

## Abstract

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**Title: "SULFIDE BASED NANOMATERIALS SYNTHESIS FOR USE AS CATALYST OF ELECTROCHEMICAL AND PHOTOCHEMICAL REDOX REACTIONS IN RELATION TO ENERGY AND ENVIRONMENTAL APPLICATIONS"**

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Energy and environment are two principal issues of the contemporary world for sustainable development. Energy is a prime entity to create acceleration in beings or objects, though the form of energy is different for various purposes. If the easily available resource of energy does not have any adverse effects on the environment, then it can play a pivotal role in bringing perfect equilibrium between energy resources and respective energy creation. The recent rise of carbon emission from limited fossil fuel resources causes environmental pollution as a result of carbon dioxide emission in the environment, which is also one of the key reasons to bring natural calamity and global warming. To counter such threats and for the sake of sustainable development, people are shifting towards renewable energy resources, which brings a sense of joy to the natural face of Mother Earth. Having characteristic features like high energy content, feasibility, storage capabilities, etc., water splitting for hydrogen generation, electrochemical fuel cells serve vital role where methanol plays a significant task to generate green, clean and sustainable energy. Electrochemical methanol oxidation overcomes some outbreaks towards direct methanol fuel cell applications due to some of special quality like less pollution, less harming, high energy density and even effective in functioning at low temperature. Direct methanol fuel cells create tremendous potentiality in the electronic field especially portable electrical device, power supplier in the automobile sectors and may play a crucial role to replace conventional use of batteries in these sectors. Electrochemical oxidation method has a significant contribution towards above-described applications which make huge differences to bring technological revolution in the coming days and this method also has environmental contribution towards waste water treatment and remove toxic component from it and also produce formate like valuable chemicals from this method. On the other hand, Water is one of the most precious, essential and subtle molecules on earth, which requires top most priority for attention and purity to maintain an equilibrium ecosystem for sustainable future. It plays like a bridge by which all beings, objects complete their life cycle path from start to end. So, development of water management and related ecosystem are much more important than that found in the present scenario to explore its highest utilization for the sake of existence of both inanimate and life.

In the context of proper conversion, storage and utilization of energy, a facile fast synthetic route is designed in our study to prepare a versatile nano electrocatalyst,  $\text{AgBi}_3\text{S}_5$  (ABS) for the generation of green fuel,  $\text{H}_2$  via water electrolysis. XRD pattern confirms the major formation of monoclinic phase  $\text{AgBi}_3\text{S}_5$  (ABS) along with binary phase  $\text{Ag}_2\text{S}$  (AS) and  $\text{Bi}_2\text{S}_3$  (BS). Another variant  $\text{CuBiS}_2$  (CBS) nanoparticle is synthesized to compare the electrochemical result with the unique sustainable as-synthesized nanoparticles of ABS compound. Microscopy (HR-TEM) as well as spectroscopy (FTIR) studies provide confirmed evidence of the syntheses of ABS, AS, BS, and CBS respectively while the XPS study confirms the presence of Ag, Bi, and S in ABS. From the electrochemical analysis, it is evident that ABS shows lower overpotential value of 47 mV compare to that of other variants (AS – 93 mV, BS – 191 mV, CBS – 603 mV), lower Tafel slope values (mV/dec) (75.99) compare to others (AS – 101.54, BS - 120.29, CBS - 265.2) which are the key aspects to analyze the catalytic activity performance of the catalyst. It is also proved that the rate-determining step of the reaction proceeds through the Volmer-Heyrovsky step. Lower EIS values of 9.84  $\Omega$  with higher active surface area value of 0.092  $\text{cm}^2$  of ABS indicate superior and effective electron charge transfer kinetics on the electrode-electrolyte interface and elevated activity compared to other electrocatalysts (AS- 15.24  $\Omega$  and 0.035  $\text{cm}^2$ , BS- 16.01  $\Omega$  and 0.014  $\text{cm}^2$ , and CBS- 19  $\Omega$  and 0.005  $\text{cm}^2$ ). On top of that acceleration degradation (AD) study before and after analysis performed at 100  $\text{mVs}^{-1}$  for 500 cycles in acidic solution disclose the fact while comparing two LSV curves a small hike (8 mV at 10

mA/cm<sup>2</sup>) suggesting higher stability and low catalyst degradation for ABS. Chronoamperometric studies with a fixed applied potential of -0.065 V vs RHE also reveal that the catalyst (ABS) shows retention of activity after a 72-hour long-term process under a cathodic environment.

To show the application of light in H<sub>2</sub> generation, the as synthesized AgBi<sub>3</sub>S<sub>5</sub>-Bi<sub>2</sub>S<sub>3</sub> nano composite is characterized by Rietveld analysis with XRD data along with FTIR and XPS studies confirming the formation of the synthesized photocatalyst. The morphological study like FESEM, TEM, EDS also support the result from the characteristic analysis of data and determines their elemental composition in the synthesized nanocomposite. The performance of this nano composite in the hydrogen production reaction in presence of light is convincible due to its catalytic ability is reported for the first time in presence of light where all the major determining factors are well synchronized and outperform in presence of light compare to that in absence of light. The robustness and longtime durability along with catalytic efficacy are also proved by the result outcome from the studied parameters like overpotential, Tafel analysis, electron charge transfer kinetics, double layer capacitance, electrochemical surface area and chronoamperometric analyses.

In search of non-noble metal anode catalyst for fuel cell applications, we synthesized Cu<sub>9</sub>S<sub>5</sub> versatile nanomaterials using a new designing synthesis route and followed by unveiling its new catalytic wing towards electrochemical methanol oxidation reaction. Cu<sub>9</sub>S<sub>5</sub> and its supported alloys in different forms and structures used in the various fields such as semiconductor, asymmetric supercapacitors, anodes for high performance lithium-ion and sodium-ion batteries, efficient catalyst for water splitting, in broad band high performance electromagnetic wave absorber, used for microfiltration, as an environmental pollution removal and photothermal conversion, as a photothermal agent with 25.7% heat conversion efficiency for photothermal ablation of cancer cells in vivo and in multimodal tumor therapy. We demonstrated electrochemical and photochemical oxidation of methanol for the first time. The increased current peak on consecutive cycling in cyclic voltammetry appears in the negative potential zone. Significantly it is achieved in absence of any noble metal in the constitution of anode. The catalyst also exhibits efficiency in presence of light. Hopefully this new insight regarding Cu<sub>9</sub>S<sub>5</sub> nanomaterials towards electrochemical oxidation helps researcher in designing the catalyst without support of any noble metal. It also enlightens new direction to better optimization of its stability and makes them feasible for commercial purpose.

In the context of remediation of atmosphere from the contamination of water by toxic dye, Rhodamine-B, nanoparticles of n-AgBi<sub>3</sub>S<sub>5</sub>, n-Bi<sub>2</sub>S<sub>3</sub> and n-n AgBi<sub>3</sub>S<sub>5</sub> - Bi<sub>2</sub>S<sub>3</sub> nanocomposite were synthesized by facile one pot hot chemical (90 °C) method using ethylene glycol as medium without further calcination. The nanocomposite on exposure to natural sunlight exhibits significant and synergistic photo-catalytic activity towards degradation of pollutant dye Rhodamine-B(Rh-B) in aqueous solution. The as synthesized monoclinic AgBi<sub>3</sub>S<sub>5</sub>, orthorhombic Bi<sub>2</sub>S<sub>3</sub>, and their nanocomposite were identified and characterized by various spectroscopic, diffraction (XRD) and microscopic techniques. The UV-visible spectroscopic study reveals significant absorption of visible light and narrow band gaps/eV: 2.8 and 1.9 for synthesized Bi<sub>2</sub>S<sub>3</sub> and AgBi<sub>3</sub>S<sub>5</sub> respectively. The spectroscopically evaluated maximum % of degradation of Rh-B (99.9) and related high-rate constant (0.059 min<sup>-1</sup>) were achieved within 25 minutes with 0.7 g/L AgBi<sub>3</sub>S<sub>5</sub>-Bi<sub>2</sub>S<sub>3</sub> nanocomposite at pH 3. The radical trapping experiments reveal that both <sup>•</sup>O<sub>2</sub><sup>-</sup> and <sup>•</sup>OH are almost equally involved in the degradation, while hole, h<sup>+</sup> is the main initiator of the degradation as usual. Studies of the products of degradation reveals both de-ethylation and ring breaking of Rh-B indicating simultaneous absorption of sunlight by it and the catalyst. The very high efficiency and synergistic effect of the nanocomposite might be due to either/ both Z scheme/ S scheme charge separation. The 95% retention of the photocatalytic activity by 5th time used catalyst, AgBi<sub>3</sub>S<sub>5</sub>-Bi<sub>2</sub>S<sub>3</sub> signifies its superiority by auto surface improvement during reaction. Hope, the present work on the sulfide-based catalyst will have significant contribution in science and build up solid edifice in the development of emission less energy converters and remediation of atmosphere for our sustainable future.

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