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Photocatalytic decomposition of A549-lung cancer cancer cells by TiO_2 nanoparticles

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ABSTRACT

A novel, less time consuming and cost ineffective Wet chemical technique (WCT) was used to synthesis TiO_2 nanoparticles at relatively low temperature, in acidic pH, using Titanium tetra isopropoxide (TTIP) as a precursor. The synthesized nanoparticles were characterized by XRD, SEM, TEM, and Uv–Visible spectroscopy. The results shows that the particle size from 17 nm to 14 nm. The Uv–Visible spectra show that blue shift was observed in TiO_2 nanoparticles. The TEM images revealed that all the particles were in nanometer size. The synthesized nanoparticles shows good photocatalytic activity and it decompose 85% of A549 (lung cancer) cells in 4 h reaction.
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1. Introduction

The rapid development of nanotechnology, nanoparticles have shown a wide range of potential applications in biological and biomedical fields [1–3]. In the past decade, the use of various semiconductor nanomaterials in biomedicine has increased owing to their controllable size, shape, and dimensionality, making them suitable for several applications, including biosensing, cell imaging, drug/ gene delivery and cancer therapy [4–7].

Titanium dioxide (TiO_2), is one of the most popular and promising materials in photocatalytic application due to the strong oxidizing power of its holes, high photo stability and redox selectivity [8,9]. Compared to other semiconductor oxides, TiO_2 has been widely used and proved to be an important potential photosensitizer because of their unique physical and biological properties [10–12], such as photostable, inexpensive, nontoxic properties, and it has high oxidative power, no secondary pollution.

TiO_2 nanocrystalline is one of the most popular photo catalysts, has long been investigated for environmental purification studies [13,14]. Recent studies show that photocatalytic activity of TiO_2 depends strongly on its grain size [15]. The decrease of grain size implies increase of surface area and high redox potential, which leads to high photocatalytic activity. Therefore, much more attention has been focused on the preparation of nanocrystalline TiO_2 with unique properties of nanoparticles and their relations to photocatalytic properties. Under the irradiation of ultraviolet (UV) light with the wavelength shorter than 387 nm (corresponding to 3.2 eV for the band gap of anatase TiO2), the electrons in the valence band of TiO_2 can be excited to the conduction band, thus creating the pairs of photo-induced electron and hole. Then, the photo-induced electrons and holes can lead to the formation of various reactive oxygen species (ROS), which could kill bacteria, viruses, and cancer cells [16–21]

Wet chemical Technique/Sol–gel technique has been widely used for the synthesis of nanophased TiO_2. Because of synthesis from atomic or molecular precursors, this technique can give better control of particle size and homogeneity in particle distribution [22–25].

In this present work we synthesis TiO_2 nanoparticles by wet chemical technique and it was characterized by XRD, SEM, TEM and Uv–Visible analysis. The photocatalytic property of the synthesized TiO_2 was studied by using A549 cancer cells.

2. Synthesis of TiO_2 and PEG modified TiO_2nanoparticles

Wet chemical (Sol-gel) technique was used to synthesis of TiO_2 nanoparticles. TTIP (Titanium tetra-isopropoxide) was used as a precursor, HCl as peptizing agent and C_2H_5OH was used as solvent medium. 5 ml of HCl was mixed with 50 ml ethanol, it was stirred

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for few minutes. To this mixture 50 ml TTIP was added and it was stirred for 1 h at room temperature. Then 100 ml of distilled water was added, the temperature was raised to 50 °C and stirring was continued for 3 h until the solution changed into colourless gel. The high viscous gel was dried at room temperature to fine powder. The resulting powder was heated at 120 °C for 1 h in a hot air oven, to remove the moisture and solvents. Finally the colourless powder was calcined at 400 °C for 1 h to increase the crystallinity and to remove the carbonaceous materials present in TTIP.

2.1. Characterization

The prepared nanoparticles were characterized for the crystalline structure using D8 Advance X-ray diffraction meter (Bruker AXS, Germany) at room temperature, operating at 30 kV and 30 mA, using CuKα radiation ($\lambda = 0.15406$ nm). The crystal size was calculated by Scherrer's formula. Surface morphology was studied by using SEM-EDS (Model JSM 6390LV, JOEL, USA), UV–Vis diffuse reflectance spectra were recorded with a Carry 5000 UV–Vis-NIR spectrophotometer (Varian, USA)

2.2. Cell culture and cellular incubation with TiO_2 nanoparticles

2.2.1. Cell line and counting method

A typical cancer cell line, A549 (lung cancer), was used in this study. The cells were cultured in a minimum essential medium (MEM, Sigma) plus 10% new born calf serum (NBS, Invitrogen Corporation, Gibco) at 37 °C under 5% CO_2. The cells were plated at a concentration of about 3×10^5 in a 60 mm Petri dish and were allowed to grow for 3 days. The old culture medium was replaced with TiO_2 colloidal solution and recultured for 24 h in an incubator. The colloidal solution was removed and washed with phosphate buffer saline (PBS, Invitrogen Corporation, Gibco). After the cells were cleaved by trypsin–EDTA (Gibco), the cells were stained with trypan blue (Nacalai Tesque, Kyoto, Japan). Then, the cells were counted under a 10× in-bright-field microscope by using a hemocytometer. The cell survival was determined as the percentage of the number of unstained (live) cells against the control dish cells.

2.2.2. Light irradiation of colloidal TiO_2 nanoparticles on cells

For the light irradiation experiment, a continuous wavelength UV lamp was used. The light wavelength was in the range of 380 nm. The maximum power of the light was 380 nm and the irradiation time was 10 min for TiO2-treated dishes. The cells were cultured for 3 days and the medium was replaced with colloidal TiO_2 solution, and then the cells were incubated for 24 h. One dish only was photo irradiated without nano particles solution (light control dish) and other dishes were photo irradiated with TiO_2. Next the colloidal solution was removed, and washed with phosphate buffer saline (PBS) and then stained with trypan blue to evaluate the cell viability. Dead cells accumulating the dye were stained with blue color while living cells have no color. The living cells were counted by using a hemocytometer and calculated as the percentage against the control dish cells.

2.2.3. Cells imaging method

The images were taken using an inverted Olympus CKX41 microscope with a numerical light field condenser, which delivers a very narrow beam of white light from a tungsten lamp (transmitted light of 6 V–30 W halogen illumination) on the top of the sample. A 40× objective was used to collect only the scattered light from the samples. The light field pictures were taken using an Olympus digital camera (model No. C-5060, wide zoom).

3. Results and discussion

The XRD patterns and UV–Visible analysis of TiO_2 nanoparticles are shown Fig. 1a and 1b respectively. In XRD spectrum sharp peak was obtained at 25.4°, which was a characteristic (101) reflection of the anatase phase and show Bragg's reflections at about $2\theta = 25.4°$, 37.8°, 48.3° and 54.3° peaks corresponding to (101), (004), (200) and (211) referred to as tetragonal crystal planes of anatase phase TiO_2 [26,27]. The crystallite size of TiO_2 was in the range of 17 to 14 nm which was calculated by using the scherrer equation.

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

where, k is the shape factor usually (k = 0.94), λ is the X-ray wavelength and β is the full width in radian at half maximum of the peak and θ is the Bragg's angle of the X-ray diffraction peak.

Fig. 1.b. shows typical absorption spectrum of TiO_2 nanoparticles. The absorption was measured in the range between 200 and 700 nm. It is shown that TiO_2 is an oxide semiconductor and its anatase form has an optical absorbance range around 384 nm, band gap 3.2 eV. In the current measurement the onset of absorption peak of maximum absorbance occurred at 372 nm. The blue shift in absorbance corresponds to smaller particle size. The optical band gap of the material was calculated by effective mass approximation and it was found to be 3.3 ev. The blue shift in absorbance

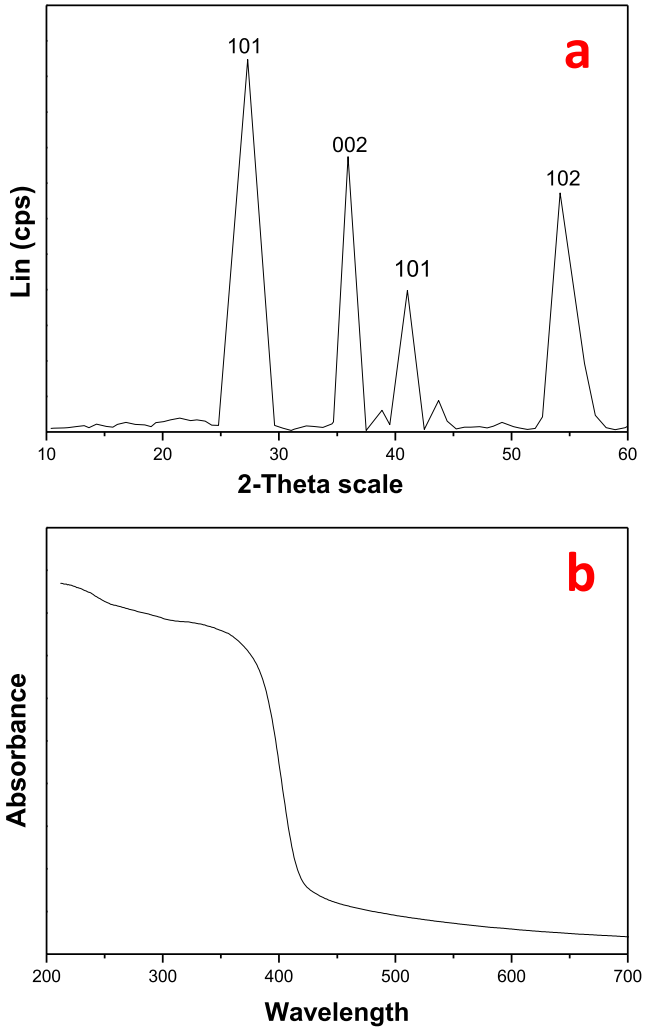


Fig. 1. a. XRD and b. Uv–Visible analysis of TiO_2 nanoparticles.

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and increased in band gap indicated the Quantum confinement effect [28]. The absorption edge shifted to the lower wavelength region confirmed the formation of nano-sized product.

3.1. Surface morphology analysis

The SEM and TEM images TiO_2 particles are shown in Fig. 2. From the SEM analysis, it is clearly observed that all the particles exhibited an irregular morphology and highly agglomerated white particles with non-uniform size distributions. The TEM analysis of the TiO_2 particles revealed highly clustered nature and strongly supported the nanophase formation of TiO_2 particles. The average particle size measured from TEM was found to be in the range of 10–20 nm, which slightly varied from the particle size evaluated from XRD analysis. It was assumed that the crystallites were formed without any local strain.

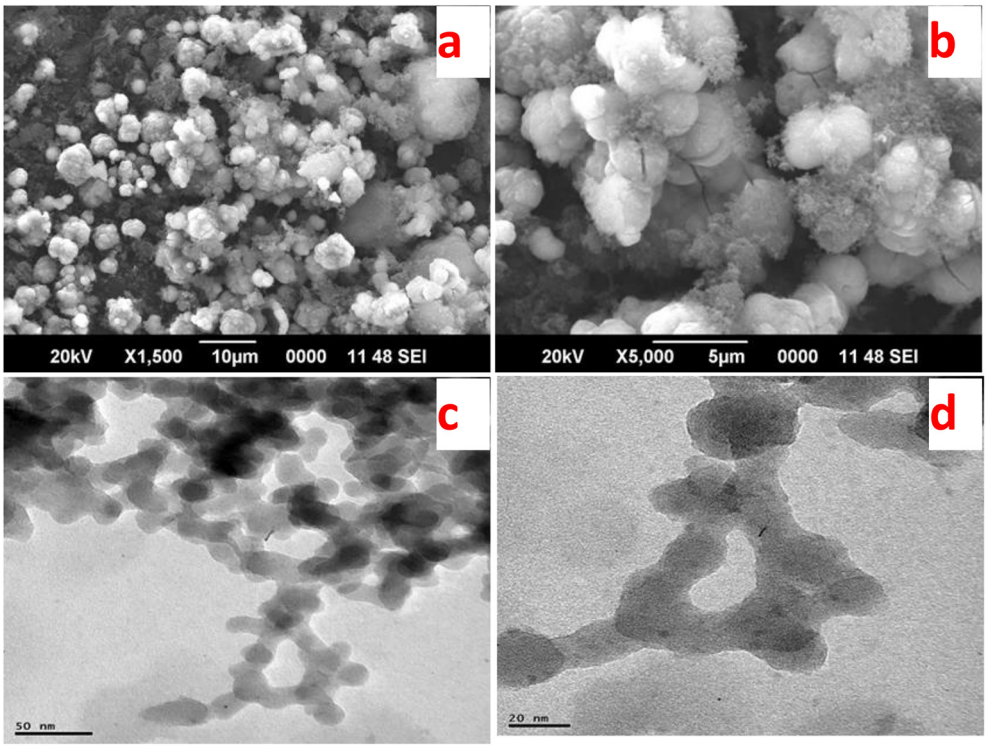


Fig. 2. SEM and TEM analysis of TiO_2 nanoparticles.

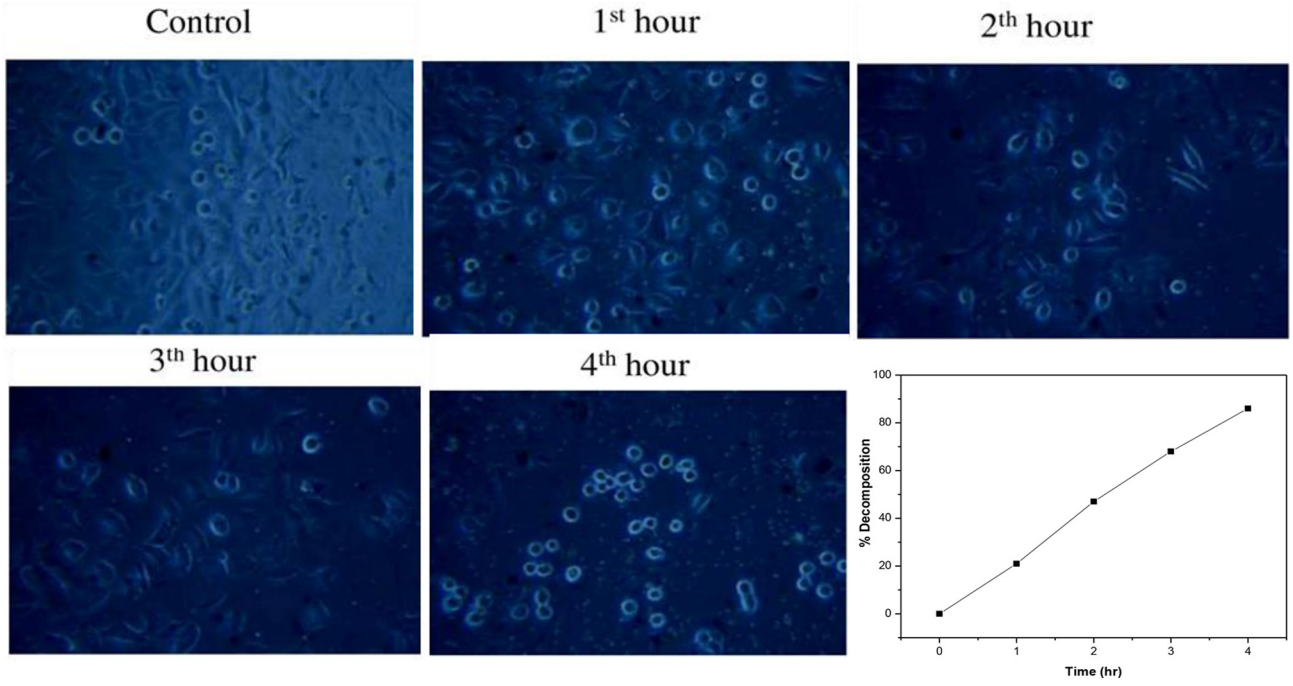


Fig. 3. The Microscopy images of A549 cells treated at 4 h UV irradiation in the presence of TiO_2 nanoparticles.

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3.2. Photokilling effect of TiO_2 nanoparticles

The photokilling effect of TiO_2 nanoparticles is shown in Fig. 3. A549 (lung cancer) cells was used to evaluate the photokilling effect of TiO_2 nanoparticles. 50μgm/L TiO_2 nanoparticles were added in the medium and it was treated with UV light in the wave length range 364 nm. Every one hour the decomposition percentage was calculated. After 4 h reaction 85% of A549 cells were decomposed by TiO_2 nanoparticles.

4. Conclusion

TiO_2 nanoparticles were synthesized by wet chemical technique. The TEM images revealed that all the particles were in nanometer size. The blue shift in absorbance and increase in bandgap shows that the nanoparticles were suitable for photocatalytic applications. The nanoparticles shows good photocatalytic activity and it decompose 85% of A549 cells in 4 h reaction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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