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Review Article

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A Review on Eco-Friendly Synthesis of $BiVO_4$ Nanoparticle and its Eclectic Applications

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ABSTRACT. The paper presents a review of green syntheses and selective applications of bismuth vanadate nanoparticles ($BiVO_4$ NPs). Generally, ample number of biomolecules exists in plant extracts and these are mainly accountable for the facile green synthesis of $BiVO_4$ NPs. Moreover, $BiVO_4$ NPs has been widely researched in chemistry, biotechnology, physics and biochemistry fields due to their interesting technological chemical, biological, ionic conductivity and ferro-elastic properties. It can also be used in diverse fields, such as sensors, photocatalysis, water splitting and antimicrobial activity. Till date, $BiVO_4$ NPs has been synthesized by various known physical and chemical approaches. The article mainly discusses the green synthesis of $BiVO_4$ NPs via plant extracts. Moreover, this article shows a detailed overview of the green synthesis, characterization and significant applications of $BiVO_4$ NPs.

Keywords: $BiVO_4$ nanoparticle; Applications; Green nanotechnology; Plant extracts.

INTRODUCTION

Nanotechnology is a multidisciplinary branch of modern research comprising of fabrication methodology and manipulation of particle's size distribution with selective morphology of functional nanomaterials. The manipulation of their biological, chemical, electrical, optical or physical properties can generate functional nanomaterials with size ranging from 1 to 100 nm. Modifications of these functional materials can create novel materials with enhanced or improved features/properties.[1-2] Functional nanomaterials have stupendous applications of areas ranging from environment, biomedical and health care, food preservation, cosmetics, fuel cells, water purification, drug delivery and gene delivery, defense, chemical industries, space industries, ceramics, electronics, energy, sensors, single electron transistors, textiles, agricultures, solar cells, catalysis, light emitters, fuel, and antimicrobial.[1-25]. This is due to progress of reactivity when compared to their bulk counterparts and/or micro-sized since functional nano-scaled materials evince larger surface area to volume ratio.[1] Hence, there is a massive interest in the production of NPs for researchers working in the discipline of nanoscience and nanotechnology.

There are two significant approaches to obtain nanomaterials, they are called the top-down and bottom-up approaches.[1-5] Top-down method incorporates breaking down bulk material into tiny particles through size reduction using different approaches such as, electric arc, grinding, sputtering, ball milling, and thermal ablation. Bottom-up approaches is basically synthesizing NPs from smaller entities such as joining atoms, molecules and tiny particles. The bottom up approach mostly relies upon

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chemical and biological approaches. This methodology has an immense advantage which is the enhanced possibility of syntheses of NPs with minimum efforts.[2]

In particular, $BiVO_4$ is a non-toxic yellow pigment and n-type semiconductor possesses diverse interesting technological properties (Fig. 1), such as ferro elasticity, photostability and ionic conductivity.[26]

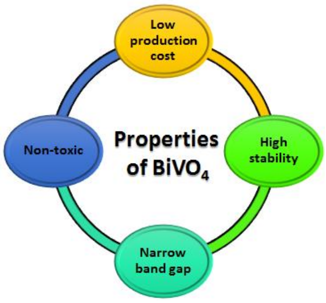

Fig. 1: Properties/features of $BiVO_4$ NPs.

Hence, $BiVO_4$ has attracted noteworthy interest due to its outstanding features, such as low band gap, resistance to corrosion, good dispersibility, non-toxicity and excellent photocatalytic result in organic pollutant degradation under visible-light.[27] Moreover, its adaptable optical and electronic properties with a band gap ~2.4 eV makes it a significant candidate for harvesting solar light.[28-29] It is notable that $BiVO_4$ mainly exists in three crystalline phases such as, tetragonal zircon phase (t-z), monoclinic scheelite phase (m-s) and tetragonal scheelite phase (t-s).[27] Heretofore, $BiVO_4$ NPs can be easily synthesized using multifarious methods such as drop casting method,[30] solution combustion method,[31] microwave-irradiation,[32] hydrothermal,[33] co-precipitation method,[34] template free approach,[35] flame-assisted,[36] thermal decomposition,[37] low temperature method,[38] ultra-sonication,[39] mechanical milling,[40] polymer assisted co-precipitation,[41] mechanochemical,[42] microemulsion,[43] ball milling,[44] molten salt method,[45] solvothermal,[46] reflux method,[47] sol gel,[48] sonochemical,[49] and metal organic decomposition.[50] Unfortunately, it often requires complicated and rigorous preparation conditions, time and energy consumption in the conventional synthesis methods. Therefore, safer, straightforward, biocompatible and economic process of uniform size distribution of $BiVO_4$ NPs still has lot of challenges.

Here, we covered the current scenario of research on the eco-friendly synthesis of $BiVO_4$ NPs with their benefits over known conventional routes. The main goal of this literature survey is to provide details of plants those are reported on biogenic syntheses and their eclectic applications. Overall, our objective is to critically describe green synthesis protocols and versatile applications of NPs that will be advantageous to researchers involved in this emerging sector. Thus, this perspective review article intends to present reports on green syntheses, characterization techniques and eclectic applications of the $BiVO_4$ NPs using plants extract.

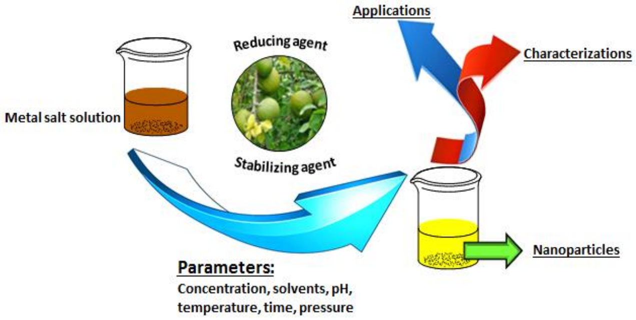

Fig. 2: Process of green synthesis of NPs.

GREEN SYNTHESIS OF METAL OXIDE NPS

Nowadays, green syntheses of functional nanomaterial imply the creating of NPs and/or nanomaterials without using noxious chemicals that generates pernicious by-products. In other words, green methodology is an eco-benevolent protocol to produce NPs where it is not ruinous to the ecosystem and human health. It is true facts that known conventional methodology can produce NPs in large quantities of desired shapes and size. Notwithstanding, these methodologies require high cost, complicated, tedious, noxious and outdated protocols.[1-10] In contrast to the conventional protocols, a green approach has immense advantages such as swift, simple manufacturing protocol, sustainable, straightforward and economically affordable. From the viewpoint of the ecosystem, green approaches for synthesizing NPs are considered, as a specific chemical it is not required to be reduced and stabilized, and furthermore its fabrication can be done under mild conditions.[2] In the green synthesis of NPs, raw materials, plants extracts (fruits, flowers, seeds, leaf, roots, etc.), enzymes, microbes, and fungi are utilized to prepare functional NPs.[3] The control of the size and morphology of green synthesized NPs and their precise mechanism of formation is still two significant challenges in nanobiotechnology.[18] In general, three routes of green syntheses using plant extracts (Fig. 2), green synthesis using microorganisms, and low-temperature synthesis have been utilized for synthesis functional NPs.

GREEN SYNTHESIS OF $BiVO_4$ NPS FROM PLANTS EXTRACT

There are very scanty reports on green syntheses of $BiVO_4$ NPs. However, employing plant extracts, natural reduction and stabilization of bismuth metal and vanadium metal into $BiVO_4$ NPs are the simplest, swift, inexpensive, sustainable and environmentally gracious procedures in green chemistry.[51] Green synthesis by plant extracts has immense benefits, including scalability, biocompatibility, and medical applicability.[4] In the synthesis of functional NPs employing selected plant extracts, the plant extract is simply mixed with the metal salt solution at proper temperature and the reaction is complete in a few minutes. The metal reduction is ascribed to the various phytoconstituents which are available in the plant extract such as tannins, polysaccharides, saponins, terpenoids, proteins, phenols and flavonoids.[3] So far, several plant extracts have been used in the synthesis of $BiVO_4$ NPs. Mohamed et al.[51] reported the green synthesis of rod shaped (Fig. 3.) $BiVO_4$ NPs by reducing bismuth nitrate and vanadium sulphate with the help of Callistemon viminalis flower extract as a reducing and stabilizing agent with an average crystallite size of $BiVO_4$ NPs in the range of 7.34 nm. At their experience, pH was kept among 3.5 and the temperature was at 100˚C during the experiment. Same author has described two more reports on green synthesis of $BiVO_4$ NPs using *Callistemon viminalis* flower extract.[53, 55]

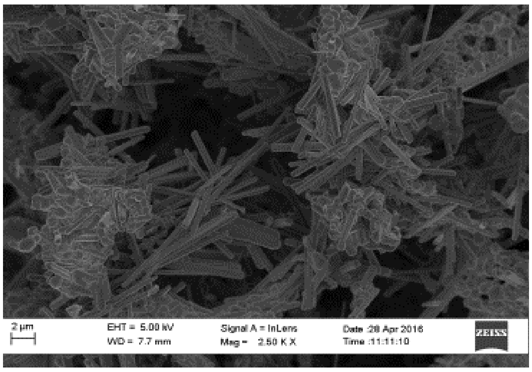

Fig. 3: TEM image of $BiVO_4$ NPs.[53]

Manjunatha et al.[52] used an aqueous fruit extract of *Citrus lemon* to produce $BiVO_4$ NPs that had an average particle size of 75 nm with a bang gap energy ranging from 2.6 to 2.8 eV. Phytosynthesis of $BiVO_4$ nanorods using a fruit extract from Hyphaene thebaica was reported by Khalil et al.[54] with an average size of 7 nm. In this research, the mixture was stirred 1 h at 100ºC. The brief protocol of phytosynthesis of $BiVO_4$ NPs by *Hyphaene thebaica* fruit extract is described in Fig. 4.

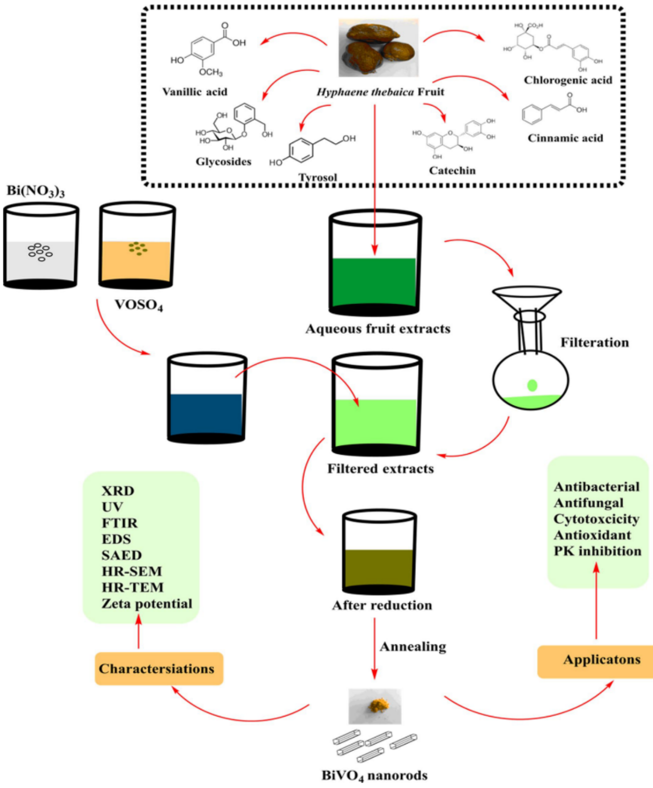

Fig. 4: Phytosynthesis of $BiVO_4$ NPs using *Hyphaene thebaica* fruit extract.[54]

In another study, Pramila et al.[56] reported the green synthesis of $BiVO_4$ NPs using *Aegle marmelos* fruit juice as a fuel. Green synthesis of $BiVO_4$ NPs using few plants extracts and their characterization techniques are summarized in Table 1.

RECENT APPLICATIONS OF BIO-SYNTHESIZED $BiVO_4$ NPS

$BiVO_4$ NPs have eclectic applications relying upon the diverse properties they manifest, which are significantly affected by their morphology, size, and optical traits. Thus, the synthesis approaches being imperative parameters for controlling all these properly. Some of these applications include sensors, photocatalysis, water splitting and antimicrobial activity etc. We have portrayed their advantageous applications to emphasize their momentous outcomes as direction to new researchers for future prospects. Mohamed et al.[51] synthesized rod shaped $BiVO_4$ NPs using *Callistemon* *viminalis* and reported their photocatalytic activity. They demonstrated that, the photocatalytic degradation of methylene blue (MB) dye up to 82% in 5 h under solar visible at room temperature by using $BiVO_4$ NPs as an efficient photocatalyst. The schematic mechanism of MB dye degradation is depicted in Fig. 5.

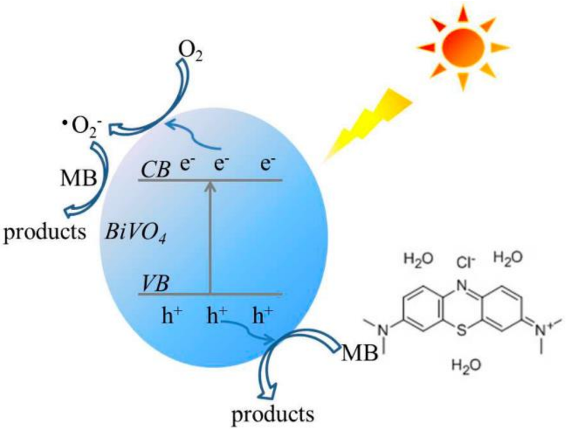

Fig. 5: Photocatalytic performance of $BiVO_4$ NPs using MB dye.[57]

Manjunatha et al.[52] reported the facile green synthesis of $BiVO_4$ NPs using Citrus lemon juice extracts and studied their photocatalytic and electrochemical activities. The synthesized $BiVO_4$ NPs catalyzed up to 90.6% degradation of *Indigo Carmine* dye within 150 min. Herewith, they also examined the electrochemical behavior of $BiVO_4$ modified electrode for the efficient detection of Hg (II) using electrochemical protocol. Khalil et al.[54] reported the phytosynthesis of $BiVO_4$ NPs using *Hyphaene thebaica* fruits extract and also described their antimicrobial, protein kinase (PK) inhibition, antioxidant, hemolysis and antiviral activities. These synthesized $BiVO_4$ NPs showed excellent antimicrobial performance against *Staphylococcus epidermidis* (ATCC 14490), *Bacillus subtilis* (ATCC 6633), *Klebsiella pneumonia* (ATCC 13883), *Escherichia coli* (ATCC 15224) and *Pseudomonas aeruginosa* (ATCC 9721), *Aspergillus flavus* (FCBP 0064), *Aspergillus fumigates* (FCBP 66), *Mucor sp.* (FCBP 300), *Aspergillus niger* (FCBP 0918) and *Fusarium solani* (FCBP 434) using simple well diffusion assay. In addition, significant and potent protein kinase inhibition is reported for $BiVO_4$ nanorods, which suggest their potential anticancer properties. Besides, phytosynthesized $BiVO_4$ nanorods exhibited good antioxidant activity using 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging potential and total antioxidant capacity protocols. Furthermore, antiviral activity of $BiVO_4$ nanorods was carried out against human rhabdomyosarcoma cells (RD), human laryngeal carcinoma (HEp-2 cells) and L20B cells (mouse fibroblast cells).

Table 1: Green synthesis of $BiVO_4$ NPs using plant extracts with size and shape.

Name of Plants	Part	Characterization techniques	Shape	Size (nm)	Ref.
Callistemon viminalis	Flowers	XRD, UV-Vis, HRTEM, SEM, EDS, FTIR, XPS	Rod	7.34	51
Citrus lemon	Fruits	XRD, FTIR, DRS, PL, SEM, TEM	Irregular	75	52
Callistemon viminalis	Flowers	UV-Vis, SEM, TEM, XRD, EDS, Raman	Rod	7.25–7.34	53
Hyphaene thebaica	Fruits	XRD, DRS, FTIR, Zeta potential, Raman, HRSEM, HRTEM, EDS	Rod	7	54
Callistemon viminalis	Flowers	XRD, PL, FTIR, SEM, TEM, EDS	Rod	54	55
Aegle marmelos	Fruits	XRD, SEM, EDS, UV-Vis	-	50	56

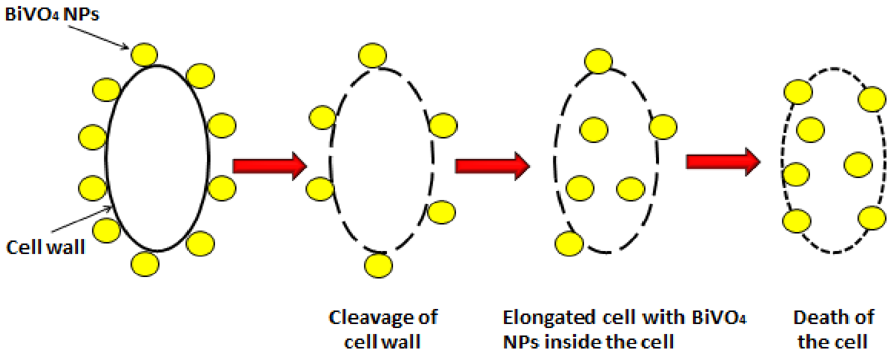

Fig. 6: Possible mechanism of antibacterial activity of $BiVO_4$ NPs.[20]

Pramila et al.[56] described the green synthesis of $BiVO_4$ NPs using *Aegle marmelos* fruit juice as a fuel and reported their photocatalytic and antimicrobial activity (Fig. 6). They reported that, the excellent photocatalytic degradation of MB dye up to 91% in 160 min under UV irradiation by using $BiVO_4$ NPs as a photocatalyst. Moreover, as-synthesized $BiVO_4$ NPs showed good antimicrobial activity against *Staphylococcus aureus*, *Klebsiella pneumonia*, *Enterobacter aerogenes*, *Micrococcus luteus*, *Salmonella typhimurium*, *Proteus vulgaris*, *Salmonella paratyphi-B*, *Candida albicans*, *Malassesia pachydermatis*, *Botyritis cinerea* and *Candida krusei* by using in vitro disc diffusion method. Overall, aforementioned results suggest that as-prepared $BiVO_4$ NPs via green chemistry approaches will play a vital role as a proper and desirable candidate for photocatalytic and antimicrobial utilization.

CONCLUSION

Green synthesis of $BiVO_4$ NPs has gained magnificent importance due to its effortlessness, sustainability, cost effectiveness and eco-benevolent nature. Few plant extracts have been successfully applied for the simple green synthesis of $BiVO_4$ NPs. The bioactive natural constituents of the plant extract were found to play double roles like natural reduction and also stabilization of $BiVO_4$ NPs. UV-Visible spectroscopy, FTIR, XRD, SEM, EDS, TEM, and XPS are the most applied analytical tools for the characterization of $BiVO_4$ NPs. Moreover, $BiVO_4$ NPs proved to be advantageous to the sector of catalysis, agriculture, defense, sensing, biomedicine, fuel, water purification with incredible future implication. Further investigation needs to depict the exact mechanism behind the green synthesis of $BiVO_4$ NPs, because no any reports are existed in literature and only few plants have been reported for green synthesis of $BiVO_4$ NPs. Thusly, further research needs to highlight the lucid mechanism behind the green synthesis of $BiVO_4$ NPs. Also, eco-friendly synthesis of $BiVO_4$ NPs using plants is an area that remains largely unexplored. Therefore, maximum numbers of medicinal plants are needed to use for the synthesis of $BiVO_4$ NPs without jeopardizing the existing plant diversity. Accordingly, several ways remain for the exploration of novel green preparatory protocols based on eco-friendly synthesis.

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