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Structural, Morphological and Antibacterial Activity of Kaolinite/TiO_2 Nanocomposites

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ABSTRACT

The development of rapid and reliable processes for the synthesis of nanomaterial is of great importance in the field of nanotechnology. In this paper, the synthesis of kaolinite/TiO_2 nanocomposite was carried out by using solvothermal method. The obtained nanocomposite was characterized by using XRD, SEM, TEM and UV-Vis absorption spectroscopy. The XRD pattern reveals that in the course of composites formation, kaolinite/TiO_2 nanocomposites containing the anatase phase of TiO_2 were found. The spherical morphology of kaolinite/TiO_2 nanocomposites were observed in SEM and TEM analysis. The UV absorption edges exhibited a blue shift, which might be caused by nanosize effect. The nanocomposites size can be calculated from Debye-Scherrer's formula. The antibacterial assay of synthesized nanocomposites was studied with the three bacterial pathogens viz., *Staphylococcus aureus, E. coli* and *Micrococcus luteus.*

1. Introduction

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range (1 nm = 10^{-9} m) [1]. Nanocomposite materials have emerged as suitable alternatives to overcome limitations of microcomposites and monolithics, while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase. They are reported to be the materials of 21st century in the view of possessing design uniqueness and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached [2], even though the first inference on them was reported as early as 1992 [3]. Nanomaterials often have a significant degree of difference in physico-chemical and biological properties to their macroscale counterpart in spite of the similar chemical composition they possess [4, 5]. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposites will differ markedly from that of the component materials [6]. In this work, kaolinite selected as the clay. Kaolin is one of the clay materials widely used for a large number of applications such as in ceramics, papercoating, paper filling, paint extender, rubber filler, cracking catalyst or cements, oil refinery and water treatment [7-10]. Kaolinite is a clay mineral with chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet of being linked through oxygen atoms to one octahedral sheet of alumina [11]. They have varying chemical composition depending on both physical and chemical changes in the environment where they are found. The industrial utilization of kaolinite is closely related to its reactivity and surface properties and depends strongly on surface modification. Several methods have been suggested in literature to improve the properties of clay materials with thermo-chemical treatment or chemical activation [12]. In Nature, titanium dioxide exists in three primary phases – anatase, rutile, and brookite – with different sizes of crystal cells in each case [13]. The popularity of titanium dioxide in materials sciences began with the first photocatalytic splitting of water in 1972 [14]. However, in recent years TiO_2 has been used widely for the preparation of different types of nanomaterials, including nanoparticles, nanorods, nanowires, nanotubes, and mesoporous and nanoporous TiO_2 containing materials [15]. Regardless of scale, TiO_2 maintains its photocatalytic abilities, and in addition, nanoscale TiO_2 has a surface reactivity that fosters its interactions with biological molecules, such as phosphorylated proteins and peptides [16], as well as some nonspecific binding with DNA [17]. In this paper, synthesis characterization and antibacterial activity of kaolinite/TiO_2 nanocomposites were studied.

2. Experimental Methods

Clay-water dispersion (1% w/w) was stirred for 2 hours. An aliquot of TiO_2 sol was added to the dispersion, to obtain a final TiO_2 content of 70% w/w. The slurry was stirred for 24 hours. The resulting dispersion was centrifuged at 3,800 rpm for 10 minutes. The solid phase was washed with ultrapure water followed by triplicate centrifugation. The resulting clay-TiO_2 composite was dispersed in 1:1 water: ethanol solution, prior to hydrothermal treatment in an autoclave at 180 °C for 5 hours. The product was centrifuged once again at 3,800 for 15 minutes, and oven-dried at 60 °C for 3 hours.

2.1 Instrumental Characterizations

For determination of crystallite size, Scherrer analysis of XRD is commonly used. XRD measurements are performed using a Philips diffractometer of 'X'pert company with mono chromatized Cu K0α (λ=1.54060 Å) radiation. A double beam UV-Vis (Jascow-500) spectrophotometer with 1 mm optical path length quart cells was used for all absorbance measurement in the range of 200 nm – 800 nm. SEM image was obtained with HITACHI-S-3400H model. The transmission electron microscopy (TEM) analysis performed using a Philips CM-200 electron microscope with operating voltages 200 KV, resolution 2.4 Å.

2.2 Agar Well Diffusion Assay

The antimicrobial activities of the clay/TiO_2 nanocomposite species were checked by using agar well diffusion method [18]. *Staphylococcus aureus, E. coli* and *Micrococcus luteus* were diluted in saline solution. A sterile swab was dipped in the diluted cultures and spread over the nutrient agar plates and wells were made in the inoculated agar medium using a sterile well puncher (6 mm in diameter) and different concentrations of the nanocomposite supernatants were pipetted out into the wells. The agar plates were incubated at 30 °C for 24 hours, after which 30 minutes of inhibition were observed and measured.

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3. Results and Discussion

3.1 XRD Analysis

The XRD pattern of the kaolinite/TiO_2 nanocomposites obtained by solvothermal method is shown in Fig.1. The diffraction peaks in Fig.1. is sharper and stronger at 25.5°, 37.8°, 47.9°, 53.59° and 62.36° were assigned to the (101), (004), (200), (105) and (204) planes. All the peaks in the XRD pattern can be indexed as anatase phases of TiO_2 and diffraction data were in good agreement with JCPDS file 21-1272 [19]. The size of nanocomposites was estimated using the Debye-Scherrer's formula. (Eq.1).

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

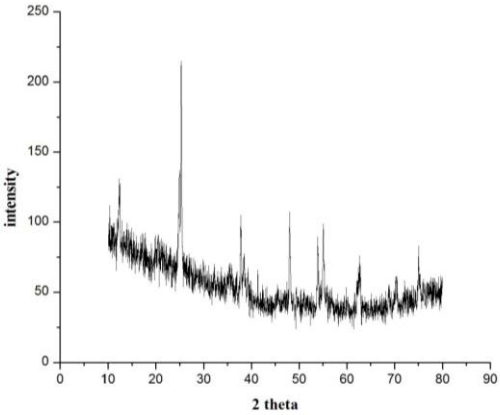


Fig. 1 XRD pattern of kaolinite/ TiO_2 nanocomposites

Where, D is the average crystallite size, β is the full width at half maximum (FWHM) of diffraction peak, λ (1.5418 Å) is the wavelength of X-ray radiation and θ is the angle of diffraction. The crystalline size was obtained as 81.61 nm.

3.2 SEM Analysis of Kaolinite/TiO_2 Nanocomposites

SEM was used to investigate the surface morphology of kaolinite/TiO_2 nanocomposites. The SEM image of the nanocomposites is shown in Fig. 2. has roughly spherical spongy shape and agglomeration nanocomposites. The SEM image of the studied sample proved matrix consisting of micro-sized kaolinite particles having layered structure with sub-micron particles of TiO_2 attached on the surface of the clay matrix.

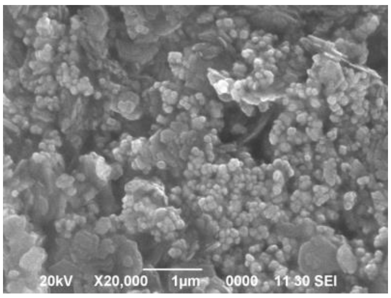


Fig. 2 SEM image of kaolinite/TiO_2 nanocomposites

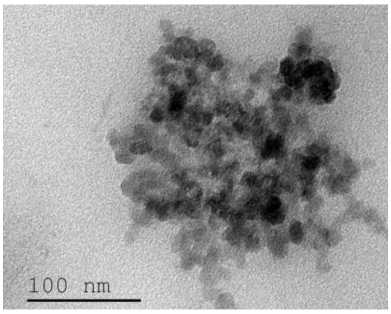


Fig. 3 TEM image of kaolinite/TiO_2 nanocomposites

3.3 TEM Analysis of Kaolinite/TiO_2 Nanocomposites

The transmission electron spectroscopic analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. Fig. 3 shows a typical TEM image of the kaolinite/TiO_2 nanocomposites. It can be seen that the particles exhibit a relatively uniform particle size distribution [20]. The average size of the nanocomposites estimated from the TEM image is around 50 nm.

3.4. UV-Vis Absorption Spectroscopy

UV-Vis absorption spectrum of kaolinite/TiO_2 nanocomposites is shown in Fig. 4. It is a useful absorption characterization to analyze nanomaterials. The UV-Vis spectral analysis was carried out between 200 nm and 800 nm. The absorption spectroscopy is very useful to calculate the optical band gap (E_g) with the help of the following equation [21].

$$\alpha = \frac{k(h\nu - E_g)^{n/2}}{h\nu} \quad (2)$$

Where, $h\nu$ is the photon energy, α and n are constants. Where n is 2 for direct energy gap and ½ for an indirect energy gap.

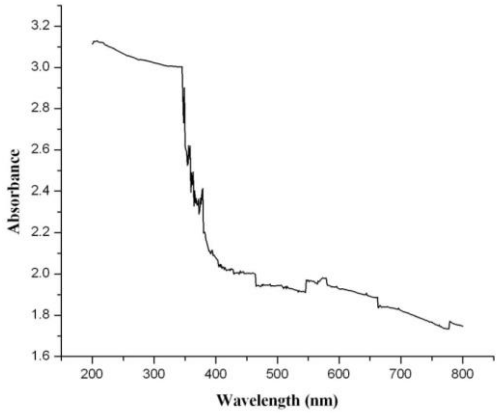


Fig. 4 UV-Vis absorption spectrum of kaolinite/TiO_2 nanocomposites

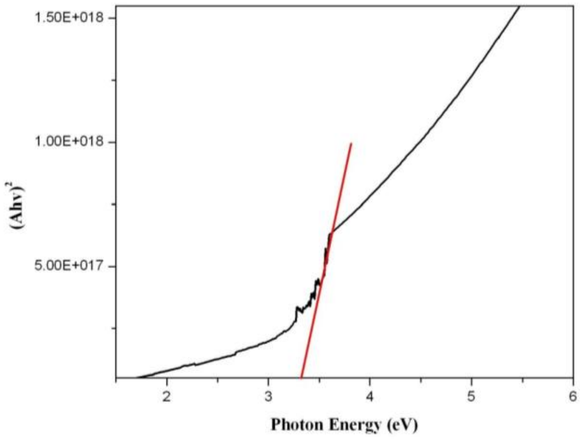
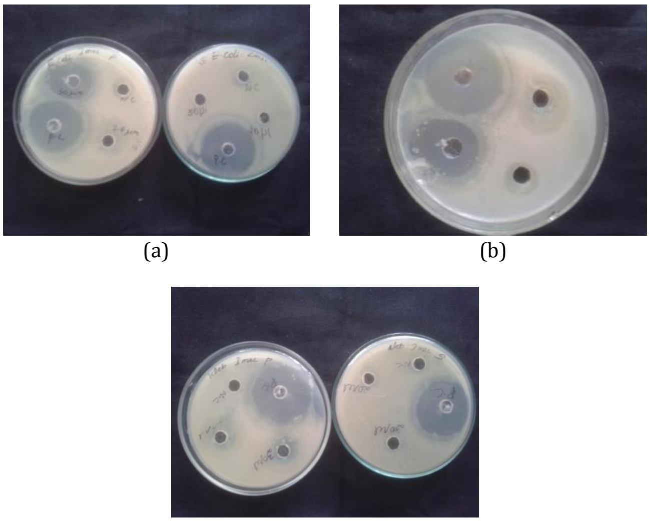


Fig. 5 Band gap energy of kaolinite/TiO_2 nanocomposites

The absorption edge is shifted to a higher energy (blue shift) and the corresponding band gap 3.3 eV for kaolinite/TiO_2 nanocomposites, which is shown is Fig. 5. The band gap energy of as prepared kaolinite/TiO_2 nanocomposites (3.3 eV), which is larger than the value of 3.2 eV for the bulk TiO_2. This can be explained because the band gap of the semiconductor has been found to be particle size dependent [12]. This nanocomposites is blue shifted (higher energy) when compared with the bulk TiO_2. The blue shift might be caused by nanosize effect and structural defect of nanomaterials [21].

3.5 Antibacterial Activity

Fresh cultures (24 h) of *Staphylococcus aureus, E. coli* and *Micrococcus luteus,* were diluted in saline solution. A sterile swab was dipped in the diluted cultures and spread over the nutrient agar. Wells were made in the inoculated agar medium, using a sterile borer (6 mm in diameter) and 30 μL of the nanocomposite supernatants were pipette into the wells. The agar plates were incubated at 30 °C for 24 hours, after which zones of inhibitions were observed and antimicrobial activity was measured in terms of zone of inhibition (mm). Antimicrobial activity of the antibiotic showed a clear inhibition zone in the media seeded with *S. aureus* (19 mm), *M. luteus* (20 mm) and *E. coli* (24 mm).



(a) (b)

(c)

Fig. 6 Antibacterial effect of nanocomposite against a) E. coli, b) M. luteus and c) S. aureus

4. Conclusion

In conclusion, the kaolinite/TiO_2 nanocomposites have been successfully synthesized by using solvothermal method. The material is characterized using various analytical tools like XRD, SEM, TEM and UV-Vis absorption spectrum. XRD result reveals that the presence of anatase phase of TiO_2. The size and morphology of the samples were characterized using scanning and transmission electron microscopy (SEM and TEM). Scanning electron microscopy proved the roughly spherical sponge shape and agglomeration nanocomposites. It is confirmed that the TiO_2 are bound onto the kaolinite surface. Transmission electron spectroscopy showed that the particles exhibit a relatively uniform particle size distribution. The band gap energy of this composite is 3.3 eV, which is larger than the value of 3.2 eV for the bulk TiO_2. This nanocomposites is blue shifted (higher energy) when compared with the bulk TiO_2. Antibacterial assays using three bacterial found the samples to have antibacterial potency. *E. Coli* has more antibacterial potency than the other bacteria.

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