Investigating photocatalytic activity of titania coated fresh water diatom frustules by the degradation of polluting dye

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Abstract: ***Silica frustules of diatoms contain nanoscale pores arranged in periodic order. In this report we have synthesized TiO_2 nanoparticles coated diatom frustules followed by annealing at 500ºC. The as synthesized DT500 catalyst is characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM) and EDX. UV-visible spectroscopy is performed to analyze the band gap (BG) energy of the material which is found to lie in the visible light range. The photocatalytic properties of the catalysts are investigated via typical polluting dye as a model organic compound under visible light irradiation. The as synthesized DT500 catalyst contains anatase phase of titania exhibited more light absorption in the visible region and found to have higher photocatalytic efficiency due to morphology of frustules and TiO_2 coating.***

Keywords: diatom frustules, photocatalysis, bandgap, anatase phase.

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1. Introduction

Dyes are one of the most discarded impurities for aquatic environment due to its direct dumping into the water bodies in a large amount by the industries. Some of them are non-self-biodegradable and toxic. Malachite green (MG) is a triphenyl methane dye used as fungicide, Parasilicide, disinfectant agent in aqua culture industries. It is also widely used in silk, wool, jute, cotton, paper, staining biological agents [1, 2]. Researchers reported that it is highly toxic to mammalians cells and may cause problems in fertility [3]. It is mutagenic and carcinogenic. MG can react with sunlight, when released into water bodies, reduce photosynthetic activity and conclusion of dissolved oxygen, and hence disturb ecological balances [4]. Thereby, effective removal of MG from water sources is of great importance. To improve the efficiency and effectiveness of water cleaning processes several physical, chemical techniques have been used. Most of the techniques are very costly, less efficient and put some undesirable effect on the environment. All of them, photocatalysis is quite promising as it is eco-friendly, low cost, light is used as energy-source to operate the reaction, that is much more green. Photocatalysis process has applications in the area of renewable energy as a photocatalyst can be used to split water into hydrogen and oxygen for energy purpose [5]. As photocatalyst various traditional semiconducting materials TiO_2, WO_3 are studied [6]. The benchmark material in the field of photocatalysis TiO_2, the BG of which lie in the UV range, so can utilize 5% of the whole solar energy [7]. In this work we have used diatoms; naturally available unicellular microscopic algae possess amorphous porous silica skeleton called frustules as template for coating of titania phases, which has periodic nano pores and can control light propagation [8] and utilize a wide range of solar radiation [9]. Taking MG as a model dye the as prepared titania coated diatom frustules is used as a catalyst that perform catalysis under visible light more efficiently instead of UV light irradiation.

2. Materials and Methods:

2 Synthesize of anatase phase diatom templates:

We collect diatom species from fresh water bodies and cultured those species using WC media [10]. After one month the diatoms are separated from the media and cleaned with distilled water. The diatoms are then immersed in gluteraldehyde solution. Titania coating is carried out by the sol-gel method [11]. 5% solution of titanium tetra isopropoxide (TTIP) in isopropanol is prepared. After that the cleaned diatom frustules are added in the slowly stirred TTIP solution. Next the samples are filtered, dried in air

and there after calcined at 500ºC. The final product was labeled as DT500.

Photocatalytic degradation of MG is done by adding 20mg of prepared photocatalyst (DT500) in 100ml of 30µM MG solution and stirred in the dark for 10h. There after the solution mixture is exposed under visible-light irradiation. At every 10 minutes during the photodegradation process, 9ml of MG suspension is taken out and centrifuged for 12mint at 7000rpm to remove the catalyst particles from the dye solution. From this we take 4ml of the aliquot for further analysis.

3 Characterization details

The morphology, identification and classifications of microbiological organisms are studied using Scanning electron microscopy (SEM) (make: JEOL JSM-6390LV scanning electron microscope). The XRD patterns of the samples are collected using a diffractometer (make: RIGAKU MINIFLEX diffractometer) with Cu-Kα radiation (λ=1.5405 A0) for structural analysis. The optical absorption spectra of diatom samples are obtained using a UV visible absorption spectrophotometer (make: UV 2450, Shimadzu Corporation). A 500W visible light source is used for irradiation purpose (Make: Xenon Lamp Zolix SLH- X500 Xenon Arc Light Source) Photocatalysis.

3. Results and discussions

2 SEM analysis

Figure 1 (a, b) show the SEM images of raw and titania coated diatom frustules. Diatoms are belonged to Achnanthidium eutrophilum species [12] having elliptical shape valves. The middle portion of the valves are slightly widen with a narrow linear axial area. Pores are elliptical and arranged in regular order with average length 164.6nm. This species of diatom cells are about 13µm to 15µm in length and their thickness is about 2µm to 2.5µm.

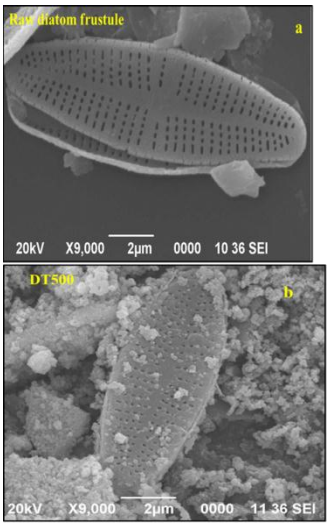

Figure 1: SEM micrographs of (a) raw diatom frustule and (b) DT500

3 EDX analysis

The SEM-EDS spot analysis has confirmed that diatom frustules are mainly composed of silica (figure 2a). The quantitative elemental analysis showed that Si in the form of SiO_2 was the major constituent of diatom frustules. EDX spectra (figure 2b) also confirmed the presence of Ti in DT500 catalyst.

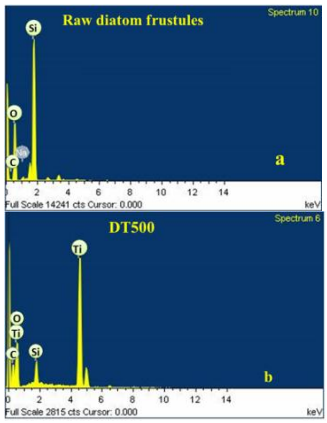

Figure 2: Energy dispersive X-ray spectra of (a) Raw diatom frustules and (b) DT500

4 XRD analysis

The structural phases of the prepared samples are studied by X-ray diffraction. The diffraction pattern of DT500 and raw diatom frustules is demonstrated in figure 3. For DT500 peaks at 25.34º, 38.01º, 48.09º, 53.9º, 55.199º, 62.78º and 68.91º correspond to diffraction planes (101), (112), (200), (105), (211), (204) and (116) (compared to JCPDS NO. 89-4921). We did not find any distinct peak for raw frustules.

This corresponds to the amorphous structure of silica. The average crystallite size is calculated to be 13.9nm for DT500, determined from diffraction peaks by using Debye-Scherer's formula.

$$D = \left(\frac{K\lambda}{\beta \cos\theta} \right) \quad \text{(Debye - Scherer's formula)} \qquad 1$$

where λ is the wavelength of X-ray radiation (Cu Kα = 0.15406), K is a constant (taken as 0.91), β is the full width at half maximum height (FWHM) of the peak, and θ is the diffraction angle.

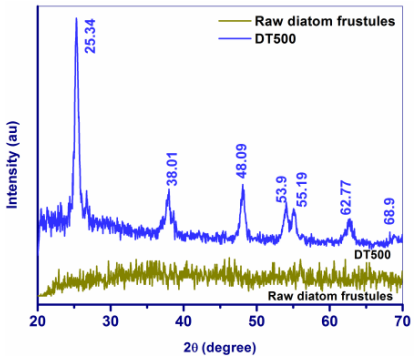

Figure 3: X-ray diffraction pattern of DT500 and raw diatom frustule.

5 UV analysis

The UV-visible absorption spectra of DT500 and raw diatom frustules are shown in figure 4. Titania coated diatoms shows significant increase in light absorption with higher intensity in the visible range compared to UV range absorption in raw frustules. Absorption near 350nm for DT500 is due to the band to band transition from Ti-3d levels to O-2p levels [13]. The increase in light absorption in the DT500 is due to diatom frustules because calcined diatom frustules can absorb light from ultra violet to far visible range [11]. In fact, absorption edge increase to visible range with higher absorption intensity is the vital factor to increase the number of electron-hole pairs on the surface of photocatalyst that improved photocatalytic activity [14].

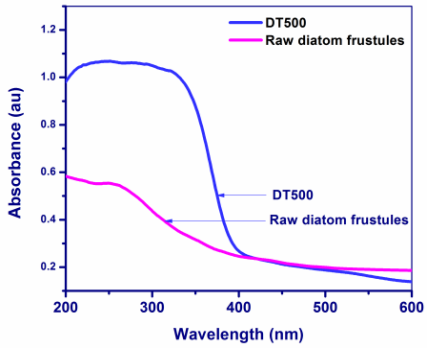

Figure 4: UV-visible absorption spectra of DT500 and raw diatom frustules

6 Determination of optical BG of the material

The optical BG can be calculated from diffuse reflectance spectrum using Kubelka-Munk (KM) plot. The BG of the material is estimated by extrapolating the straight line in the plot of $[F(R)h\nu]^{1/2}$ vs hν [13] where F(R) is KM function. The calculated bandgap value for DT500 is 3.08eV (figure 5).

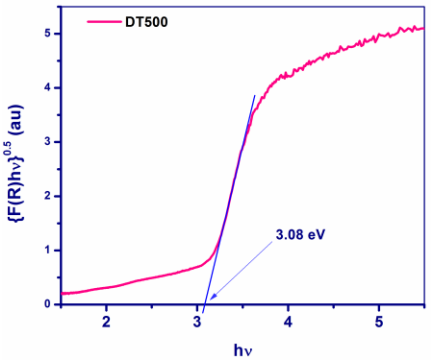

Figure 5: KM plot for BG determination.

7 Photocatalytic degradation measurement of MG

The photocatalytic activity of the as-synthesized materials is studied by observing the degradation of absorption peak in UV-Vis spectra of MG under visible light irradiation using DT500 catalyst. The absorption spectra of MG in presence of DT500 under visible light irradiation are shown in figure 6. The spectrum ranges from 520nm to 700nm with maximum absorption at wavelength 616nm. The characteristic absorption peak intensity of MG

decreases with the increase of irradiation time. At 60 minutes of irradiation, the degradation of MG becomes about 97% where the absorption peak is almost vanished.

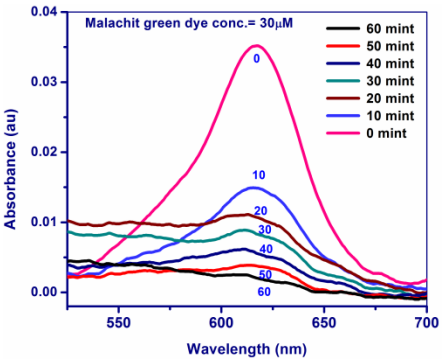

Figure 6: absorption spectra of MG by DT500 under visible light irradiation

In the photocatalytic process, the catalysts absorb light and electrons and holes are generated and combine with water and OH-group and water dissolved oxygen get adsorbed on different active sites of the photocatalyst to form the hydroxyl radicals and super oxide anions. These hydroxyl radicals and super oxide anion act as the potential agents in the photodegradation process [15]. Here we use diatom as template for coating of titania phases. Diatom frustules contain regular pores. The inner chamber of these pores can trap dye molecules when the molecules pass through them. So the coated titania inside the chambers of the frustules can react with dye molecules and degrade them more effectively.

The mechanism of the photodegradation of MG by using our as prepared catalysts is proposed as follows:

$$DT500 \xrightarrow{h\upsilon} DT500(e^-, h^+) \quad 2$$

$$h^+ + H_2O \rightarrow H^+ + \bullet OH \text{ (hyper-reactive hydroxyl free radical)} \quad 3$$

$$e^- + O_2 \rightarrow \bullet O_2^- \quad 4$$

$$MG + \bullet OH \rightarrow \text{Degraded products} \quad 5$$

$$MG + \bullet O_2^- \rightarrow \text{Degraded products} \quad 6$$

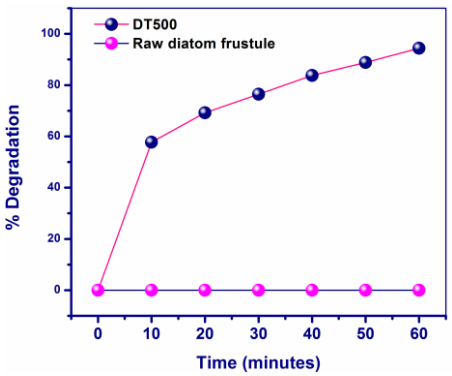

Figure 7: Degradation curve of MG under visible light irradiation

The degradation efficiency is calculated using the following formula:

$$\%D = \left(\frac{A_0 - A_t}{A_0}\right) \times 100\% \quad 7$$

where A_0 is the initial absorbance and A_t is the absorbance at time t. The photocatalytic performances of DT500 under visible light were evaluated by degradation of MG. In figure 5, the percentage of degradation of the catalysts in various degradation time is shown. 97.38% of

degradation was observed for DT500 after 60 minutes irradiation time. The photocatalytic activity is also performed using raw diatom frustules but no degradation is observed which revealed the enhanced efficiency of DT500 as catalyst .

4. Conclusions

The coating of titania nanoparticles in the pores of diatom frustules is successfully performed by using simple sol-gel techniques. In the photodegradation experiments, titania coated diatom frustules show photocatalytic activity, with about 97% dye degradation within 60minutes. As diatoms are naturally occurring species and there is no harm in using TiO_2 nanoparticles, the process is a promising way to degrade polluting dyes with minimal cost.

5. References

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