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Research Article

Effects of Calcination Temperature, pH and Irradiation time on Photocatalytic Activity of Pure and Doped Titanium Dioxide Nanopowders

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Abstract

Titanium dioxide nanopowders were fabricated by using sol-gel method process using titanium isopropoxide as a precursor, ethanol as a solvent and ferric chloride, copper chloride and pomegranate rind extract (PRE) as dopants. The formation mechanism was investigated by scanning electron microscopy (SEM) in which the shape control is influenced by pH under acidic range. The effect of calcination temperature, pH on the phase structure and photocatalytic activity of pure and doped TiO_2 were investigated using X-ray diffraction (XRD) results indicates that the phase transformation of anatase tetragonal crystal structure of TiO_2 occurs at 400°C and the calcined samples shows crystallinity with (101) preferred orientation, which the higher crystallinity shows better transmittance. Also the doped samples exhibit highest photocatalytic activity due to the good crystallization and the photo degradation degree for organic compounds increase with decreasing the pH value and due to the effects of pH and irradiation time.

Keywords: Titanium dioxide; X-ray diffraction; Photodegradation; Irradiation time.

Introduction

A large number of investigations have focused on the semiconductor photocatalyst for its applications in solar energy conversions and environmental purification since FUJISHIMA and HONDA discovered the photocatalytic splitting of water on TiO_2 electrodes in 1972. [1-3]. Among the metal oxide nanostructures, titanium dioxide has specific chemical and physical properties that make it an attractive material for various applications such as catalysis, white pigment for paints or cosmetics, electrodes in lithium batteries, dye-sensitized solar cells, photocatalyst to deal with environmental pollution, waste water treatment, antibacterial activity and air purification. Many researchers have paid much more attention to the use of inorganic antibacterial agent due to its stabilization compared with organic antibacterial agent. Among them, anatase titania (TiO_2) as one of the most promising inorganic antibacterial agent has been widely investigated because of its high efficiency, good chemical stability, safety and inexpensiveness. But anatase titania is with large band gap (3.2eV), which limits its application [4,5]. Titania (TiO_2) is a cheap and innocuous inorganic material extensively employed in industrial and commercial applications such as pigment in the paint industry, as sun blocking material in cosmetics, as a binder in medicinal fields and so on.Using the superb photocatalytic effect of titanium dioxide (TiO_2) is a conceptually feasible technology for this material is easy and inexpensive to produce in industrial scale. Photocatalytic TiO_2 samples have been shown to eliminate organic compounds and to function as disinfectants [6].

Traditional TiO_2 photocatalyst, however, is effective only upon irradiation of UV-light at levels that would also include serious damage to human cells. This greatly restricts the potential application of TiO_2 for use in our living environments. Recently metal-ion doped or Herbal and Fruit extract doped anatase based TiO_2 photocatalysts have been identified to be active upon visible-light illumination [7,8], offering the possibility to overcome this problem. It is believed that nanometer-sized anatase phase particles have large surface area are efficient for the decomposition of pollutants in air and water [9]. Furthermore it is also found

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that the presence of anatase phase is important in some of the photocatalytic reactions where oxygen is used as electron acceptor [10]. The antibacterial activity of visible light responsive photocatalysts has been reported by several groups [11-13]. The peel of fruits can be used for waste water treatment and photocatalytic activity [14, 15]. In the present study, the metal (Fe/Cu) and organic dopants (Pomegranate Rind Extract) were used for the degradation factor of dyes. The effect of dopants in TiO_2 photocatalyst onTiO_2, crystallite size, surface morphology and photocatalytic reaction were tested with respect to pH and irradiation time.

Materials and methods

Synthesis of TiO_2

Firstly, Titanium Tetra Isopropoxide (TTIP) was dissolved in ethanol, mixed with Ferric chloride/Copper chloride/pomegranate rind extract (PRE) by stirring for 15 min at room temperature and followed by adding droplets of 4 M NH_3 into the solution until pH about 3 - 4. Finally, distilled water was slowly added to the solution by stirring for 30 min. The solution was dried at 105°C for 24 hrs and calcined at the temperature 400°C for 2 hrs. The synthesized powder was ground and submitted for the application of titanium dioxide.

Characterization techniques

The XRD spectra of the TiO_2 films were recorded by using an X-ray diffractometer (model-D5oo, Siemens) using CuK_α radiation (λ=0.15406 nm) and operating at an accelerating voltage of 40Kv and an emission current of 40 mA. Data were acquired over the range of 2θ from 20 to 80° at a sampling width of 0.1° C and a scanning speed of 5° min^{-1}. The crystalline structure was studied using XRD spectra. SEM image were recorded using a SEM JSM 6400 JEOL scanning microscope, for morphological studies.

Photocatalytic reaction test

The photocatalytic activities of the array of synthesized TiO_2 samples were quantified by measuring degradation of MeO. Synthesized TiO_2 samples were dispersed in distilled water (1 g/L). This was followed by the addition of an aliquot of the target substrate stock solution to the catalyst suspension to give a specific substrate concentration. The reaction suspensions pH were circum-neutral at t=0. Before irradiation, the suspension was stirred in the dark for 30 min to obtain a state of sorption equilibrium of the specific substrate on TiO_2 [16-19]. A high-pressure Hg (Xe) Arc lamp (500 W) was used as the light source. The incident light beam was passed through an IR water filter and a UV cut-off filter giving λ>320 nm for UV irradiation λ>400 nm for visible irradiation before being focused onto a cylindrical Pyrex reactor through a quartz window. The reactor was open to ambient laboratory air during photolysis with a few exceptions. Time-sequenced sample aliquots were collected from the reactor during the time-course of illumination for analysis and filtered through a 0.45 μm PTFE syringe filter to remove TiO_2 particles. Multiple photolysis experiments were performed under the identical reaction conditions to determine reproducibility.

Result and discussions

X-ray diffraction

The pH value of the solution and annealing temperature have been great effects on the crystal phase composition and crystalline of the final products. Fig. 1 and 2 shows the XRD patterns of the substrates immersed in (pH=3) for as-prepared and annealed TiO_2 samples. Results revealed that for as-deposited film at room temperature and the heat treated film at 100°C shows amorphous in nature.

All the TiO_2 samples are pure tetragonal anatase phase exhibits good crystallinity. As the annealing temperature increases from 200 to 300°C it changes its structure from amorphous to polycrystalline and the exhibited characteristic peaks of anatase crystal plane are (101), (004) and (200) respectively [20-22]. For the samples annealed at 400°C, and above upto 600°C other characteristic peaks of anatase crystal plane (105) and (204) appeared, but the intensity of these peaks is very weak. It was observed that the intensities of the peaks of few anatase planes increased slightly with the increase of annealing temperature, i.e. crystallinity increases at the pH=3.

Scanning electron microscopy

It is observed that role of pH is not only the formation of structure but also the smoothness

enhancement of TiO_2 films. The shape control was preformed in an acidic range of pH [23, 24] shown in the Fig. 3. For the precise morphological control of oxide particles, pH control is another key factor, since the adsorption of the shape controllers is strongly affected by pH.

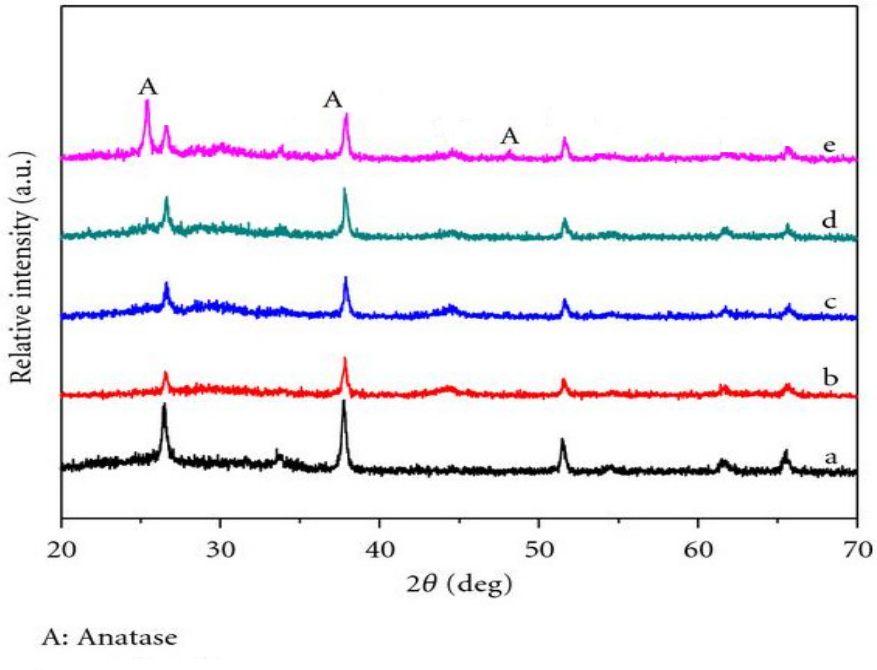

Fig 1. XRD patterns of pure TiO_2 sample for pH=3 annealed at temperatures from 300-400°C

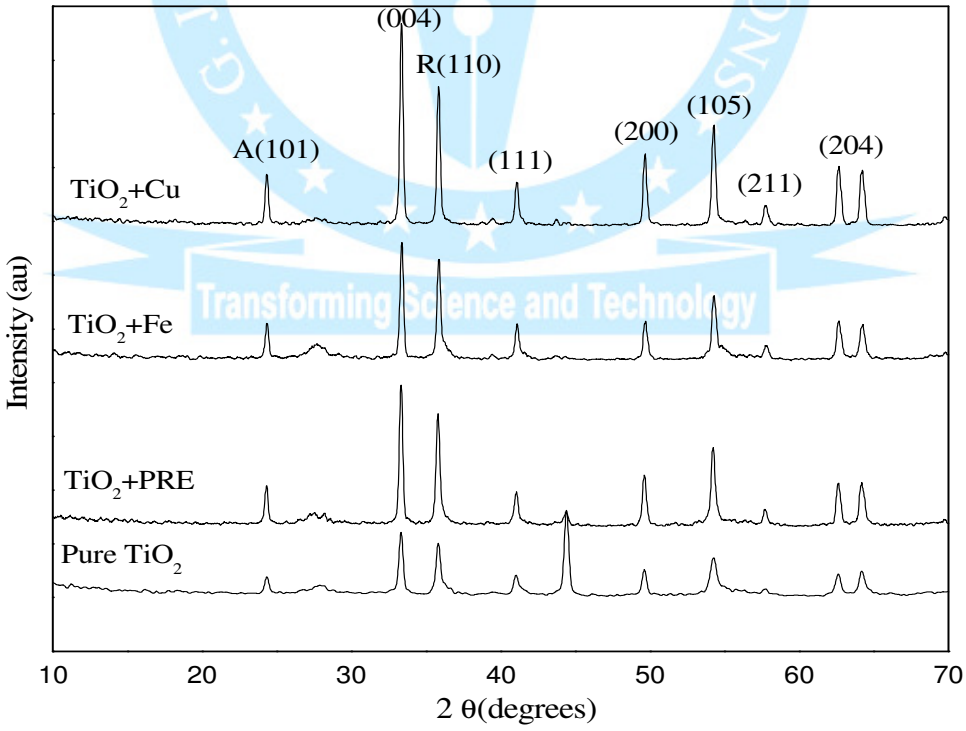

Fig 2. XRD patterns of pure and doped TiO_2 sample for pH=3 annealed at 400°C

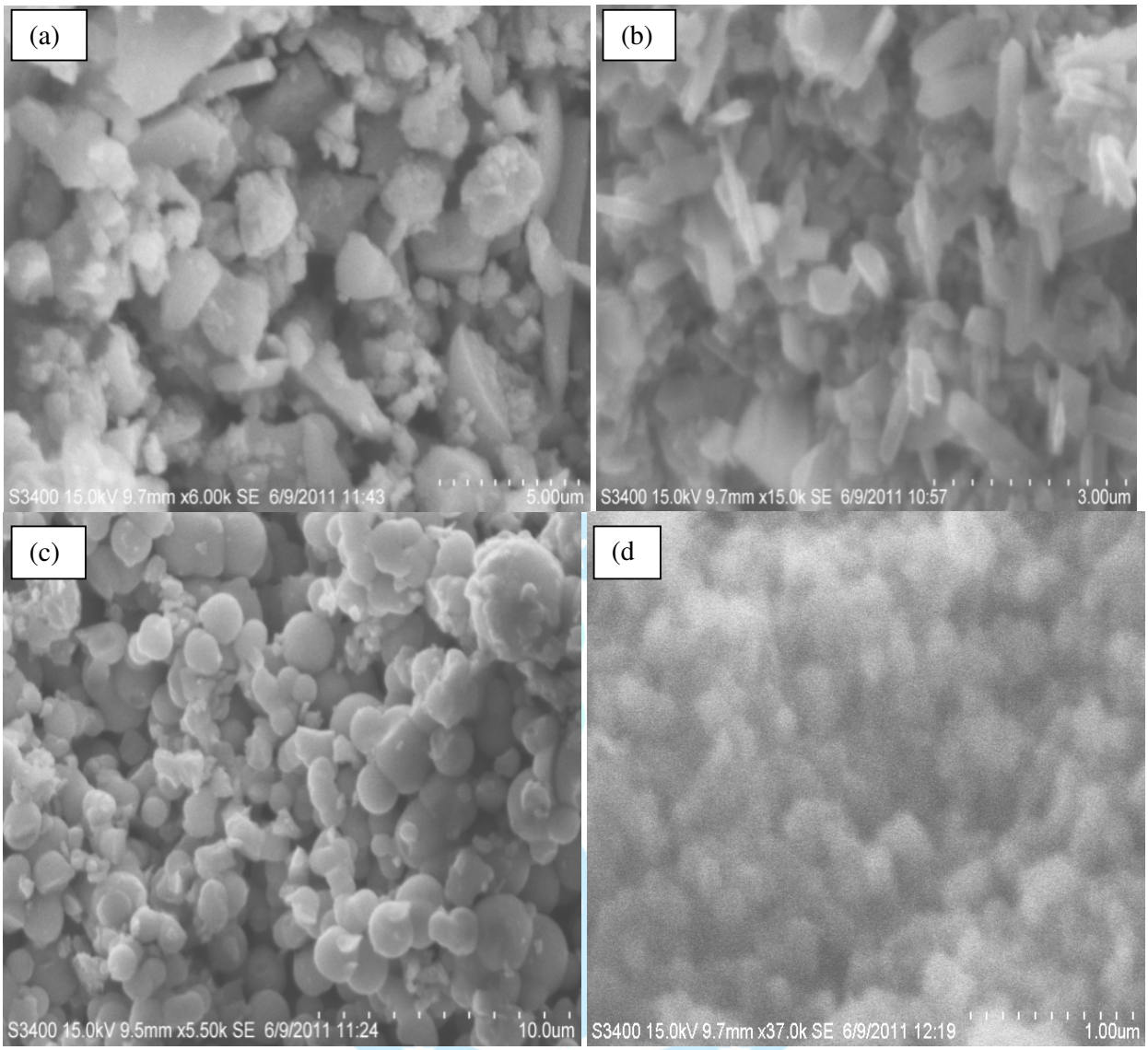

Fig 3. SEM image of doped TiO_2 sample for pH =3 annealed at 400°C (a) Pure TiO_2 (b) TiO_2 + Cu (c) TiO_2 + Fe (d) TiO_2 + PRE

Photocatalytic degradation

Effect of PH variation

TiO_2 phase composition and reuse of TiO_2 catalyst on the Methyl Orange photo degradation were investigated to analyze the photocatalytic activity of the as-synthesized TiO_2 nanoparticles. The photodegradation of Methyl orange solution with TiO_2 powders as photocatalyst was analyzed previously for different acidic pH's [25]. The relationship between the degradation degree of MeO and the pH value of the solution indicated that a low pH value can facilitate the decolorization reaction. The remarkable sonocatalytic degradation ratios of MeO in the presence of TiO_2 powder indicate that the treatments of some organic pollutants like MeO should be performed in highly acidic system in order to obtain a perfect photodegradation degree [26].

In general, it is expected that the photo degradation degree for most organic compounds increase with decreasing the pH value, which indicates the number of OH radicals increase on the surface of TiO_2 particles in solution by trapping electrons. The acidic pH value of the dye solution has maximum degradation efficiency compared to aqueous pH reported earlier.

Effect of irradiation time

The relationship between the percentage degradation and irradiation time plays a vital role. As the irradiation time increases, the formation of intermediates and its competitiveness with parent dye molecules in the

photocatalytic degradation process have attributed the slow kinetics of dye degradation after certain time limit due to the difficulty in converting the N- atoms of dye into oxidized nitrogen compounds. This has been observed during photocatalytic degradation of C- N bonds in aliphatic compounds like form amide. Under the given experimental conditions the complete degradation has occurred within 90 minutes using immobilized Dowex-11 photocatalyst. The photocatalytic degradation of the dye occurs on the surface of catalyst where $OH^{\cdot}$ and O_2^{-} radicals are available for photocatalytic degradation [27-29]. Hydroxyl radicals are formed from the holes in the valence band reacting with either water OH^{-} adsorbed on the catalyst surface. The $OH^{\cdot}$ radicals are strong enough to break the different bonds in the dye molecules (N=N, C-C, C=N, C-S and C=N) adsorbed on the surface of the catalyst which lead to the formation of carbon dioxide and inorganic ions such as NH^{+},NO^{3+}, Cl^{-} and SO_4^{2-}, the formation of $OH^{\cdot}$ radicals and $O_2^{\cdot}$ increases with increase in irradiation time and hence the dye is completely degraded in the course of time.

Mechanism of TiO_2photocatalyst

The transition metal ion used as dopants is able to enhance the attachments of the functionalized organic pollutants to the doping ion active sites[30-32]. Fig.5. shows the degradation of methyl orange solution using doped TiO_2 powders, pure TiO_2 and doped TiO_2 powders under UV light for 15 minutes until 90 min. The degradation effect of methyl orange for different doped TiO_2 in some concentrations was better than those of pure TiO_2. After 90 min of testing, the percentage degradation was 30.0 (pureTiO_2), 32 (PRE + TiO_2) 65 (Cu +TiO_2), 45 (Fe +TiO_2), respectively. This increase in photocatalytic activity with doping is related to shift in optical absorption of the catalyst in visible region. TiO_2 absorbs only UV energy (below 400nm) whereas doped catalyst absorbs UV and portion of visible energy hence there is increase in photo-catalytic activity. The presence of metal ions on the surface of the photocatalyst particles improves the rate of electron transfer to O_2 and consequently has a beneficial effect on the photo- oxidation rate of organic species. The more number of pores increases the hydroxyl content as like in Fig.4. In heterogeneous photo catalysis, the illumination of semiconductor produces electrons (e^{-}) and holes (h^{+}). The holes (h^{+}) are combining with OH^{-} ions and there is formation of hydroxyl radicals

$$(h^{+}_{vb} + OH^{-} \longrightarrow \bullet OH).$$

These surface hydroxyl radicals formed on the surface of the photo-catalyst are oxidizing species which ultimately affects the photo-catalytic activity. This suggests that the increase in hydroxyl content of the film increases the photo-catalytic activity. Also, stated that this dopant exists only as the recombination centre for the electron /holes, thus having no noticeable effect on the reaction rate [33-37].

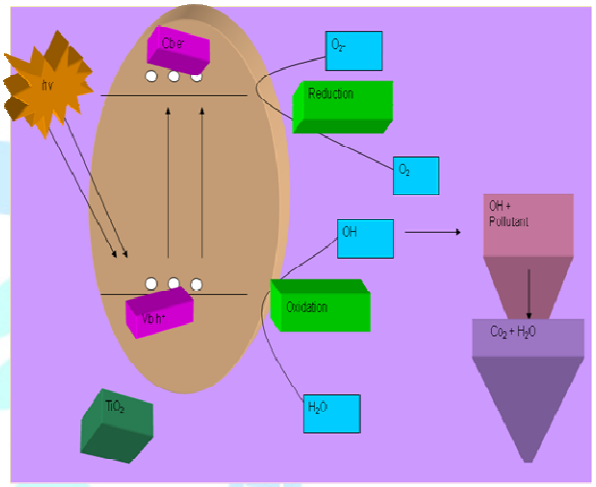

Fig 4. General mechanism of TiO_2 photocatalyst

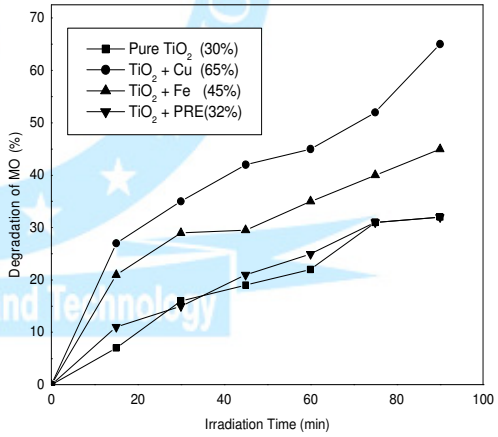

Fig 5. Rate of decomposition of methyl orange for pure and doped TiO_2 samples

Conclusions

The enhancement of photocatalytic activity and disinfection efficiency is due to their large surface area. Metal-ion doped TiO_2 nanomaterials have strong antimicrobial properties through a mechanism including photocatalytic production of reactive oxygen species that damage cell components and viruses, its potential to be activated by visible

light or sunlight.The more number of pores increases the hydroxyl content as the surface hydroxyl content increases the photocatalytic activity of photocatalysts also increasesThe percentage of degradation for pure TiO_2 is nearly 30 and for dopants of Pome granate rind extract, iron and copper increases as 32, 45 and 65 percentages respectively. So the inorganic dopant has high degradation efficiency but the organic extract from fruits showed less efficiency than metal dopants it has good antioxidation property. Pomegranate fruit, which contains high proportion of polyphenolic compounds show strong antioxidant potential against lipid peroxidation etc. justifies for biopreservative in food. Also its peel provides protection against hepatoxicity. Further it is used as an antibacterial agent in high ratio.

Conflict of interest

Authors declare there are no conflicts of interest.

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