



## YASHWANTRAO CHAVAN COLLEGE OF SCIENCE, KARAD

### CRITERION-III

### RESEARCH, INNOVATIONS AND EXTENSION

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# The Promise of Molecular and Genomic Techniques for Biodiversity Research and DNA Barcoding of the Arabian Peninsula Flora

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The Arabian Peninsula is known to have a comprehensive and rich endowment of unique and genetically diverse plant genetic resources. Analysis and conservation of biological diversity is a crucial issue to the whole Arabian Peninsula. The rapid and accurate delimitation and identification of a species is crucial to genetic diversity analysis and the first critical step in the assessment of distribution, population abundance and threats related to a particular target species. During the last two decades, classical strategies of evaluating genetic variability, such as morphology and physiology, have been greatly complemented by phylogenetic, taxonomic, genetic diversity and breeding research molecular studies. At present, initiatives are taking place around the world to generate DNA barcode libraries for vascular plant flora and to make these data available in order to better understand, conserve and utilize biodiversity. The number of herbarium collection-based plant evolutionary genetics and genomics studies being conducted has been increasing worldwide. The herbaria provide a rich resource of already preserved and identified material, and these as well as freshly collected samples from the wild can be used for creating a reference DNA barcode library for the vascular plant flora of a region. This review discusses the main molecular and genomic techniques used in plant identification and biodiversity analysis. Hence, we highlight studies emphasizing various molecular techniques undertaken during the last 10 years to study the plant biodiversity of the Arabian Peninsula. Special emphasis on the role of DNA barcoding as a powerful tool for plant biodiversity analysis is provided, along with the crucial role of herbaria in creating a DNA barcode library.

**Keywords:** Arabian Peninsula, molecular markers, genomic techniques, plant biodiversity, DNA barcoding, herbarium collections



# Development of Porous Manganese Oxide/Polyaniline Composite Using Electrochemical Route for Electrochemical Supercapacitor

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Manganese oxide (MnO<sub>2</sub>)/polyaniline composite thin films were deposited using the electrochemical route for the fabrication of supercapacitor devices. The MnO<sub>2</sub> polyaniline composite was prepared with different percentages of MnO<sub>2</sub> and polyaniline and its structural, morphological, electrochemical, wettability and supercapacitor properties have been studied. The effects of the different percentages of MnO<sub>2</sub> and polyaniline on the supercapacitor have been investigated. The thin film containing 80% polyaniline and 20% MnO<sub>2</sub> shows relatively better supercapacitance, i.e., 409 F/g as compared to other composite thin films. The same film shows the retention of 92% of its original specific capacitance value after 1000 cycles. Similarly, after 2000 cycles, this value is still 84%.

**Key words:** MnO<sub>2</sub>/polyaniline composite, supercapacitance, electrochemical route

## INTRODUCTION

Electrochemical supercapacitors are charge storage devices possessing high power density. They exhibit excellent reversibility and a very long cycle life. The majority of the research in this particular area has targeted the development of new electrode materials. The criterion is a high specific surface area in order to enhance the performance.<sup>1–3</sup> Transition metal oxides such as MnO<sub>2</sub> exhibit great promise for use in capacitors as well as having low cost, low toxicity, and an environment-friendly nature.<sup>1,4</sup> The cost factor has inspired many researchers to look at alternative materials for pseudo-capacitive behavior. Manganese oxide is used in various types of batteries and is less harmful than some battery compounds such as cadmium.<sup>2</sup> For the last two decades, a wide variety of electrically conducting polymers have been

extensively studied due to their exclusive physical properties. Polymers possess good environmental stability and controllable electrical and optical properties,<sup>3</sup> and have high electrical conductivity and mechanical flexibility.<sup>4</sup> Composites of conjugated polymers are of great interest because of their potential for combining properties that are difficult to attain separately with the individual components. Recently, nanocomposites based on conducting polymers and transition metal oxides have been intensively investigated because of their potential applications as supercapacitor electrode materials.<sup>5–7</sup> Conducting polymers have shown great promise in a variety of applications, such as light-emitting diodes, chemical sensors, anti-corrosion coatings, batteries, and capacitors. Among the family of conducting polymers, polyaniline (PANI) is one of the most widely studied due to its stability.<sup>8</sup>

The hierarchical core-shell structure of MnO<sub>2</sub>/PANI nanosheets has successfully deposited by Yang et al.<sup>9</sup> The electrochemical performance of MnO<sub>2</sub>/PANI has revealed that the electrodes have 437 F/g of specific capacitance at 1 A/g with 62.4%

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## Uranium and Thorium Anomalies in the ~2.5 Ga Vendodu Leucogranite, Nellore Schist Belt, SE India and its Potential to Generate Uranium Deposits

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### ABSTRACT

The Vendodu intrusive, emplaced at  $2483 \pm 3$  Ma within the Nellore schist belt, SE India, is a K-rich per-aluminous A-type leucogranite composed of quartz and alkali feldspar (essential minerals), biotite, zircon, allanite, titanite, magnetite and apatite (magmatic accessory minerals) and muscovite, haematite, fluorite and uraninite (hydrothermal accessory minerals); zircon and uraninite could be both magmatic and hydrothermal. The Vendodu leucogranite is characterized by high Rb, Zr, Nb, Th, U and REE, low Ca, Al, Ba and Sr abundances, and large negative Eu anomalies. U content in the Vendodu leucogranite averages 17.63 ppm and is 6 to 11 times higher than average concentration of U in Upper Continental Crust (UCC) and Archaean granitoids. Similarly, Th content averages 61.38 ppm and is 3 to 20 times higher than average concentration of Th in Archaean granitoids and UCC. The U distribution in the Vendodu leucogranite is influenced by both magmatic and high-temperature hydrothermal processes. Processes that have enriched U have also increased LREE, Nb and Cr contents in the leucogranites. Geochemical proxies including Th/U, Zr/U and V/Yb suggest both magmatic and high-T hydrothermal (deuteric) enrichment of U over a wide range of temperatures and oxygen fugacities. High Th/U ratios in the Vendodu leucogranite (1.62-9.76) hint that the hydrothermal (deuteric) fluids were possibly magmatic. Petrographic and geochemical evidences suggest that the Vendodu leucogranite experienced magmatic and deuteric U enrichment that has potential to form mineralized zones either *in situ* or in pegmatitic veins.

### INTRODUCTION

Archaean granitoids record evolution of the early continental crust and its ore deposits. Sites, rates and processes of crust formation significantly changed at the Archaean-Proterozoic boundary: the Na-rich granites of the early Archaean are largely succeeded by late Archaean K-rich granites (Kemp and Hawkesworth, 2003), which make up 20% of presently exposed Archaean cratons (Condie, 1993). The K-rich leucogranites contain high proportions of radioactive elements and are considered to have increased the upper crustal budget of K, Rb, Cs, U, Th, LREE, Zr, and Hf, and possibly form the sources for Palaeoproterozoic uraniferous conglomerates as well as unconformity-related U deposits in the Palaeoproterozoic intra-cratonic basins (Taylor, 1987; Cuney, 2014).

Uranium ores are characterized by a spectrum of compositions resulting from different geologic origins (Cuney, 2009). Spatio-temporally, the U-deposits range from Archaean-Proterozoic boundary

to Recent and deep-seated magmatic cumulates to surface regoliths (Sarangi and Krishnamurthy, 2008; Cuney, 2009). The International Atomic Energy Agency (IAEA) proposed 15 distinct types of U deposits (Hore-Lacy, 2016). Granite-hosted uranium mineralization is one of the important U-deposits (magmatic and hydrothermal vein-type) (Cuney, 2009). Leucogranite hosted U deposits, in general, are low grade (<0.1 wt.% U) but large tonnage (>100 Mt) (Cuney, 2014). Four types of U deposits associated with leucogranites include: (1) primary disseminations and segregations, (2) primary mineralization in aplites and pegmatites (late differentiates; syngenetic), (3) high-T hydrothermal deposition in veins and fractures (epigenetic) and (4) low-T hydrothermal deposits due to meteoric water interaction (Cuney, 2009 and 2014).

In the present study, positive uranium anomalies in circa 2.5 Ga Vendodu leucogranite from the Nellore schist belt, SE India and highlight its potential to host U-deposits is reported.

### GEOLOGY AND PETROGRAPHY

The curvilinear Nellore Schist Belt (NSB) is the easternmost greenstone belt within the eastern Dharwar craton (Fig. 1A) and is sandwiched between the granulitic rocks of the Eastern Ghats belt (EGB) to the east and the intracratonic Cuddapah basin and TTG gneisses to the west (Fig. 1B). The NNE-trending NSB is up to ~600 km long and 30 to 130 km wide, and is composed of amphibolites, granite gneisses and metasediments, including banded iron formations (Vijaya Kumar et al. 2006). The present study area in the southernmost part of the NSB occurs between 2.7-2.6 Ga Archaean TTG to the west and the arc-related 1.8-1.7 Ga Eastern Ghats granite-migmatite complex to the east (Fig. 1C). Contacts between the different formations are either thrust or high-angle reverse faults (Fig. 1C). Hornblende- and biotite-granodiorite and leucogranite bodies are dispersed within the amphibolites and schistose rocks around the Kandra area (Fig. 1C). Leucogranites occur as domical stocks and elongate plutons within the schistose rocks. The strike directions of the host NSB terrane and the linear trails of leucogranite are conformable. A younger (1.85 Ga) ophiolite (Leelanandam, 1990; Sesha Sai, 2009; Vijaya Kumar et al., 2010; Saha, 2011), also occurs in the area, suggesting that the zone experienced repeated tectonothermal events. The leucogranites show intrusive relationships with the NSB, but thrust and sheared contacts with the Kandra ophiolite complex (Fig. 1C).

The Vendodu leucogranite, member of the circa 2.5 Ga K-rich leucogranite magmatism (Vijaya Kumar et al., 2011), occurs as an isolated stock to the southwest of Kandra ophiolite complex within the Nellore schist belt (Fig. 1C). SHRIMP U-Pb dating of magmatic zircons indicate that the Vendodu leucogranite was formed at  $2483 \pm 3$



# Enhanced Saccharification and Fermentation of Rice Straw by Reducing the Concentration of Phenolic Compounds Using an Immobilized Enzyme Cocktail

Virendra Kumar, Sanjay K. S. Patel, Rahul K. Gupta, Sachin V. Otari, Hui Gao, Jung-Kul Lee,\* and Liaoyuan Zhang\*

The production of bioethanol from rice straw can contribute to the rural economy and provide clean fuel in a sustainable manner. However, phenolic compounds, which are mostly produced during acid pretreatment of biomass, act as inhibitors of fermenting microorganisms. Laccase is well known for its ability to oxidize lignin and phenolic compounds derived from lignocellulosic biomass. In the present study, an immobilized enzyme cocktail containing laccase was evaluated in regard to its ability to enhance the saccharification and fermentation processes by reducing the amount of phenolic compounds produced. Saccharification of rice straw with the laccase-supplemented immobilized enzyme cocktail reduced phenolic compounds by 73.8%, resulting in a saccharification yield of 84.6%. In addition, improved yeast performance was noted during the fermentation process, resulting in a 78.3% conversion of sugar into ethanol with an ethanol productivity of 0.478 g/L/h. To the best of our knowledge, this is the first description of the use of an immobilized enzyme cocktail comprised of Celluclast 1.5L,  $\beta$ -glucosidase, and laccase for the production of bioethanol from rice straw. This study details a potential approach to producing biofuels from agricultural biomass, the applicability of which can be improved through up-scaling.

be a very suitable alternative to fossil fuel while contributing to biowaste management. Generally, the lignocellulosic biomass produced from agriculture has been recognized as a cheap source of feed to produce bioethanol due to its high availability worldwide.<sup>[3]</sup> As agricultural waste, rice straw is an attractive source of bioethanol production because it is one of the major crops in the world and is used to produce copious number of residues. According to the Food and Agriculture Organization, USA, the world's rice production was 759 million tons in 2017, and this generated approximately 1140 million tons of rice straw.<sup>[2]</sup> Based on the maximum theoretical ethanol production from rice straw, 350 million liters of ethanol can be produced in Asia only.<sup>[2]</sup> This large amount of rice straw can contribute significantly to bioethanol production and can reduce fossil fuel consumption to some extent.

Bioethanol production from lignocellulosic biomass such as rice straw has several challenges associated with it. The high complexity and strong association of the

## 1. Introduction

Biofuels as a source of renewable energy can replace gasoline and reduce greenhouse gas emission.<sup>[1,2]</sup> Production of biofuels such as bioethanol using lignocellulosic biomass has been hypothesized to

components of lignocellulose (cellulose, hemicellulose, and lignin) result in a compact structure and cause hindrance in every step (pretreatment, saccharification, and fermentation) of bioethanol production. The crystallinity of cellulose has been reported to be one of the factors negatively affecting the saccharification of lignocellulosic biomass.<sup>[4]</sup> However, hemicellulose favors saccharification by reducing the cellulose crystallinity.<sup>[5]</sup> The most complex component of lignocellulose is lignin, which is a hydrophobic heteropolymer composed of three major phenylpropane units: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S). Lignin content and composition also affect the saccharification of biomass.<sup>[6]</sup> During the pretreatment of biomass, lignin and hemicellulose are degraded, making the cellulose component more accessible for the enzyme to convert it into fermentable sugar. A wide range of phenolic compounds are released as a result of pretreatment, which further inhibits the processes involved in bioethanol production such as the hydrolysis of biomass and the fermentation of sugars.<sup>[7–11]</sup> In contrast, saccharification and fermentation of lignocellulosic biomass were enhanced after removal of inhibitors.<sup>[12,13]</sup>

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# Facile Chan-Lam coupling using ferrocene tethered *N*-heterocyclic carbene-copper complex anchored on graphene

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Ferrocene tethered *N*-heterocyclic carbene-copper complex anchored on graphene ([GrFemImi]NHC@Cu complex) has been synthesized by covalent grafting of ferrocenyl ionic liquid in the matrix of graphene followed by metallation with copper (I) iodide. The [GrFemImi]NHC@Cu complex has been characterized by fourier transform infrared (FT-IR), fourier transform Raman (FT-Raman), CP-MAS <sup>13</sup>C NMR spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), energy dispersive X-ray (EDX) analysis, X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area analysis and X-ray diffractometer (XRD) analysis. This novel complex served as a robust heterogeneous catalyst for the synthesis of bioactive *N*-aryl sulfonamides from variety of aryl boronic acids and sulfonyl azides in ethanol by Chan-Lam coupling. Recyclability experiments were executed successfully for six consecutive runs.

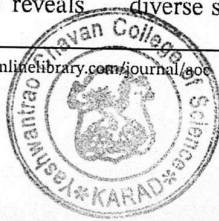
## KEYWORDS

ferrocene, graphene, *N*-aryl sulfonamides, *N*-heterocyclic carbene, reusability

## 1 | INTRODUCTION

*N*-Heterocyclic carbenes (NHCs) have emerged as the powerful spectator ligands in transition metal (TM) catalysis.<sup>[1]</sup> NHCs are electron-rich, excellent  $\sigma$ -donors and moderate  $\pi$ -acceptors, which make them ideal ligands for complexation with transition metals. An important attribute of NHC-TM complexes is their unexceptional stability that is often cited as one of the key advances of these ligands over their phosphine counterparts.<sup>[2]</sup> In addition, they are remarkably stable towards air, heat and moisture. Moreover, their steric and electronic properties can be fine-tuned with the help of wingtip substituents in the ligand backbone thereby making them process compatible.<sup>[3]</sup> The scrutiny of literature reveals

that majority of the NHC-TM complexes are homogenous in nature. The insight into these complexes has revealed some basic problems in terms of separation and recycling.<sup>[4]</sup> In addition, the contamination of ligand residue in the product causes inevitable pollution and unfavorable economics when the precious metals are employed during complexation. These inherent limitations associated with homogenous NHC-TM complexes have sparked major research activity in the field of heterogeneous analogs of these complexes.<sup>[5]</sup> The heterogeneous NHC-TM complexes are usually prepared by immobilizing NHCs on high area support materials. A plethora of distinct protocols for synthesis of heterogeneous NHC-TM complexes by employing structurally diverse supports have been reported.<sup>[6]</sup> However, despite





## Supplementary Material

### Cellulose supported ionic liquid phase catalyst mediated Mannich reaction

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231 2692333.

#### Spectral data of synthesized compounds

1,3-Diphenyl-3-(phenylamino)propan-1-one, C<sub>21</sub>H<sub>19</sub>NO; (**Table 3, entry 14a**): IR (KBr, thin film):  $\nu = 3384, 3098, 3023, 2878, 1669, 1598, 1509, 1448, 1369, 1290, 1176, 1001, 743, 687$  cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (d,  $J = 9$  Hz, 2H), 7.59-7.40 (m, 5H), 7.34-7.24 (m, 4H), 7.14 (t,  $J = 9$  Hz, 2H), 6.85-6.75 (m, 3H), 5.04 (t,  $J = 6.6$  Hz, 1H), 3.68 (d,  $J = 6.3$  Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  190.5, 144.8, 136.6, 134.9, 133.4, 129.1, 128.9, 128.8, 128.6, 128.4, 127.6, 126.8, 122.2, 55.3, 46.0; MS (EI):  $m/z = 301$  (M<sup>+</sup>); Anal. Calcd. for C<sub>21</sub>H<sub>19</sub>NO (301.15): C, 83.69; H, 6.35; N, 4.65. Found: C, 83.65; H, 6.31; N, 4.67.

1-(4-Methoxyphenyl)-3-phenyl-3-(phenylamino)propan-1-one, C<sub>22</sub>H<sub>21</sub>NO<sub>2</sub>; (**Table 3, entry 4b**): IR (KBr, thin film):  $\nu = 3383, 3026, 2928, 1663, 1660, 1514, 1458, 1401, 1219, 1021, 832, 741, 682$  cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.97-7.82 (d,  $J = 8.9$  Hz, 2H); 7.42-7.41 (m, 2H), 7.31-7.28 (m, 3H), 7.18-7.03 (m, 2H), 6.98 (d,  $J = 8.9$  Hz, 2H), 6.72-6.66 (m, 3H), 4.92 (t,  $J = 6.8$  Hz, 1H), 3.81 (s, 3H), 3.66-3.42 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  196.5, 163.3, 146.2, 143.9,



# Facile synthesis of $\beta$ -cyclodextrin-grafted solid silica nanoparticles

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## Abstract

In this work, a simple and reliable method for the synthesis of  $\beta$ -cyclodextrin ( $\beta$ -CD)-grafted silica nanoparticles (SiNPs) is developed. The synthetic protocol included postsynthesis functionalization of silica nanoparticles with aminopropyl trimethoxysilane (APTES) followed by the condensation of the amino groups with imidazole carbamate ester of  $\beta$ -CD. The activated  $\beta$ -CD (carbamate ester) was prepared by reacting it with carbonyldiimidazole (CDI). The grafting of ( $\beta$ -CD) on SiNPs was confirmed by ATR-IR, DLS, and TGA analyses. The method developed can be easily reproduced with any other oxide nanoparticles for the preparation of  $\beta$ -CD-grafted nanoparticles.

## KEYWORDS

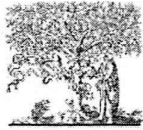
$\beta$ -cyclodextrin, grafting, hybrid nanoparticles, silica nanoparticles, surface modification

## 1 | INTRODUCTION

The cyclodextrins (CDs) are cyclic oligosaccharides made of 1,4 linked glucopyranose subunits.<sup>1</sup> The glucopyranose subunits are joined together by oxygen bridges and this structure forms hydrophilic outer surface and lipophilic central cavity.<sup>2</sup> The main characteristic property of CDs is their ability to form inclusion complexes with several compounds especially with drug molecules.<sup>3</sup> The drugs which are insoluble in water when complexed inside the hydrophobic cavity of CDs they form a soluble complex hence CDs are used to improve the solubility of drugs.<sup>4</sup> In addition, the CDs are also used extensively in various other applications such as food, cosmetics, and chromatography.<sup>5</sup> There are three main cyclodextrins, namely  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrin. Out of these, the  $\beta$ -CD is the most common CD in pharmaceutical formulations, and it is the most studied CD for drug delivery applications.

The grafting of  $\beta$ -CD molecules on the surface of nanoparticles produces hybrid core-shell nanomaterial which combines the inclusion complex formation property of  $\beta$ -CD and the intrinsic property of the nanoparticle on which it is grafted. Therefore, a continued interest to prepare  $\beta$ -CD-grafted nanoparticles is observed. Some representative examples of the  $\beta$ -CD-grafted materials include the synthesis of  $\beta$ -CD-grafted magnetic nanoparticles for drug delivery,<sup>6,7</sup>  $\beta$ -CD-grafted TiO<sub>2</sub> nanoparticles for improved dispersability in polymer nanocomposites,<sup>8</sup>  $\beta$ -CD-grafted barium titanate nanoparticles for improved colloidal or dispersion stability,<sup>9</sup> and  $\beta$ -CD-grafted chitosan nanoparticles for drug delivery.<sup>7,10</sup> The previous works reported in the literature about grafting of  $\beta$ -CDs on various nanoparticles used multi-step and complicated synthetic protocols. So, there is a need to develop new, fast, and efficient method for rapid and reliable grafting of  $\beta$ -CDs on nanoparticles. For this purpose, in the present work, a relatively simple, short, and reliable method for grafting of  $\beta$ -CD on silica nanoparticles by preparing the carbamate ester of  $\beta$ -CD and its grafting on amino-functionalized silica nanoparticles (SiNPs) is developed. The importance of the work lies in the fact that the synthetic protocol developed can be easily reproduced with any other oxide nanomaterials to prepare  $\beta$ -CD-grafted nanoparticles.

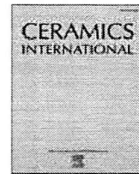




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# Biomolecule-entrapped SiO<sub>2</sub> nanoparticles for ultrafast green synthesis of silver nanoparticle-decorated hybrid nanostructures as effective catalysts

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## ARTICLE INFO

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Nanocomposite

## ABSTRACT

Noble-metal hybrid nanostructures have gained tremendous attention due to their potential roles in biomedical and catalytic applications. In this study, for the synthesis of silver nanoparticles (Ag NPs)-silica (SiO<sub>2</sub>) NPs, a novel green chemistry approach was employed, in which green tea biomolecule-encapsulated SiO<sub>2</sub> nanostructures were used for the reduction of silver ions to produce hybrid nanostructures within 300 s. The high-resolution transmission electron microscopy (HRTEM) revealed the formation of uniform ultrafine spherical Ag NPs that were evenly distributed in the nanostructures. The formed nanohybrid structures showed efficient catalytic activity for the formation of derivatives of dihydroquinoline, and retained 91% of their reusability capacity, even after 5 repeated cycles. Hence, this work provides a novel synthesis method not only for the synthesis of biomolecule-entrapped SiO<sub>2</sub> nanostructures, but also for the rapid formation of catalytically active hybrid nanostructures.

## 1. Introduction

Noble metal-based nanostructures have been proven to have potential applications in the fields of catalysis, medicine, energy storage, sensors, electronics, etc [1]. Owing to their large surface areas, and electrical and optical properties, noble metals such as silver (Ag) nanoparticles (NPs), Au NPs, and Pd- and Pt-based nanostructures have been studied extensively [1]. Comparing the cost and availability of these noble metal NPs, Ag is less expensive and available in abundance in the earth crust. Ag and Ag-based materials have been studied and used since ancient times as storage materials, antimicrobial agents, etc [2]. Extensive research is underway for the fabrication of ideal support materials for bio, organic, and inorganic catalysts, to maintain their effective activity, stability, and reusability [3]. Silicon dioxide nanoparticles (SiO<sub>2</sub> NPs) have been the choice of many researchers, as support materials, due to their chemical inertness, thermal stability, high stability when carrying a negative charge in neutral pH, low van der Waals interactions, non-interference with magnetism and light, etc [4,5]. Recently, we demonstrated the use of SiO<sub>2</sub> NPs as support for the immobilization of a multi-enzyme catalyst to produce acetoin, 2,3-butanediol, and 2-butanol [6]. Therefore, in this study, efforts were made to construct noble metal NP-immobilized SiO<sub>2</sub> hybrid nanostructures as effective catalysts.

Several methods have been reported for the synthesis of Ag NP-supported SiO<sub>2</sub> NPs and Fe<sub>2</sub>O<sub>3</sub> NPs, in which time-consuming reactions, hazardous chemicals, sophisticated instruments, or harsh reaction conditions were employed. Das et al. used a protein extract of *Rhizopus oryzae* to prepare Ag@Nanosilica in a 72 h incubation period [7]. Kaloti et al. reported excess concentrated glucose-mediated synthesis of Ag-γ-Fe<sub>2</sub>O<sub>3</sub> nanocomposites at high temperature [8]. Tzounis et al. reported Ag NP-decorated SiO<sub>2</sub> spheres using polyethyleneimine (PEI) as coating molecules for the spheres and sodium borohydride (NaBH<sub>4</sub>) as the reducing agent [9]. To the best of our knowledge, this is the first report on the synthesis of SiO<sub>2</sub> NPs using a green tea leaf ethanolic extract to entrap biomolecules, and their use for the synthesis of ultra-small uniform Ag NPs on and in the surface of the SiO<sub>2</sub> NPs in a very short time. As this synthesis method was optimized for the encapsulation of biomolecules in the SiO<sub>2</sub> nanostructure, it minimizes the complexity, cost, use of cumbersome SiO<sub>2</sub> functionalization steps, and addition of hazardous chemicals for the reduction of Ag<sup>+</sup> ions, making the synthesis process cost-effective, non-toxic, and eco-friendly.

In this study, we developed an ultrafast, green synthesis method, in which the biomolecules of the green tea leaf extract of *Camellia sinensis* (*C. sinensis*) were entrapped in SiO<sub>2</sub> NP structures to produce BSiO<sub>2</sub>

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## Antimicrobial Activity of Biosynthesized Silver Nanoparticles Decorated Silica Nanoparticles

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**Abstract** The production of cheap and effective compound for medicinal application is a major challenge for scientific community. So, several biological materials have been explored for the possible application in material synthesis which are useful in biomedical uses. Here, biomolecules from green tea leaves were functionalized on the surface of silicon dioxide nanoparticles (GSiO<sub>2</sub> NPs). Next, the decoration silver (Ag) NPs on the surface of the GSiO<sub>2</sub> NPs was observed in very short time of incubation in aqueous AgNO<sub>3</sub>. Ultraviolet–visible spectroscopy confirmed the formation of Ag NPs and the high-resolution transmission and scanning electron microscopies confirmed the decoration of spherical Ag NPs of 10 to 15 nm size on the surface of GSiO<sub>2</sub> NPs. The antimicrobial activity of the Ag–GSiO<sub>2</sub> NPs was determined against *Staphylococcus aureus* and *Escherichia coli*. The Ag–GSiO<sub>2</sub> NPs displayed sustainable antimicrobial activity compared to Ag ions. The results indicate the potential value of Ag–GSiO<sub>2</sub> NPs in surgical material and food processing.

**Keywords** Biosynthesis · Silver nanoparticles · Green tea · Biomolecules · Antimicrobial

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The various forms of the nanoparticles have been demonstrated for the different applications as the physical, chemical and biological properties of the nanoparticles varies with their shapes, size and surface properties [1–3]. Among the various nanomaterials, noble metals and noble metal-based nanomaterials have been not only synthesized and studied also extensively applied in various industrial and healthcare fields like medicinal, catalyst, energy, diagnostic, electronics, and other fields [4]. The platinum (Pt), palladium (Pd), silver (Ag) NPs, and gold (Au) NPs based nanomaterials have gained most interest due to their optical, physical and electrical properties over the other metal nanoparticles [5]. Among the various supporting materials, silicon dioxide (SiO<sub>2</sub>) NPs have the most favored inorganic material, which is inert, thermally stable, carry negative change in neutral pH, and less interference in magnetic and optical fields [6–9]. Synthesis of Ag NPs to decorate the surface of SiO<sub>2</sub> NPs has been explored in the application of coating on antimicrobial materials. Several reported methods for formation of Ag–SiO<sub>2</sub> NPs have involved the use of hazardous chemicals like sodium borohydride [10], expensive instruments like microwave devices [11] and sonicators [12], and time-consuming microbial methods [13]. Thus, to date, the approaches to synthesize Ag–SiO<sub>2</sub> NPs have proven to be expensive and potentially hazardous. With the goal of devising a rapid, safe, and cost-effective method for Ag–GSiO<sub>2</sub> NP synthesis, active reducing molecules were used for the functionalization of SiO<sub>2</sub> NPs in this study. These molecules were then used for the reduction of Ag<sup>+</sup>. The biosynthesized silver–silica composite was tested against *Staphylococcus aureus* and *Escherichia coli* to demonstrate the its effective antimicrobial activity. The Ag@GSiO<sub>2</sub> nanostructure formation was achieved as demonstrated in the schematics using biofunctionalized SiO<sub>2</sub> NPs (Fig. S1).



## FULL PAPER

# Intramolecular O-arylation using nano-magnetite supported *N*-heterocyclic carbene-copper complex with wingtip ferrocene

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Nano-magnetite supported *N*-heterocyclic carbene-copper complex with wingtip ferrocene has been prepared *via* multi-step procedure. The complex has been characterized by various analytical techniques such as fourier transform infrared (FT-IR), fourier transform Raman (FT-Raman), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) analysis. The catalytic activity of the complex has been exploited in intramolecular O-arylation of *o*-iodoanilides under heterogeneous conditions. The complex could be successfully recycled up to twelve consecutive cycles.

**KEYWORDS**

ferrocene, intramolecular O-arylation, nano-magnetite, *N*-heterocyclic carbenes, reusability

## 1 | INTRODUCTION

*N*-Heterocyclic carbenes (NHCs) have emerged as a versatile class of ligands with enormous applications.<sup>[1]</sup> The selection of NHCs as best ligands can be rationalized by their coordinative unsaturation, incomplete electron octet, which promise comparatively weak  $\pi$ -acceptor property, strong  $\sigma$ -donor capability, strong binding with transition metals and sterically demanding structure.<sup>[2]</sup> In addition, owing to flexible design of NHCs and ease of convenience to their azolium salt precursors, tailor made NHCs are readily offered.<sup>[3]</sup> Moreover, the steric and electronic properties of NHCs can be systematically fine-tuned with the assistance of wingtip substituents on the ligand backbone.<sup>[4]</sup> It is well recognized that tethering organometallic fragment like ferrocene at wingtip site in ligand backbone can have notable influence on steric and spatial properties of NHCs.<sup>[5]</sup> Ferrocene, by virtue of its unique cylindrical shape and powerful electron donor capacity causes expedient stabilization of NHCs. Additionally, ferrocene is non-toxic, easily

accessible and can be installed by simple synthetic manipulation in backbone of NHCs.<sup>[6]</sup> These unique properties of ferrocene have focused a quest towards progress of new methods for synthesis of ferrocenyl NHC-transition metal complexes in the field of catalysis.<sup>[7a-f]</sup>

In recent years, magnetic nanoparticles (MNPs) are intensely researched in the catalysis arena, as magnetic based nanocatalysts have been contributing significantly to meet requirements of green chemistry standpoints.<sup>[7g-o]</sup> The bridge between heterogeneous and homogeneous catalysts can be accomplished through the use of MNPs.<sup>[7p]</sup> Out of various MNPs, nano-magnetite finds a myriad of applications in the diverse areas including catalysis,<sup>[8]</sup> bioengineering,<sup>[9a-d]</sup> drug delivery,<sup>[9e]</sup> sensing,<sup>[9f]</sup> environmental treatment,<sup>[10]</sup> bioseparation,<sup>[11]</sup> biomaterials<sup>[12]</sup> and food analysis.<sup>[13]</sup> The ease of surface functionalization of nano-magnetite with desired precursors have provided significant versatility to design task specific catalytic systems.<sup>[14a]</sup> Amongst various precursors, organosiloxane precursors have been



# Prospects of genomic resources available at the global databases for the flora of United Arab Emirates

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## Abstract

This article emphasizes available genomic resources at the global databases National Center for Biotechnology Information (NCBI) GenBank, Gramene and Phytosome for the selected 378 plant taxa of the United Arab Emirates (UAE). Germplasm of these species was collected and banked at the Sharjah Seed Bank and Herbarium (SSBH) along with their related information on habit, habitat and occurrence. The occurrence statistics exhibits almost 19.84% species under rare-to-very rare category, the GenBank search statistics for this category indicates 17.72% species as studied and 2.11% as not studied. Overall, from the global search statistics for 378 plant species, it seems that about 40 (10.58%) species remained unstudied. Most of the unstudied species were herbaceous plants belonging to the mountainous habitat. Moreover, full genomes were recorded for 7 species at NCBI GenBank, 2 species at Phytosome and 1 species at Gramene database. The local search statistics (for UAE) exhibits about 10.58% of the flora that still remained unstudied and only 11 (2.90%) of the recorded species were having genomic information at NCBI GenBank. It is necessary to prioritize studies on such species that could provide valuable insight on their genetic composition in order to understand their adaptation to the natural environment. At present, the SSBH is cataloguing UAE's flora using core barcode and assisted markers that could provide a robust DNA barcode library for native plants of UAE. Our study appeals researchers to recognize and prioritize the species that need attention to enrich their genomic resources at the global databases by supporting nucleotide libraries with their conspecifics. At present, genomic resources for UAE plant taxa are limited, but with the advent of low-cost sequencing technologies these resources would flourish in the near future. Nevertheless, the information generated through genomic studies could be utilized for conservation and management of threatened and endangered plant species. Crop Wild Relatives and medicinal plants. We hope this article will promote interest in conducting additional studies in genomics of desert plants by encouraging researchers to participate in this emerging field.

**Keywords** Genomic resources · Global databases · UAE plants · Nucleotide libraries · DNA barcoding

## Introduction

The United Arab Emirates (UAE) is situated in the eastern Arabian Peninsula, bordering Oman and Saudi Arabia. Currently, about 830 plant taxa are known to occur in the UAE (Gairola et al. 2016). These plants have evolved highly diverse traits to thrive in the often harsh, unpredictable desert climates. Botanical studies in the UAE are increasing, as the knowledge of the richness and diversity of the flora is understandably still limited. The UAE's terrestrial environments faces a variety of pressures and threats, the plant life is under threat as native vegetation has an impact of varying degrees of disturbances mainly land use and overgrazing. Genomic approaches can enhance an understanding of plant evolution and adaptation, and offer the possibility of

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Research Article



# A green tactic for the synthesis of classical 3,3-bisindolylmethanes in waste curd water

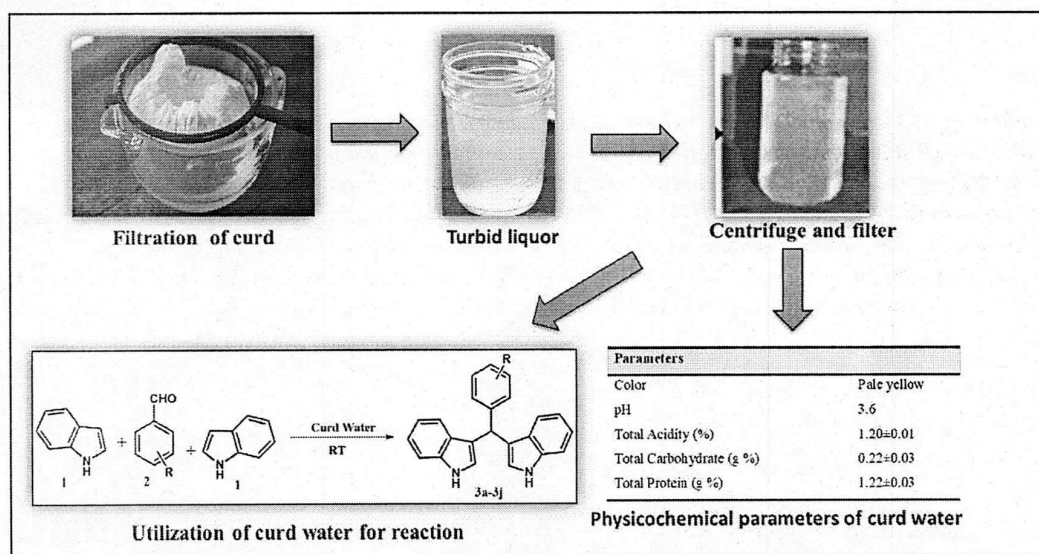
Jamatsing Rajput<sup>1,2</sup> · Sunil Koli<sup>1</sup> · Bhavana Mohite<sup>1</sup> · Ratnamala Bendre<sup>2</sup> · Satish Patil<sup>1</sup> · Vikas Patil<sup>3</sup>

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## Abstract

The biowaste curd water generated after the curd formation was utilized as an acid catalytic green solvent for the synthesis of 3,3-bisindolylmethanes derivatives. The soluble organic acid (i.e. lactic acid) responsible for the acidity to curd water which adequately fulfills the purpose of acid catalyzed reaction, where 2 mol of indole reacted with an aldehyde in the presence of curd water at a low temperature and yields classical 3,3-bisindolylmethanes derivatives. During the reaction, continuous product formation and isolation was observed. The product precipitate was separated by the successive method of filtration. This biowaste water catalyzed method is highly retrievable and advantageous over the trend of high-temperature inorganic acid catalyzed reaction offering the effortlessly separable product.

## Graphic abstract



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# Production and characterization of multifacet exopolysaccharide from an agricultural isolate, *Bacillus subtilis*

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## Abstract

This study aims to explore the fermentative production and physicochemical properties of an exopolysaccharide (EPS) produced from agricultural isolate, *Bacillus subtilis* S1 in submerged culture. The structural characterization (Ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, and <sup>13</sup>C Nuclear magnetic resonance spectrometry) revealed that the EPS is an acidic heteropolymer consisting of glucose, glucuronic acid, pyruvic acid, and succinic acid. The non-Newtonian shear thickening nature of EPS with a  $1.55 \times 10^7$  Da molecular weight is confirmed by rheology analysis. The extracted EPS was 61.3% amorphous with partial crystallinity (38.7%) as confirmed by

X-ray diffraction analysis. The EPS shows two-step decomposition and thermal stability up to 300 °C as confirmed by thermogravimetric analysis and differential scanning calorimetry analysis. The EPS has a small Z-average particle size (74.29 nm), high porosity (92.99%), high water holding (92.39%), and absorption capacity (1,198%). The biocompatible nature is confirmed by cytotoxic testing on the human keratinocytes cell line. The demonstrated unique characteristics of *Bacillus* EPS presents it as a choice of biomaterial for diverse applications. © 2019 International Union of Biochemistry and Molecular Biology, Inc. Volume 00, Number 0, Pages 1–14, 2019

**Keywords:** biopolymer, extracellular polymer, rhizosphere, polyanionic, biodegradable, biocompatible

## 1. Introduction

The microbial polymers are biocompatible and biodegradable in contrast with synthetic polymers. Therefore, the interest in the production of large quantity of known microbial

exopolysaccharide (henceforth EPS) by fermentation is boosted in the past few years [1]. The physiological role of EPS producing bacteria is very diverse, for instance, stress tolerance, protection against drying, grazing protozoan, bacteriophages, antimicrobial agents [2–4], and toxic metal ions [5] along with nutritional benefits like carbon source, chemoattractant, and surface active agent [6].

Bacteria have better EPS secreting ability as compared with fungi and algae [3]. Among which, in particular, Gram-positive *Bacillus* spp. are known to produce a high quantity of EPS. The *Bacillus subtilis* is adapted to the formation of biofilm, which is the intricate community of bacteria formed at air–liquid interface or solid surfaces [7]. The cells in the biofilm are held together by an extracellular matrix consists of amyloid-like fibers and an EPS [8, 9]. In aerobic organisms like *B. subtilis*, the energy created is reliant on the coupling efficacy of ATP synthesis and respiration. In the excess of carbon source, the respiration rate leads to high metabolic activity for the higher production of EPS [6]. The biofilm formation and porous nature of EPS help in the formation of stable colonies that mediate

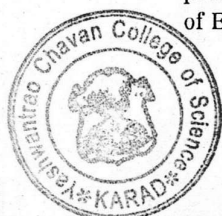
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## ON-TYPE SPATIAL POSTPOSITIONS IN MARATHI: A COGNITIVE SEMANTIC APPROACH

Arvind Jadhav

### Abstract

The present paper explores the linguistic encoding of ON-TYPE spatial relations in Marathi. The data is elicited from ten native speakers of Marathi using Bowerman & Pederson (1992) stimuli. Besides introspection as a method of analysis, Talmy's FIGURE/ GROUND and SCHEMATIC SYSTEMS are used for its analysis.

The ON-TYPE spatial relation is a generalized semantic relation denoting the ON-ness. It does not directly correspond to English preposition 'on'. It is demonstrated that the ON-TYPE spatial relations are encoded by the four postpositions in Marathi such as *war* 'on', *lā* 'to', *bhowati* 'around' and *sabhowati* 'surround'.

Factors such as FIGURE and GROUND geometry, PLEXITY, ANIMACY, ORIENTATION, BOUNDEDNESS, CONTACT, SUPPORT, PROXIMITY, ATTACHMENT as well as PROTOTYPICALITY, CONVENTIONALITY, PART-WHOLE relations and FORCE DYNAMICS are the significant factors which influence the use of postpositions in the spatial descriptions.

**Keywords:** cognition; cognitive semantics; spatial relations; Marathi postpositions; figure/ ground; Leonard Talmy; Bowerman & Pederson stimuli

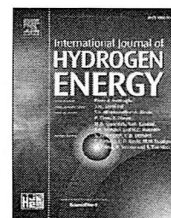
### 1. Introduction

Spatial cognition is an integral part of a comprehensive human cognition. Linguistic systems like linguistic structures and cognitive systems such as perception, attention, etc. are interdependent and complementary. These cognitive and linguistic systems play a vital role in spatial cognition.

The early attempts on spatial studies are seen in Gruber (1965); Clark (1968, 1973); Leech (1969); Catford (1969); Fillmore (1968); etc. In these studies, we find some common principles such as the distinction between static scenes and dynamic events, spatial and temporal relations, the linguistic representation and underlying conceptual structures, the relation between language and perception, etc. Later, Jackendoff

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## Co-generation of hydrogen and electricity from biodiesel process effluents

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### HIGHLIGHTS

- Application of external voltage to a microbial fuel cell (MFC) during acclimatization improves bioelectrogenesis.
- Dark fermentation with synthetic wastewater yields high H<sub>2</sub> production.
- Higher power generation is noted with crude glycerol (CG) dark fermentation effluent over CG.
- Enhanced performance of MFC is proved at an applied voltage of 0.8 V after 24 h acclimatization.

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### ABSTRACT

In this study, we apply a short-term voltage (0.2–0.8 V) to both crude glycerol (CG) and an anaerobic digestion (AD) effluent in a single-chamber microbial fuel cell (MFC) for power production. This improves the bioelectrogenesis in both CG (in MFC-1) and the AD effluent (in MFC-2), but higher power generation is attained in MFC-2. The use of domestic and synthetic wastewaters in the AD process leads to the generation of 195 and 350 mL H<sub>2</sub>/L-medium, respectively. MFC-2 performs better than MFC-1 in terms of both voltage generation and chemical oxygen demand (COD) reduction. The application of 0.8 V yields a power density of 311 mW/m<sup>2</sup> (1.94 times higher than that of the control (160 mW/m<sup>2</sup>)). In addition, MFC-2 exhibits a 70% COD removal at 0.8 V, which decreases to 56% at 0.2 V. Thus, the application of a short-term voltage in MFC can stimulate both bioelectrogenesis and COD removal.

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Abbreviations: CG, Crude glycerol; MFCs, Microbial Fuel cells; H<sub>2</sub>, Hydrogen; COD, Chemical oxygen demand; CV, Cyclic voltammetry; EIS, Electrochemical impedance spectroscopy; VFAs, Volatile fatty acids; AD, Anaerobic digestion; PD, Power density; DC, Direct current; NE, Net energy; PBS, Phosphate buffer solution; DW, Domestic wastewater; SW, Synthetic wastewater; PW, Petroleum wastewater; I, Current; V, Voltage; W, Power; Ω, Resistance; R<sub>oh</sub>, Ohmic resistance; R<sub>ct</sub>, Charge transfer resistance; R<sub>in</sub>, Internal resistance.

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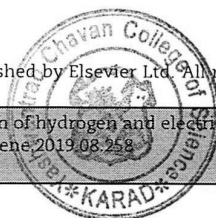
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# Prospective of *Monascus* Pigments as an Additive to Commercial Sunscreens

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## Abstract

Red and yellow pigments from *Monascus purpureus* (NMCC-PF01) were evaluated to enhance sun protection factor (SPF) of commercial sunscreens and *Aloe vera* extract. The extracted *Monascus* pigments contain rubropunctamine (red pigment) and the mixture of monascin and ankaflavin (yellow pigment) as major components. Antioxidant activity and *in-vitro* safety of the pigments were assessed by ferric reduction potential and DPPH radical scavenging assays, human keratinocytes (HaCaT), and erythrocytes (RBCs) cytotoxicity assay, respectively. In results, SPF of commercial sunscreens showed an increase of 36.5% with red pigment compared to the 13% increase by yellow pigment. The *in-vitro* studies showed 67.6% ferric reducing potential and 27% DPPH radical scavenging activity, neither cytotoxic effect against human keratinocytes nor haemolytic activity. These results confirmed the safe nature of the *Monascus* pigments; however, *in-vivo* studies merit further research. In conclusion, screened pigments from *Monascus purpureus* may act as potential candidates to increase SPF of commercial sunscreen naturally.

## Keywords

SPF, commercial sunscreens, *Monascus* pigments, antioxidant, *Aloe vera* extract

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Ultraviolet (UV) radiation can damage the skin by multiple modes like mutations in cell DNA, the formation of reactive oxygen species, changes in histochemistry of cell, increased expression levels of the p53 gene, and/or influencing the immune system.<sup>1</sup> Increased consciousness about skin exposure to ultraviolet radiation has tempted the use of commercial sunscreen products. The commercial sunscreen is generally composed of organic, inorganic UV absorbers like aminobenzoates, cinnamates, avobenzonone, oxybenzone, and oxides of zinc, titanium, iron. However, increasing side effects of some sunscreen components has made it indispensable to search for natural photoprotectants.<sup>2</sup> The most commonly utilizing sunscreen ingredients such as oxybenzone linked to sun exposure triggered allergic reactions, generating free radicals, which may be associated with cell damages.<sup>3,4</sup> While the nanoscale TiO<sub>2</sub> and ZnO are responsible for the generation of a substantial amount of reactive oxygen species, which upon UV illumination causes modifications in nucleic acid bases and eventually cell death.<sup>5,6</sup> Consequently, it is the need of an hour to look for other options to replace harmful components of sunscreens.

Nature is an abundant source of metabolites, considering the fact that UV damage is not only limited to humans but also to microbes. In continuation of our research on natural UV protectants,<sup>7</sup> we targeted pigments from *Monascus purpureus*, which are well known for their multifaceted use in food

coloration and range of other bioactivities. The selection of these pigments was rationalized on their variable bioactivity after linking with different amino acids.<sup>8</sup> This amino acid-based derivatization of *Monascus* pigments may change their absorption maxima in the UV region. Here we sought to study the ability of food-grade pigments from *Monascus purpureus* (NMCC-PF01) (i) to increase the SPF of commercially available sunscreens, (ii) evaluation of their antioxidant potential, and (iii) cytotoxicity testing on human keratinocytes and erythrocytes cells.

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