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Challenges in Biochemical Engineering and Biotechnology for Sustainable Environment

Albizia saman: A Green Route for the Reduction of Bulk TIO₂

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Abstract : Recently, Metal oxide nanoparticles have been paid much attention as they are possessing fascinating properties such as semiconducting, photovoltaic, photocatalytic, magnetic, electronic and antimicrobial activity. This is due to their high fraction of atoms and their high surface area. Each and every nanoparticle differs in their size, shape, composition and crystalline nature. Among the metaloxides, TiO₂ has its applications in degrading dyes and in purifying water. In this present investigation, an eco-friendly method was adopted to reduce the bulk TiO₂ to nanoscale by using the aqueous leaf extract of *Albizia saman*. The reduced particle was characterized by performing XRD. The average grain size formed after the bioreduction was determined by using the Scherrer's formula, $d = 0.89\lambda / \beta \cos\theta$. The estimated size for the bulk TiO₂ was 79nm whereas the bioreduced TiO₂ nanoparticle possessed the grain size of 41nm. The bioreduced TiO₂ should be explored for its potential applications in the future.

Keywords: Metaloxide nanoparticles, TiO₂, Albizia saman, Bioreduction, XRD

Introduction

Nanotechnology is one of the growing interdisciplinary areas covering all fields of science and technology. Now-a-days, nanoparticles made its foot prints in most of the applications as they possess considerable surface area to volume ratio. This determines their characteristics properties such as catalytic, mechanical, thermal, antimicrobial, degrading dyes, etc.

Metaloxides plays a critical role in major areas of physics, chemistry and material science¹. Particles in bulk materials are highly unstable as they possess high surface free energy. Those particles once synthesized as individual nanostructure may have low surface free energy, which makes them to acquire structural stability. Such stability has been found in TiO_2 and few more metal oxides.

 TiO_2 are versatile metal oxide as they have wide range of applications from sunscreen lotions to wall paints. Apart from the commercial applications, they too possess biological applications, which includes degradation of organic dyes such as ethidium bromide in aqueous solution², anthraquinone dye³, organic pesiticidal pollutants like aldicarb⁴, Alachlor and Fenitrothion⁵, penicillin in water⁶, etc.,

Generally, Metal and metaloxide nanoparticles can be synthesized by physical and chemical methods. But, both the methods employs the usage of expensive substrate, higher temperature, higher pressure and also results in the generation of harmful end products. To overcome such complications, there should be an alternative method, which should be cost effective, easy to handle, simple to perform and should result in the environmentally benign by products. Such conditions can be fulfilled by the diversified presence of microbial and plant sources on our planet. Synthesizing nanoparticles using the plant system is currently under exploitation as the method does not cause lethal effects to the environment. Few researchers has been reported the biosynthesis of TiO_2 nanoparticles using the leaf extract of *Nyctanthes*⁷, *Eclipta prostrata*⁸, *Cantharanthus roseus*⁹. *Albizia saman* is a rain tree, which is not so far exploited for the green synthesis of TiO_2 nanoparticles. This tree exhibits antioxidant, antiplasmodial and cytotoxic properties^{10,11,12}. It was reported that its aqueous leaf extract contains tannins, flavonoids, saponins, steroids, cardiac glycosides and terpenoids¹³. The as-said extract was validated for antimicrobial activity against *E. coli, S. aureus* and *C. albicans* and the investigated data has confirmed their activity¹³. Such tree can be used for the green synthesis of metaloxide nanoparticles. Hence, the present work was focused to utilize the leaves of *A.saman* as a considerable source to bioreduce bulk TiO₂.

Materials and methods

Collection and processing the leaves of A.saman



Fig. 1(a)Fig. 1(b)Fig. 1(c)Fig. 1(d)Fig. 1(a): Fresh leaves of Albizia saman, Fig. 1(b): 5mM TiO2 solution, Fig. 1(c): Aqueous leaf filtrates of
Albizia saman, Fig. 1(d): Dirty, white deposits of TiO2 nanoparticles

The fresh leaves of *A.saman* were collected in a polythene bag from the university campus of Sathyabama and were processed in the university laboratory. As an initial step, the leaves were washed thoroughly in running tap water and were rinsed with sterile distilled water twice. The spills of water were blotted and dried for 2-3 minutes. Then, the leaves (Fig 1(a)) were used for preparing the aqueous extract.

Preparation of 5mM TiO₂ solution

0.039 g of TiO₂ was weighed and it was mixed in 100 ml of distilled water in 250 ml Erlenmeyer flask. The preparation was mixed and swirled properly. The flask was then plugged with non-absorbent cotton, covered with aluminium foil and stored at 4^oC for future use (Fig 1(b)).

Preparation of aqueous leaf filtrate of A.saman

About 2gms of leaves were taken and were homogenized in mortar and pestle by adding 5 ml of distilled water .The resultant solution was made upto 20 ml and was kept in the water bath at 65° C for 30 minutes. The solution was filtered using whatmann no.1 filter paper and the resulting filtrate (Fig 1(c)) was used for the bioreduction of bulk TiO₂.

Bioreduction of TiO₂ nanoparticles

The leaf filtrate was taken in an Erlenmeyer flask and TiO_2 solution was added in drops under constant stirring at room temperature. Then, the mixture was left in the magnetic stirrer at 50^oC for 24 hours.

Characterization of TiO₂ nanoparticles

The TiO_2 solution treated with the aqueous leaf extract of *A. saman* was observed after 24 hrs. There was a change of colour from milky white to dirty, white deposits. In order to confirm the as so formed nanoparticle, the sample was subjected to XRD measurements.

Results and Discussion

The aqueous leaf extract of *A. saman* was mixed with 5mM TiO_2 solution. To which, a magnetic pellet was added and kept on the magnetic stirrer for the reduction of TiO₂. During the reaction, the milky coloured TiO₂ solution was gradually changing its colour to dirty-white deposits (Fig 1(d)).

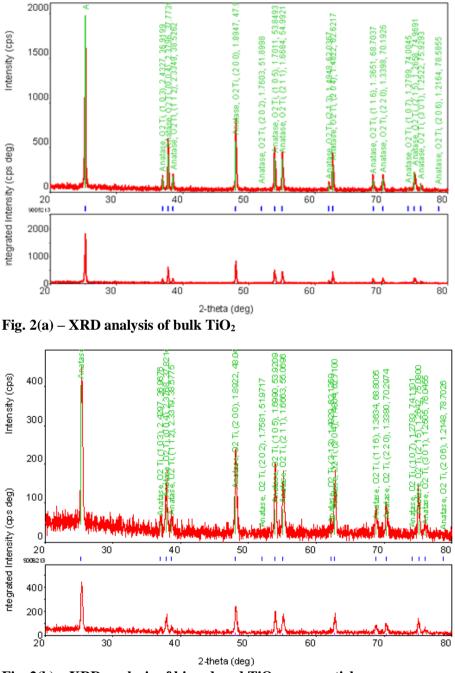


Fig. 2(b) – XRD analysis of bioreduced TiO₂ nanoparticles

The bulk TiO₂ as well the bioreduced TiO₂ nanostructure synthesized by employing the aqueous leaf filtrate of *A.saman* were characterized with the aid of X-ray diffraction measurements. The bulk TiO₂ showed crystalline nature with 2θ peaks lying at $2\theta = 25.347^{\circ}$ (Fig. 2(a)) and at 25.257° (Fig. 2(b)) for the bioreduced TiO₂ nanoparticles. The preferred orientation corresponding to the plane (101) is observed in the TiO₂ NPs. The result is in same proximity with the XRD peak at $2\theta=25.25^{\circ}$ (101), which confirm the characteristic facets for anatase form of TiO₂ [14].

All the peaks in the XRD pattern can be indexed as anatase phase of TiO₂ and the diffraction data was in good agreement with the COD (Crystallography Open Database) file no. 9008213. The crystalline size was obtained by Debye-Scherrer's formula, which is given by the equation, $d = k\lambda / \beta \cos\theta$, Where, d = crystal size,

 λ = wavelength of the x-ray radiation (λ = 0.15406nm) for CuK_a. k is normally considered as 0.89 and β is the line width at half-maximum height.

The crystallite size obtained by using this formula ranged between 34nm and 58nm for the bioreduced TiO_2 nanoparticles whereas in the case of the bulk TiO_2 nanoparticles, the size was ranged between 68nm and 83nm. The average grain was estimated as 41nm for the bioreduced TiO_2 nanoparticles and 79nm for the bulk TiO_2 nanoparticles. The aqueous leaf extract of *Eclipta prostrata* mediated synthesis of titaniumdioxide nanoparticles ranged from 36 to 68nm with an average grain size of 49.5nm [9].

The sharp peaks confirmed the crystallinity of the bulk TiO_2 as well the bioreduced TiO_2 nanoparticles. The unidentified peaks assured the absence of other biomolecules in the aqueous plant extract, which in turn indicates the purity of the bioreduced nanoparticles.

Conclusion

The current study suggests that the aqueous leaf filtrate of *A.saman* can be used to bioreduce the bulk TiO_2 nanoparticles even less to nanoscale level as the method is simple, easy and eco-friendly. Further, these TiO_2 nanoparticles should be subjected to SEM and FTIR analysis in order to find out the surface topography and the biomolecules of leaf filtrate involved in the reduction reaction respectively. The potential application of nano sized TiO_2 nanoparticles should be explored in the near future.

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