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Synergistic effect of sodium and yeast in improving the efficiency of DSSC sensitized with extract from petals of *Kigelia Africana*

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ABSTRACT

TiO_2 nanostructures with two different dopants, sodium and yeast have been successfully synthesized by hydrothermal method. Doping sodium is found to extend the absorbance of TiO_2 into the visible region as well as it acts as mordant in fixing and improving the absorption of dye. Yeast, as a dopant, can help in absorption of more anthocyanins from the natural dye extract by TiO_2 and also aids in retaining the colour of the dye and increases the stability of the dye at varying pH. Anthocyanins are the major class of pigment present in the newly addressed maroon, velvety and trumpet shaped flower "*Kigelia Africana*". X-ray diffraction analysis revealed the formation of rutile phase for all the samples. Field Emission Scanning Electron microscopy images revealed the formation of nanorods and nanoflowers with change in dopant as well as their concentration. The photoelectric conversion efficiency of DSSC with undoped TiO_2 photoelectrode is 0.87% and DSSC with 6% Na doped TiO_2 photoelectrode is 1.56%. The efficiency of DSSC with 6% Na + 6% yeast doped TiO_2 photoelectrode is found to increase from 2.09% (DSSC with 6% Na + 4% yeast doped TiO_2 photoelectrode) to 2.31% on varying the dopant concentration. Doping is also found to increase the dye absorption and superior charge transport efficiency which in turn helps to improve the performance of DSSC.

1. Introduction

DSSC sensitized with natural dyes are widely researched due to their large absorption coefficients in visible region, relative abundance, ease of preparation, and environmental friendliness [1,2]. Most importantly, DSSC involving natural dyes are cost effective and do not involve harmful and toxic elements like ruthenium. Generally, titanium dioxide (TiO_2) is employed as photoelectrode in DSSC due to its large band gap (3.1 eV), natural abundance, non-toxicity, low cost, chemical stability, extraordinary ability to oxidize photo-generated holes and suitable band edge levels for efficient charge injection [3,4]. The morphology of TiO_2 plays a vital role in determining the photoelectric conversion efficiency of DSSC [5]. Recently, one-dimensional (1D) nanostructures such as nanorods (NR), nanowires (NW), nanotubes (NT) etc are found to be more promising due to their enhanced electron transport phenomenon and also their ability to retard the recombination of electron-hole pairs by separating the photo-generated electrons and holes in opposite direction [3]. In particular, nanorods have the following advantages, (i) higher surface-to-volume ratio that guarantees a high density of active sites for surface reactions (ii) reduces the electron loss during the transfer of photo generated electrons (iii) high interfacial charge carrier transfer rate that can enhance the device efficiency [3,5].

Firstly, doping is found to be a promising method to tune the optical and electronic properties of TiO_2. Doping can (i) easily shift the absorption band edge and Fermi level of the material [6] (ii) effectively extend the absorption of TiO_2 from UV to visible region [7] (iii) improve the dye absorption and can lead to superior charge transport efficiency [8]. There are several dopants including alkali metals, metalloids, non-metals and transition metals that are used to dope TiO_2. Among the dopants, alkali metals consist of outer shell that contains an electron that can be easily donated. This property makes alkali metals like calcium, sodium, magnesium and lithium as good dopants for TiO_2. Amongst all alkali metals, sodium is chosen as the dopant as it is easily available in large quantities, cheap and non-hazardous. Moreover, to the best of our knowledge there is only limited literature available for sodium (Na) doped TiO_2 [9]. We have already reported on the synthesization of Na doped TiO_2 nanorods with different amount of sodium by hydrothermal method [3].

Secondly, sensitizer plays an important role in determining the performance of DSSC. There is a need for selecting a right sensitizer and natural dyes with anthocyanins as the major pigments are proved to be versatile in improving its performance. In our study, we have addressed

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the use of dye from a maroon and velvety flower *"Kigelia Africana"*. This dye has been reported for the first time in the literature and the results are encouraging. This dye is found to show good colour stability (visual examination) with time when compared to few other reported dyes that causes browning or formation of some kind of precipitates in the solution. The important chemical constituents present in the dye that contribute to the colour stability and improved performance of DSSC will be discussed in the forth coming sections.

From our previous work [10], the efficiency values obtained for 2%, 4% and 6% Na doped TiO_2 based DSSC was 1.09%, 1.36% and 1.56% respectively. Based on the efficiency results, we have chosen 6% of sodium as dopant concentration and with the aim to further improve the efficiency of DSSC, an attempt has been made to introduce one more dopant into the lattice of TiO_2. Yeast (Baker's yeast) has been chosen as the new dopant as there are no reports on yeast doped TiO_2 based DSSC. For the first time, we are reporting on the effect of co-doping sodium and yeast into TiO_2 and its effect in improving the performance of DSSC.

2. Choice and need of Na and yeast as dopant

The motivation behind doping is to improve the conversion efficiency of DSSC. The efficiency of DSSC can be improved with improved dye absorption by TiO_2. Doping of TiO_2 with sodium (Na) is believed to solve two issues. Firstly, doping Na is found to extend the absorption from UV to visible region and also tends to modify the morphology of nanostructures. Secondly, Na acts as mordant. Mordants are water soluble substances that combine with natural dye molecule by forming covalent and coordination bonds. It is believed that mordants are capable of fixing and improving the dye absorption by the film. The most important class of mordant includes tannic acid, sodium chloride, ferrous sulphate, stannous chloride etc. Amongst all, sodium chloride is found to be a safe mordant as it is easily available, non-hazardous and is a neutral catalyst that helps to speed up the dye uptake by the film [3,11]. The next dopant chosen in this study is yeast. The implication of doping yeast has two benefits. On one hand, yeast helps in absorption of more anthocyanins from the natural dye extract by TiO_2 which can help in enhancing the efficiency of DSSC. On the other hand, yeast can participate in certain interactions with pigments and forms stable anthocyanins on to the surface of TiO_2 [12,13]. These stable anthocyanins contribute to the colour stability of the dye and are stable at a wide pH range. Interactions of yeast with natural dye pigments will be discussed in the forthcoming sections.

3. Chemical constituents of *Kigelia Africana* and its significance in improving the performance of DSSC

Kigelia belong to genes of flowering plants in the family 'Bignoniaceae'. *Kigelia Africana* contains anthocyanins which are glycosides in which sugar molecule is bound to a functional group via a glycosidic bond. This functional group greatly contributes to the stability of the dye colour. Two predominant anthocyanin pigments; peonidin and peonidin-3-*O*-glycoside are derived pigments of cyanidin which has methoxy bonds on hydroxyl groups. These bonds are responsible of solubility of anthocyanins. Peonidin is responsible for the purplish-red colour of this flower. These peonidin derivatives are glycosides with acyl sugars attached at the positions 7 and 3′ of the basic ring. Strong intramolecular association between these molecules helps in maintain the stability of the flower extract without help of any other co-pigment or metal cation [19]. Chemical structures of (a) peonidin, (b) peonidin-3-*O*-glucoside and (c) complexation of anthocyanins with TiO_2 are shown in Fig. 1.

Like most anthocyanins, peonidin is sensitive to pH and changes from red to blue as pH increases. This is because most of the anthocyanins are conjugated chromophores and are most stable at varying pH values. When pH changes, the conjugation of bonds get altered and change in colour occurs. At pH 2, peonidin possess cherry red colour and changes to yellowish pink at pH 3. At pH 5, the peonidin is red-purple colour and at it becomes deep blue at pH 8. Then the colour changes to yellow on increasing the pH to 9. The significance of these chemical constituents in stabilizing the dye is described in detailed in our previous reports [10].

4. Materials and method

4.1. Materials

Titanium (IV) isopropoxide (Ti $[OCH(CH_3)_2]_4$, 97% purity), Hydrochloric acid (HCl, 98% purity), Sodium Hydroxide (NaOH, 98% purity), Sodium Chloride (NaCl, 98% purity) and Baker's yeast were used as precursors for the synthesis of undoped and doped TiO_2 nanostructures. All the chemicals used in this study were purchased from Sigma-Aldrich and used without any further purification. FTO (fluorine doped tin oxide) of sheet resistance 7 Ω/□, iodide-triiodide (0.6 M tetrapropylammonium iodide, 0.1 M iodine, 0.1 M lithium iodide, 0.5 M 4-*tert*-butylpyridine (TBP) in 3-ethoxypropionitrile) electrolyte and platinum coated glass was used for the fabrication of DSSC.

4.2. Method

In this experiment, undoped and doped TiO_2 nanostructures have been fabricated by hydrothermal method. Initially, FTO substrates were cleaned ultrasonically using soap solution, distilled water, acetone and ethanol for 10 min and finally dried.

4.2.1. Synthesis of undoped TiO_2 nanostructures

For the preparation of undoped TiO_2 nanostructures, required quantity of HCl and deionized water was mixed and stirred for 10 min. Then Ti $[OCH(CH_3)_2]_4$ was added as droplets to the stirring mixture and stirred for another 10 min. Then the solution was transferred into teflon-lined stainless steel autoclave (50 mL) with substrates pre-loaded into it. The autoclave was sealed and hydrothermally treated in a muffle furnace at 170 °C for 4 h. At the end of growth time, the autoclave was cooled down to room temperature and the samples were washed with deionized water several times and dried at room temperature overnight.

4.2.2. Synthesis of Na-doped TiO_2 nanostructures

Typically, required quantity of HCl and deionized water was mixed and stirred for 10 min. Ti $[OCH(CH_3)_2]_4$ was added as droplets to the stirring mixture and stirred for another 10 min. Finally, to synthesize Na doped TiO_2 nanostructures, 6% of NaCl salt was dissolved with required amount of distilled water and added to the mixture and stirred again for 30 min. The solution was then transferred into teflon-lined stainless steel autoclave (50 mL) with substrates pre-loaded into it. Then the autoclave sealed and hydrothermally treated in a muffle furnace at 170 °C for 4 h. After the growth time, the autoclave was cooled and the substrates were washed and dried.

4.2.3. Synthesis of Na and yeast-doped TiO_2 nanostructures

For the synthesis of Na and yeast-doped TiO_2 nanostructures, 200 mg of yeast was washed with distilled water followed by ethanol and dried at 70 °C for 0.5 h. In a separate beaker, required quantity of yeast was taken and necessary amount of ethanol was added to it. The mixture was stirred for 20 min. Then, 6% of NaCl salt was dissolved with required amount of distilled water and added to the mixture. Finally, Ti $[OCH(CH_3)_2]_4$ was added as droplets. After 1 h of stirring, 0.01 M NaOH was added to the mixture till the pH of the solution becomes somewhere around 3.5–4. Stirring was continued for another 0.5 h to allow the solution achieve homogeneity and then transferred into 50 mL autoclave with substrates pre-loaded into it. The autoclave was sealed and hydrothermally treated at 150 °C for 4 h. The samples were cooled, washed and again dried at 70 °C for 10 min.