent research impact in the environmental field.

1. Introduction:

Nano-science and nanotechnologies are getting valuable attention in the field of research and development at the present time. In the field of nanotechnology, the metal-metal oxides (MM_xO_x) nanoparticles appear as a challenging prospect due to having amazing synthesis, characterization, and fabrication as well as their wide range of applications. The synthesis of nano-particles has received remarkable attention in view of the size, shape, structural arrangement, properties and potential applications in advance level. Metal oxides nano-particles have wide range of applications e.g. sensors, batteries, photoluminescence etc. [1–4].

Semiconductor materials have played a potential role as promising host material for transition doped materials and have attracted insightful research exertion due to their excellent properties and multidimensional applications [5,6]. Recently, a broad research has been made on the advancement of doped nano-materials by both basic sciences and potential sophisticated technologies. It has been discovered that numerous dopants such as Cr, Co, Si, Mn, Mg, Cu, Fe, In, Al, and Ga) can enhance the surface area of metal oxide nanostructure. These dopants alleviated the surface and encouraged the decrease in size as well as change the orientation, shapes and morphologies of the nano-materials. Doping of nano-materials can also improve their physical and chemical properties such as resistivity, diffuse reflectivity and chemical sensing properties. Doped nanomaterials, large band-gap material are conductive in natures which are due to the formation of oxygen vacancies and tin interstitials in nano-materials. These oxygen vacancies and tin interstitials readily form in nano-materials because of its low energy formation and resulting in the conductivity of doped nano-materials. These dopants can enhance the conductivity, electrical and especially sensing and catalytic properties of the nonmaterial which plays a vital role in environmental applications which has beneficial effects on human health [7,8].

The soil, water and air pollutants are heavy metals, solvents, hydrocarbons, volatile organic compounds, chemical waste, carbon monoxides, sulfur oxide, nitrogen dioxide, airborne particles, ozone, and radioactive. All these pollutants and fossil fuel are cause for environmental pollution which affects humans, animals, trees and plants [5,8]. Environmental pollution has received considerable attention due to their harmful effect on human health and living

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organisms. The industrial progress causes several severe environmental problems by releasing wide range of toxic compound to the environment. Thousands of hazardous waste locations have been produced worldwide consequential from the accumulation of xenobiotics in soil and water over the years. Monitoring of environmental pollution is therefore one of the most important needs for selecting pollution controlling option. A present demand is how to control the environmental pollutants or organic pollutants. Sensor technology and photo-catalysis plays an important role in environmental safety that normally caused by environmental pollution and accidental leakage of hazardous chemicals which is a big threat for environment [5,8].

Dichloromethane chemical is toxic, inhalation hazardous, skin irritant, and may cause of cancer of pancreas, liver and lungs [9]. It is challenge to detect the hazardous chemical like dichloromethane to protect the environmental pollution which is harmful for human and surrounding. Electrochemical sensors have gained great attention in the detection and determination of risky compounds because of their simple and fast operation, response and detection. The metal oxides have been studies as a chemical sensor to detect the hazardous chemicals. Metal oxides have proven their self a representative resource for chemical sensing to detect hazardous chemicals. Photo-catalytic degradation is a method of treatment of wastewater in presence of metal oxides. This is a thrilling choice for the detoxification of organic pollutants which help to cleanse common toxins from our surrounding [1–4].

In this research, $CoSb_2O_6$ nano-particles were synthesized and characterized by FE-SEM, XRD, FT-IR, and UV. Further we aimed to investigate applications of $CoSb_2O_6$ nano-particles as a novel electrochemical sensor material for the detection of dichloromethane and an active photo-catalyst for the degradation of acridine orange. $CoSb_2O_6$ nano-particles exhibited excellent performance in terms of chemical sensing and photo-catalytic activities.

2. Experimental details

2.1. Materials

Cobalt chloride ($CoCl_2$), antimony chloride ($SbCl_3$), ammonium hydroxide, acridine orange, butyl carbitol acetate, ethyl acetate and dichloromethane were purchased from Sigma–Aldrich. All reagents used were of analytical grade. Doubly distilled water was used in synthesis.

2.2. Preparation of $CoSb_2O_6$ nano-particles

Cobalt antimony oxide nano-particles were simply prepared by addition of cobalt chloride (0.1 M) and antimony chloride (0.1 M) in double distilled water (100 ml). The pH was adjusted 10.55 by adding ammonium hydroxide. The resultant solution was transferred in Teflon autoclave and put in oven at temperature of 150 °C for 16 h. Brown precipitate was obtained after cooling and then washed with acetone for three times. The brown precipitate was dried at room temperature and grind into fine powder. $CoSb_2O_6$ powder was heated in oven at 400 °C to remove the moisture and form the uniform crystalline nanostructures.

2.3. Structural characterizations

The structural characterizations of the cobalt antimony oxide nano-particles were investigated using Field Emission Scanning Electron Microscope (FE-SEM; JSM-7600F, Japan). The powder X-ray diffraction (XRD) patterns were measured with a X-ray diffractometer (XRD; X'Pert Explorer, PANalytical diffractometer) equipped with Cu-Kα1 radiation (λ = 1.5406 nm) using a generator voltage of 40 kV and a generator current of 35 mA were applied for the determination. Fourier Transforms Infrared spectrometer (FT-IR; Perkin Elmer), spectrum was recorded in K-Br dispersion. The UV/visible spectrum were recorded in the range of λ 200–800 nm (Perkin Elmer-Lambda 950-UV–visible spectrometer).

2.4. Fabrication of glassy carbon electrode using $CoSb_2O_6$

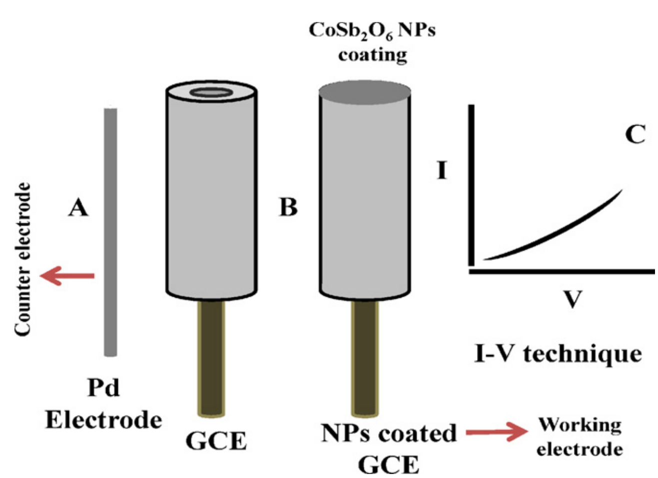
The $CoSb_2O_6$ nano-particles mixed with butyl carbitol acetate (BCA) and ethyl acetate (EA) both chemicals were used as a conducting binder on a glassy carbon electrode (GCE, surface area 0.026 cm^2). The glassy carbon electrode put in oven at 60 °C for few hours until film is dried and uniform. The 0.1 M phosphate buffer solution at pH 7.0 was made by mixing of 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 solution in 100.0 ml de-ionize water. I–V techniques have been used for dichloromethane sensing with coated electrodes. The chemical sensing of $CoSb_2O_6$ electrodes have been primarily investigated, where dichloromethane used as a target compound. The GCE was fabricated on electrode substrate by $CoSb_2O_6$ nano-particles with coating for developing the sensor substrate.

2.5. Detection of dichloromethane by I–V technique

The glassy carbon electrode modified with $CoSb_2O_6$ nano-particles was used as working electrode and Pd wire was used as reference electrode (Scheme 1). The different concentrations of dichloromethane prepared in DI water were added to beakers containing 20.0 ml of 0.1 M phosphate buffer solution. Then electrode is immersed in each beaker one by one and measured the I–V curves by using electrometer. The ratio of voltage and current (slope of calibration curve) were used to measure the dichloromethane sensitivity.

2.6. Photo-catalytic experiment

For photo-catalytic reaction, 150 ml of acridine orange solution having 0.03 mM concentration was taken in 250 ml beaker and then added 150 mg of $CoSb_2O_6$ nano-particles. Before irradiation, the solution was stirred and bubbled with oxygen for at least 15 min in the dark to allow equilibrium of the system so that loss of compound due to the adsorption can be taken into account. The reaction was constantly purged with oxygen bubbling and irradiated by using 250 W high pressure mercury lamp. 5.0 ml samples were taken before and at regular time during the irradiation and centrifuged to separate acridine orange solutions from the photocatalyst. The clear solution of acridine orange was analyzed by



Scheme 1. Fabrication of chemical sensors using $CoSb_2O_4$ nano-particles and its detection methodology.