Structural, Optical and Photocatalytic Activity of α - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ Ternary Multi-heterojunction Nanoflakes Synthesized via Submerged DC Electrical Discharge in Urea Solution

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Research Article

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Abstract

In this research, novel $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ multi-heterojunction photocatalytic nanoflakes are fabricated via submerged DC electrical arc discharge in urea in water solution. FT-IR, XRD, EDS and PL results conform the formation of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ multi-heterojunction. Formation of nanoflake morphology are revealed by FE-SEM, TEM images. Based on UV-visible results the calculated band gap energies are in the range between 2.7 and 3.0 eV for fresh sample and after one month. The photocatalytic performance of sample is investigated via degradation of methylene orange (MeO) under visible light irradiation. $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ exhibited much higher photocatalytic activity than $\text{Bi}_2\text{O}_2\text{CO}_3$, Bi_2O_3 and $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$. Also, stable photodegradation efficiency of sample after four cycles reveal the long term stability and reusability of synthesized photocatalyst. PL intensity show improved separation rate of electrons and holes and so better photocatalytic performance of multi-heterojunction in compared to single phase photocatalyst. The enhanced photocatalytic activity can be ascribed to the formation of multi-heterojunctions, flake morphology and intrinsic internal electric field (IEF). Multi-heterojunction nanoflakes enhance the absorbance of visible light and facilitate the separation and transport of photogenerated electron-holes through large IEF which enhance the photocatalytic activity. Our work offers an effective method for production of innovative bismuth based photocatalyst with excellent prospective for degradation of environmental pollutions and light harvesting for renewable energy generation under visible-light.

Introduction

Energy crisis and environmental pollution are one of the major global problems in the present century¹. Hence, semiconductor photocatalysts attracted great attention in this matter. Photocatalysis with solar energy, is one of the most advanced and encouraging techniques in reducing energy crisis and environmental pollutions¹⁻⁴. The light of sun as an inexhaustible energy source are used for removal of environmental pollutants as well as water splitting and CO_2 photoreduction to generate hydrogen and carbon containing fuels to overcome the energy scarcity⁵⁻⁸. So, synthesis of efficient photocatalysts with high performance in absorbing visible light and charge separation as well as photochemical stability is a key challenge⁹. Visible-light-driven photocatalysts with heterojunctions has found much attention in degradation of wide range of toxic compounds especially hazardous dyes in wastewater^{10,11}. The photocatalytic activity depends not only on the material but also on the dimensions and structure as well as the composition of the photocatalysts^{12,13}. Bismuth based complex oxide semiconductors are new promising materials for environmental remediation, water splitting and photocatalytic applications, which show a good photocatalytic performance under visible light¹⁴. Among the diverse photocatalytic materials such as TiO_2 , ZnO , SnO_2 , WO_3 and CeO_2 , bismuth-based photocatalysts are important group with low toxicity in compared to other photocatalysts which have photocatalytic performance for degradation of organic pollutants in the environment as well as industrial hazardous wastes^{15,16}. In the electronic structure of bismuth oxide, the valence band consist of O 2p and Bi 6s hybrid orbitals. The Bi 6s orbital

rises the mobility of photo-generated charge carriers and thus lead to decrease in the band gap^{14,17}. Bi_2O_3 is a p-type semiconductor, which has a direct band gap energy with less than 3.0 eV¹⁸. There are six main polymorphs for Bi_2O_3 , which crystallize into different crystal structures¹⁹. The monoclinic $\alpha\text{-Bi}_2\text{O}_3$ phase is the most stable phase at room temperature²⁰. Thermodynamically $\alpha\text{-Bi}_2\text{O}_3$ is stable between 25°C and 730°C and then transformed to face centered cubic $\delta\text{-Bi}_2\text{O}_3$ phase at 730°C and remains stable up to its melting point at 825°C^{19,21}. The tetragonal $\beta\text{-Bi}_2\text{O}_3$ and body centered cubic $\gamma\text{-Bi}_2\text{O}_3$ are metastable phases, which formed at high temperature and can be stabilize down to room temperature or transform to $\alpha\text{-Bi}_2\text{O}_3$ at high cooling rates^{22,23}. In addition, thermal transformation of $\alpha\text{-Bi}_2\text{O}_3$ and $\beta\text{-Bi}_2\text{O}_3$ to $(\text{BiO})_2\text{CO}_3$ and $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ were reported previously^{24,25}. Bismuth oxides including $\alpha\text{-Bi}_2\text{O}_3$, $\beta\text{-Bi}_2\text{O}_3$, $\gamma\text{-Bi}_2\text{O}_3$ and $\delta\text{-Bi}_2\text{O}_3$ as well as $(\text{BiO})_2\text{CO}_3$ and $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ show photocatalytic activity^{19,22,25-28}. Whereas, the small specific surface area, chemical instability and high recombination rate of photo-generated carriers of Bi_2O_3 demonstrate the main problem for applications of Bi_2O_3 as a photocatalyst merely¹⁴. Several approaches are developed to overcome the drawbacks of using single-phase semiconductor as photocatalyst namely metal or ion doping, establishing composites or formation of multi-junctions^{20,29-31}. Among them, formation of multi-junctions has gained much attention and has used widely³¹. The construction of a heterojunction can efficiently improve the photocatalytic activity by increasing the separation of photo-generated electrons and holes effectively. In addition, multi heterojunctions can show better charge transport mechanism and thus higher photocatalytic activity, for instance, visible light photo-response AgI loaded BiOI, $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ ternary nanocomposites, Z-scheme Ag-AgI/BiOI- Bi_2O_3 photocatalysts and $\text{SnO}_2/\text{Bi}_2\text{O}_3/\text{BiOI}$ nanofibers with enhanced photocatalytic performance³²⁻³⁵. IEF is a factor in improving photocatalytic activity by means of simplifying transformation and separation of the photo generated carriers. The alternative layer structure of $(\text{Bi}_2\text{O}_2)^{2+}$ fluorite flake and $(\text{MO}_6)^{2-}$ perovskite layers in bismuth-based binary metal oxides form IEF that enhanced separation efficiency of photo generated charge carriers^{25,36}. Bismuth subcarbonate with $(\text{BiO})_2\text{CO}_3$ chemical formula is a n-type photocatalyst and has shown photocatalytic performance in decomposition of pollutants in wastewater and polluted air^{14, 37,38}. The electronic structure of $(\text{BiO})_2\text{CO}_3$ is comprised of hybridized O 2p and Bi 6p orbitals in conduction band and O 2p, Bi 6p and C 2p orbitals in valence band¹⁴. The structure of $(\text{BiO})_2\text{CO}_3$ is composed of $(\text{Bi}_2\text{O}_2)^{2+}$ slabs that are intertwined by means of CO_3^{2-} layers, which lead to IEF and improve photocatalytic performance^{25,39}. However, the photocatalytic application of $(\text{BiO})_2\text{CO}_3$ under the solar spectrum is limited due to the wider band gap between 2.8 eV and 3.5 eV and lower charge separation efficiency^{25,39,40}. Hence, formation of junctions between $(\text{BiO})_2\text{CO}_3$ and other visible responsive photocatalytic semiconductors like $\alpha\text{-Bi}_2\text{O}_3$ is an appropriate way to extend the photocatalytic activity even under visible light, such as $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ and $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{S}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3/\text{BiOCl}$ ⁴⁰⁻⁴². $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ as an Aurivillius oxide with 2.17 eV band gap is a promising visible-light driven photocatalyst²⁵. $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ has the same structure as $(\text{BiO})_2\text{CO}_3$ and can be formed through replacing of CO_3^{2-} layers of $(\text{BiO})_2\text{CO}_3$ by OH^- layers which are more polar and

increased IEF of photocatalyst and thus lead more photocatalytic performance⁴³. Therefore, $(\text{BiO})_2\text{CO}_3$ and $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ are suitable candidate for construction of layered nanostructures with large IEF and high ability to separate photo generated carriers³⁹. Consequently, formation of junctions between $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ and $(\text{BiO})_2\text{CO}_3$ can improved visible light photocatalytic activity^{25,44}. The interfaces between $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ and $(\text{BiO})_2\text{CO}_3$ which are contacted nearly and have efficient built-in electric field improve photogenerated carriers separation and lead better photocatalytic performance. $(\text{BiO})_4\text{CO}_3(\text{OH})_2/(\text{BiO})_2\text{CO}_3$ with internal polarized heterojunction was synthesized and shows enhanced photocatalytic activity due to synergetic effect between IEF and carriers separation and indicated great potential in application in wastewater treatment²⁵. There are many growing number of methods for preparation of single phase or multi-heterojunctions of bismuth oxide based nanostructures. Hydrothermal synthesis of $\alpha\text{-Bi}_2\text{O}_3$ photocatalysts with nanosheet structure, Bi/ Bi_2O_3 nanoparticles synthesis by Nd:YAG laser ablation, solvothermal preparation of Bi/ $\text{Bi}_2\text{O}_2\text{CO}_3$ heterojunction photocatalyst, synthesis of photocatalytic dendritic $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures with facile transformation, two-dimensional $(\text{BiO})_4\text{CO}_3(\text{OH})_2/(\text{BiO})_2\text{CO}_3$ heterostructure photocatalyst formation by in-situ photosynthesis and flower-like Au/ $\text{Bi}_2\text{O}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ multi-heterojunction photocatalysts preparation by one-pot in-situ growth were reported elsewhere^{25,39,45-48}. Compared with several conventional techniques for nanostructures synthesis, DC electrical arc discharge in liquid provides a straightforward, flexible and cost-effective method for mass production nanomaterials without environmental footprints. There are some experimental parameters including electrical current, composition of electrodes and chemical nature of liquid environment, which impress arc discharge process, as well as nanomaterials formation both during and after synthesis in liquid^{49,50}. Chemical nature of liquid environment is determining factor in final composition of synthesized nanomaterials through electrical arc discharge. For instance, TiC nanoparticles synthesis via electrical arc discharge in organic liquids⁵¹. Furthermore, Bi/ Bi_2O_3 rod like nanostructures were prepared via oriented aggregation of bismuth based nanoparticles synthesized by DC arc discharge in water, where water act as both synthesis medium and oxidative environment⁵².

In this research, novel $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ multi-heterojunction nanoflakes with considerable photocatalytic performance have been synthesized via DC electrical arc discharge in urea in water solution for the first time. By applying an appropriate DC current between bismuth electrodes, electrical arc discharge cause plasma generation in the solution and form $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ nanoflakes. This compound exhibit enhanced photocatalytic performance toward degradations of MeO, compared with $\alpha\text{-Bi}_2\text{O}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3$ and $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ single phases. The photoactivity enhancement can be attributed to the formation of multi-heterojunctions flake morphology and improved IEF in $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ nanostructure. To the best of our knowledge, no research has been conducted around the investigation of photocatalytic performance of synthesized ternary $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ nanocomposite by electrical arc discharge in liquid with an efficient photocatalytic activity under visible light for energy and environmental application.

Experimental

Multi-heterojunction $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ nanoflakes were synthesized by facile DC electrical arc discharge method in liquid⁵². The nanostructures synthesis part comprised of a heat-resistant glass container filled with urea in water solution by concentration of 10 g/L. The urea was Merck with more than 99% purity. Two 99.9% purity bismuth electrodes placed in front of each other in vertical mode while the one electrode was held fixed the other one was movable to make electrodes close each other. The diameter and length of both electrodes were about 5 mm and 30 mm respectively. The synthesis parts were connected to ARC 200 DC power supply and a 40A DC current was applied to synthesis of nanostructures. The synthesis process begins by bringing electrodes close together. When electrodes were brought into contact electrical arc discharge generated and nanostructures formed. Each discharge lasted about 1 to 2 second and emitted a very shiny blue lights. By establishing electrical discharge the surface of electrodes is eroded through evaporation and sputtering, and then bismuth atoms and dispersed clusters are formed in the solution with so lower temperature than arc hot zone. The suspension of dark nanostructures formed through synthesis and the colour of suspension became lighter during time passing due to the oxidation of nanostructures.

FTIR spectroscopy was used to determine the functional groups on the surface of the sample. FTIR spectra was conducted by a PerkinElmer spectrometer on samples using standard KBr pellets. To investigate the crystallographic and phase characteristic of the sample the powder specimen was analyzed by X'Pert MPD system with Co K α radiation at 1.78897 Å wavelength. To identify the microstructure, chemical compositional properties, morphology and size distribution of nanostructures a MIRA TESCAN field emission scanning electron microscope and a Zeiss EM900 transmission electron microscope were measured at room temperature with different magnification. The optical properties of colloidal sample were determined by SCO-TECH SP UV-26 UV-visible spectrophotometer at wavelength between the 190 and 1100 nm at different times. To investigate the photocatalytic activity of synthesized sample, the powder specimen was carried out from solution by using KTS 5000 rpm centrifuge. PL spectra were recorded by an Avaspec2048Tech spectrofluorophotometer. A Nd-YAG laser with 3rd harmonic crystal was used for excitation of the samples at wavelength of 355 nm.

The MeO was used as the model pollutant to investigate the photocatalytic activity. The photocatalytic activity was done through dispersing of 45 mg photocatalyst powder in 160 mL solution of MeO (2.5 mg/L) in a glass reactor. It should be noticed that, the solution was stirred in darkness for about 30 minutes to establish adsorption–desorption equilibrium between MeO molecules and surface of photocatalysts. Then the solution was under irradiation about 180 minutes while stirring constantly during irradiation, to make uniform mixture. The photocatalytic tests applied at room temperature and the setup was held in a chamber under visible light. During the photocatalytic experiment, each 15 minutes 3mL of the solution taken out to measure optical transmission spectra to reveal the concentration of MeO by determining the maximum absorption wavelength of MeO at 464 nm. For evaluate the reusability of synthesized sample cyclic photodegradation experiments of MeO by $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ nanocomposites were done at the same conditions. For doing cyclic photocatalysis tests, photocatalyst

was withdrawn from solution by means of centrifuge after each cycle. The solution sample centrifuged at 4500 RPM for 10 min, then washed and cleaned via ultra-sonicating of sample in deionized water several times and after drying reused again in a new solution of MeO with photocatalyst. The photodegradation procedure of MeO by sample was redone in four cycle. Furthermore various scavengers were used to investigate the role of reactive oxidative species in degradation process. To capture the generated holes, hydroxyl and superoxide radicals ethylenediaminetetraacetic acid (EDTA), isopropyl alcohol (IPA) and benzoquinone (BQ) were respectively used in photocatalytic process.

Results And Discussion

The type of functional groups on the surface of synthesized nanostructures were identified by FTIR spectrum, as illustrated in Figure 1. It reveals characteristic vibrating modes of the free carbonate ion with point group symmetry D_{3h} . This is engrossed several internal vibrations including, symmetric stretching mode ν_1 at 1066 cm^{-1} , out-of-plane bending mode ν_2 at 848 cm^{-1} , antisymmetric vibration ν_3 at 1460 and 1384 cm^{-1} , in-plane deformation ν_4 at 695 and 673 cm^{-1} and symmetric stretching plus in-plane deformation modes, $\nu_1 + \nu_4$, at 1756 and 1730 cm^{-1} ^{137,38,43}. The band groups of CO_3^{-2} at ν_1 , ν_2 , ν_3 , ν_4 and $\nu_1 + \nu_4$ reveal the formation of $\text{Bi}_2\text{O}_2\text{CO}_3$. Moreover, the bands at 844 cm^{-1} and $300 - 800\text{ cm}^{-1}$ are corresponded to Bi-O-C and stretching modes of the Bi-O bonds in $\text{Bi}_2\text{O}_2\text{CO}_3$, and Bi_2O_3 , respectively⁵³. The bands at 3455 cm^{-1} and 1400 cm^{-1} are corresponding to O-H stretching vibration and O-H bending vibration respectively, suggest the presence of $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ in composition^{54,55}.

The XRD pattern of synthesized sample is illustrated in Figure 2. It is observed that there are forty nine different peaks in the pattern which are related to the crystallographic characteristics of $\alpha\text{-Bi}_2\text{O}_3$, $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ and $\text{Bi}_2\text{O}_2\text{CO}_3$ phases. The crystal system of Bi_2O_3 is monoclinic with $a = 5.8480$, $b = 8.1660$ and $c = 7.5100\text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 113^\circ$ crystallographic parameters and is according to 00-027-0053 reference code⁵⁶. The $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ phase is relevant to 00-038-0579 reference code with orthorhombic crystal system with $a = 10.7716$, $b = 5.4898$ and $c = 14.75740\text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ crystallographic parameters⁵⁷. The crystal structure of $\text{Bi}_2\text{O}_2\text{CO}_3$ is orthorhombic with $a = 5.4680$, $b = 27.3200$, $c = 5.4680\text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ crystal parameters and is based on 01-084-1752 standard card⁵⁸. Based on calculation of semi quantitative analysis of multiphase systems the $\alpha\text{-Bi}_2\text{O}_3$, $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ and $\text{Bi}_2\text{O}_2\text{CO}_3$ phases have 44%, 36% and 20% share of structure respectively. To describe mechanism of multiphase nanostructures formation, it should be noticed that, establishing electrical arc discharge leads to formation of a high temperature plasma⁵⁹. The plasma formation process dissociates the solution molecules and produces neutral, ionic and molecular species of bismuth, water and urea constituent atoms. Formation of Bi, O, C and H ions or OH, H_2 , O_2 , CO and CO_2 molecules in their ground or excited state in the plasma of electric arc discharge has been reported before^{51,52}. Follow these radicals the formation of oxide, oxide carbonate, hydroxide and carbonate oxide of bismuth could be explained.

Figure 3 shows the FE-SEM images of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ with nanoflakes structures and the approximate average thickness of nanoflakes were demonstrated by size distribution histogram. The size distribution histogram was obtained by applying a gaussian curve on the size histograms. The average thickness of nanoflakes is almost 22 nm. Furthermore, FE-SEM elemental mapping and energy dispersive spectrometry (EDS) of synthesized nanoflakes indicated the uniform distribution of Bi, O, C and N elements in structures, as shown in Figure 4.

Figure 5 (a) and (b) shows the TEM image of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ nanoflakes with different magnification, which confirms the SEM observation. There is a strong correlation between morphology and light harvesting performance of a multi-heterojunction nanostructure. Morphology can affect light absorption and electron-hole transport dynamics. Flake structure can enhance carrier extraction via an efficient electron-hole separation which results in an optimal charge transport properties. Reduction of electron-hole recombination rate could be attributed to the enhancement of the electron-hole separation due to the formation of electrical dipole in nanostructures with flake morphology^{60–62}.

Optical properties specially UV–vis spectrum of the nanoflakes is an effective way to evaluate photocatalytic activity via measuring light harvesting efficiency over different range of visible spectrum⁵². The optical absorption spectra of colloidal sample over different times immediately after synthesis, 15 min, 30 min, 1 hour, 4 hours, 4 days and after 1 month are shown In Figure 6a. The spectra are measured in wavelength between 190 and 1100 nm. The optical absorption spectra of the sample show an absorption peak at wavelengths between 190 nm and 400 nm, which is explained by electron transitions from the valance band to conduction band and bandgap absorption of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$, which is the feature of semiconductor materials^{25,39,53}. According to Tauc model the optical absorption coefficient of semiconductors with indirect transition band gap near the band edge follows the subsequent equation:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g)$$

1

where α is absorption coefficient, h is Plank constant, ν is light frequency, E_g is band gap energy and A is a constant^{53,63}. The calculation band gap diagrams of colloidal sample over different times after synthesis are indicated in Figure 6b. The estimated band gap energies are in the range between 2.7 eV and 3.0 eV for as prepared sample and after one month. The optical properties of colloidal sample show that synthesized nanoflakes can be good candidate for visible light harvesting and possible photocatalytic activity.

The photocatalytic activity of the novel $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ nanoflakes with multi heterojunctions was evaluated by the degradation of MeO solution under visible light irradiation for 180 minutes. The optical transmission spectra of MeO solution during degradation process by $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ nanoflakes exhibited considerable photocatalytic activity and the MeO absorption peak at 464 nm was considerably reduced.

The concentration of the dye at different times during degradation can be obtain by Langmuir–Hinshelwood model⁶⁴:

$$r = - \frac{dC(t)}{dt} = k_{abc}C(t)$$

2

where r is the degradation rate of the dye, $C(t)$ reveals concentration at time t and k_{abc} is a constant for reaction rate. The degradation kinetics of the dye can be described by following equation at low concentration of the dye:

$$\ln \left(\frac{C_0}{C} \right) = k_{abs}t$$

3

where the C_0 is initial concentration of MeO. The photocatalytic activity and MeO degradation kinetics for the sample are presented in Figure 7 that obtained at different reaction times during the photo degradation process. Figure 7a illustrates C/C_0 plot vs irradiation time and as obviously seen the sample shows highly efficient degradation rate. Figure 7b shows the degradation reaction kinetics, which was measured from the slopes of the $-\ln(C/C_0)$ plots versus irradiation time⁶⁵. The calculated k_{abs} value for synthesized nanoflakes is $5.5 \times 10^{-3} \text{ min}^{-1}$. The promoted photocatalytic performance of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ can be attributed to its flake morphology and multi-phase structure. Based on previous reports, the large surface area can helps to increase the photocatalytic reaction by means of rising active photocatalytic sites and the promotion of the efficiency of the electron-hole separation^{60–62}. Based on the obtained results of this research, it can be concluded that, the formation of multi-junction flakes can efficiently improve the photocatalytic activity of multi-heterojunction $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ photocatalyst in comparison with single $\alpha\text{-Bi}_2\text{O}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3$ and $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ photocatalysts^{25,45,66}.

The recyclability and reusability of photocatalysts are important factors in practical application^{6,67}. The stability of the photocatalytic activity of a photocatalyst can be evaluated through the monitoring of photocatalytic degradation of MeO under light over several cycles. In fact, the stability of a photocatalyst will be proved by stability in efficiency over every cyclic photocatalytic degradation test⁶⁸. Hence, the efficiency should not decline noticeably with each cycle. The degradation efficiency of the recovered $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ photocatalyst after four cycles are shown in Figure 8. As it clear, after each cycle the photocatalytic activity of sample was almost unchanged, which demonstrates a high stability of photocatalyst after multiple reuse.

Possible photocatalytic degradation mechanism of MeO by $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ under visible light irradiation were investigated through trapping experiments of reactive species in

photocatalytic tests by using different radical scavengers namely EDTA, IPA and BQ for scavenging the active h^+ , $\cdot OH$ and $\cdot O_2^-$ during the photocatalytic reaction^{25,39}. Based on Figure 9 degradation values of the MeO decreased in all capturing experiments which reveals all the generated reactive species are effective in photodegradation of MeO. However, BQ as superoxide radicals scavenger, more affected the MeO degradation efficiency. As shown in Figure 9, by capturing $\cdot O_2^-$ the dye degradation will eliminate more than other h^+ , $\cdot OH$ species.

According to absolute conduction and valence band energy positions of α - $Bi_2O_3/Bi_2O_2CO_3/(BiO)_4CO_3(OH)_2$ nanocomposite and the energy levels of literature, three possible degradation mechanism for α - $Bi_2O_3/Bi_2O_2CO_3/(BiO)_4CO_3(OH)_2$ multi-heterojunctions before and after junction are proposed in Figure 10^{25,69,70}. The Fermi level of α - Bi_2O_3 and $(BiO)_4CO_3(OH)_2$ which are p-type photocatalyst are close to the valence band and the Fermi level of p-type $Bi_2O_2CO_3$ is close to the conduction band^{25,71}. By formation of multi-heterojunction the energy band of α - Bi_2O_3 , $(BiO)_4CO_3(OH)_2$ and $Bi_2O_2CO_3$ will move upward or downward to lineup the Fermi level of the multi-heterojunction structure²⁵. Under visible light irradiation, the photogenerated electrons on the conduction band of component with less negative edge potential will transfer to upper CB, while the holes in the valence band with more positive edge potential are likely to transfer opposite position⁷⁰. In this situation, the recombination of photogenerated carries in photocatalyst will reduce and thus formation of p-n-p or p-p-n α - $Bi_2O_3/Bi_2O_2CO_3/(BiO)_4CO_3(OH)_2$ multi-heterojunctions nanoflakes will improve the separation efficiency of the photogenerated electron and holes which lead better photocatalytic performance⁶⁰⁻⁶².

PL spectrum of the α - $Bi_2O_3/Bi_2O_2CO_3/(BiO)_4CO_3(OH)_2$ with the excitation wavelength at 355 nm was measured and compared with PL spectrum of Bi_2O_3 to display the photoactivity enhancement mechanism. Broad emission peaks in the range between 2 and 3 eV are found in the PL spectra at the samples which is agreement with the documents^{23,39,47,72}. In general, a superior PL intensity shows an upper recombination rate of photo generated electron and holes, and thus lower PL intensity express lower recombination rate of photo generated electrons and holes which means improved separation rate of electrons and holes and so better photocatalytic performance³⁹. Based on PL spectra shown in Figure 11, the PL intensities of the multi-heterojunction α - $Bi_2O_3/Bi_2O_2CO_3/(BiO)_4CO_3(OH)_2$ nanoflakes are all lower than that of the Bi_2O_3 at the same condition, which means the efficient separation rate of the carriers in α - $Bi_2O_3/Bi_2O_2CO_3/(BiO)_4CO_3(OH)_2$. The formation of the multi-heterojunction reduce the recombination rate of photo-generated electrons and holes and then was favorable to improve photocatalytic activity.

Conclusion

In summary, a new multi-heterojunction α - $Bi_2O_3/Bi_2O_2CO_3/(BiO)_4CO_3(OH)_2$ nanoflakes was prepared by applying a 40 A DC currents between two bismuth electrodes through DC electrical arc discharge in liquid and investigated for using as visible light photocatalyst. FT-IR, XRD and EDS results revealed the

formation of $\alpha\text{-Bi}_2\text{O}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3$ and $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ phases. FE-SEM and TEM analysis revealed the flake morphology of sample with thickness of about 22.0 ± 0.5 nm. Formation of nanoflakes enhance surface area which lead more active photocatalytic areas and increase the separation efficiency of the photo-generated carriers and thus enhanced photocatalytic performance. The optical absorption spectra of sample show an absorption edge at wavelength between the 190 and 400 nm. The electronic structure of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ with a proper band gap less than 3.0 eV, makes it an appropriate photocatalyst in visible range. Additionally, XRD and PL results confirm the formation of multi-heterojunction between $\alpha\text{-Bi}_2\text{O}_3$, $\text{Bi}_2\text{O}_2\text{CO}_3$ and $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ phases. The lower PL intensity of $\alpha\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ in compared to single phase $\alpha\text{-Bi}_2\text{O}_3$ photocatalyst reveal lower recombination rate for this sample and thus better photocatalytic activity. The results of this research introduce a novel multi-heterojunction compound with considerable photocatalytic performance with an appropriate and cost-effective synthesis method.

Declarations

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Figures

Figure 1

FT-IR spectra of synthesized nanostructures by electrical arc discharge.

Figure 2

XRD pattern of synthesized nanostructures by electrical arc discharge.

Figure 3

FE-SEM images and size distribution histograms of synthesized nanostructures by electrical arc discharge.

Figure 4

FE-SEM image and EDS maps of Bi, O, C and H atoms in synthesized nanostructures by electrical arc discharge.

Figure 5

TEM images of synthesized nanostructures by electrical arc discharge with different magnification, (a) 200 nm and (b) 50 nm.

Figure 6

UV-vis optical absorption spectra (a) and the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot (b) of synthesized nanostructures by electrical arc discharge over different times.

Figure 7

(a) Photocatalytic degradation of MeO and (b) Liner curves of $\ln(C/C_0)$ vs. the irradiation time for the photodegradation reaction kinetics of MeO by synthesized nanostructures by electrical arc discharge.

Figure 8

Photocatalytic stability test of synthesized nanostructures by electrical arc discharge.

Figure 9

Degradation curves of MeO with different scavengers under the visible-light by synthesized nanostructures by electrical arc discharge.

Figure 10

Schematic diagram of three possible photogenerated charge separation for $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3/(\text{BiO})_4\text{CO}_3(\text{OH})_2$ multi-heterojunctions

Figure 11

The photoluminescence spectra of synthesized nanostructures by electrical arc discharge.