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Aluminium, cooper and ironsalts doped TiO_2 films abilities in self-cleaning application

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ABSTRACT

Three types of metals, Al, Cu and Fe,doped TiO_2 thin filmsat deferent concentrations were prepared via sol-gel method achieves using dip-coating technique. All the samples were undergone to calcination in a furnace at (450ºC) with temperature rate of 20ºC/min for three hours.

XRDtest show anatase crystal phase for all films. The absorption spectra were adopted for calculation the band gap. Noticeable UV to visible red shifts was recordedin Fe-doped TiO_2samples (absorption edge reach 418.92 nm),while minor shift were observed in both Al-doped TiO_2 and Cu-doped TiO_2 samples. Systematic absorption edges shifting with concentration dependence were realized for all adopted samples. Self-cleaning capability of the prepared samples were examinedinterrelated to the hydrophilicity using contact angle measurements.

KEYWORDS

Metal- doped TiO_2;
Self-cleaning;
Hydrophilicity.

INTRODUCTION

Hydrophilic as well as hydrophobic surfaces offer advantages for leaning of technical surfaces[1, 2]. Humans have pursued synthetic hydrophobicsurfaces for decades[3]. The following properties of hydrophilic coatings are interesting: less dirt, easy to clean, antifogging and inhibition of growth for vegetation and bacteria[4-7]. Light photons of energy greater than the band gap can excites an electron from the valence band to the conduction band then the photo-generated electron/hole pair causes redox reactions. The band gap width of anatase TiO_2(3.2 eV) determines the light absorption resulting in low efficiency of solar energy conversion[8]. Usually, doping involves; the use of metals or non-metals and designed to extend the photocatalytic activity of a semiconductor to the visible region. Technically, doping is the introduction of foreign elements into the parent photocatalyst without giving rise to a new crystallographic forms, phases or structures[9]. The most commonly utilized method for measuring surface hydrophobic or hydrophobicity is through analysis of the water contact angle. The sessile drop method involves the placement of a droplet of liquid onto a horizontal surface and measuring the contact angle.

There are many possible mechanisms, which have been proposed for the photo-induced hydrophilicity effect on TiO_2 surfaces. The famous one is

based on induced defect production. It is involves the production of Ti^{3+} ions at the surface because of oxygen atom ejection from the lattice. The defects, known as oxygen vacancies or Ti^{3+} sites, when produced on the surface are known to cause water dissociation. As well as the production of adsorbed OH^- species that is known to be hydrophilic in nature[10]. Another mechanism is based on the photo-induced rupture of Ti—OH bonding. This model suggests that the photo-induced hydrophilicity effect is due to surface modifications. This modification leads to an increased surface coverage by Ti—OH groups in the presence of H_2O. The–OH groups bound in 2-fold coordination to Ti atoms are converted by H_2O adsorption into two –OH groups, which are singly coordinated each to their own Ti atom[11]. In photocatalytic reactions, the band gap energy principally determines which light wavelength is most effective. Hence the position of the highest point in the valence band is the main determinant of oxidative decomposing power of photocatalyst. In this work the hydrophilic ability of aluminium, copper and iron salts doped TiO_2 films were examined.

EXPERIMENTAL

Chemical materials

These chemical materials were adopted in this work:Aluminium nitrate $Al(NO_3)_3$, Nitric acid (HNO_3), Cupper chloride $CuCl_2$, Iron chloride $FeCl_3$ all supplied from Merck Co. Titaniumtetraisopropoxide (TTIP), Ti [OCH $(CH_3)_2]_4$, purity 97%, from Sigma-Aldrich and deionized water (18.2MΩ.cm).

(TiO_2) Sol preparation

(TiO_2)sol was prepared using the following procedure: Deionized water was mixed with (TTIP) in terms of a molar ratio of Ti: H_2O=1:4. Nitric acid was used to adjust the pH at (1.5) for restrain the hydrolysis process of the solution. The solution was put on a magnetic stirrer for (24 hours). The resultant sol was aged for six hours at (55ºC) yielding a transparent sol.

Metal doped TiO_2sol preparation

Nitric acid was mixed with deionized water to adjust PH value at (1.5),this mixture is denoted as mixture (A). Meanwhile, taking about (5ml) from (A) and mix with several weights percentage of (2.21, 6.40, 10.16and 18.50 %) of each of $Al(NO_3)_3$, $CuCl_2$ and $FeCl_3$, These mixtures was denoted as mixture B_1, B_2 and B_3 respectively. Slightly, TTIP was added to the first mixture (A). Separately mixturesB_1, B_2 and B_3were added to mixture (A) drop by drop, this processes were done at room temperature. The resultant sol was stirred for (24 hours),and then aged for six hours at (55ºC), yielding a White,light green and lightorange all transparent solsrelated to Al, Cu and Fe doped samples respectively.

RESULTS

Structural characterizations

The X-Ray Diffraction patterns for the optimized samples were achieved. The positions of the diffraction peaks in the films were compared with those given in ASTM data card (# 96-900-9087) for anatase[12]. X-ray pattern for all samplesare shown in the Figure (1). This figure shows that, the films were polycrystalline having totally anatase phase. It is observed that all films exhibited characteristic peaks of anatase crystal plane (010), (004), (200), (105) and (211).

Scanning electron microscopyimages (Figure 2) are present the surface profile and grain size for the optimized prepared thin films.

Optical characterizations

Optical characterizations were achieved by means of the absorption spectra, where the band gap energieswere calculated for the optimum prepared samples. The Absorbance of bare and metal doped TiO_2samples in the spectral range of (200–800) nm is shown in the Figure (3). From this figure, it is clear that the absorption edge are red shifted with respect to the bare sample in the direction of Al-doped TiO_2, Cu-doped TiO_2 and Fe-doped TiO_2.

Band gap energy

The calculated band gap energy for bare and

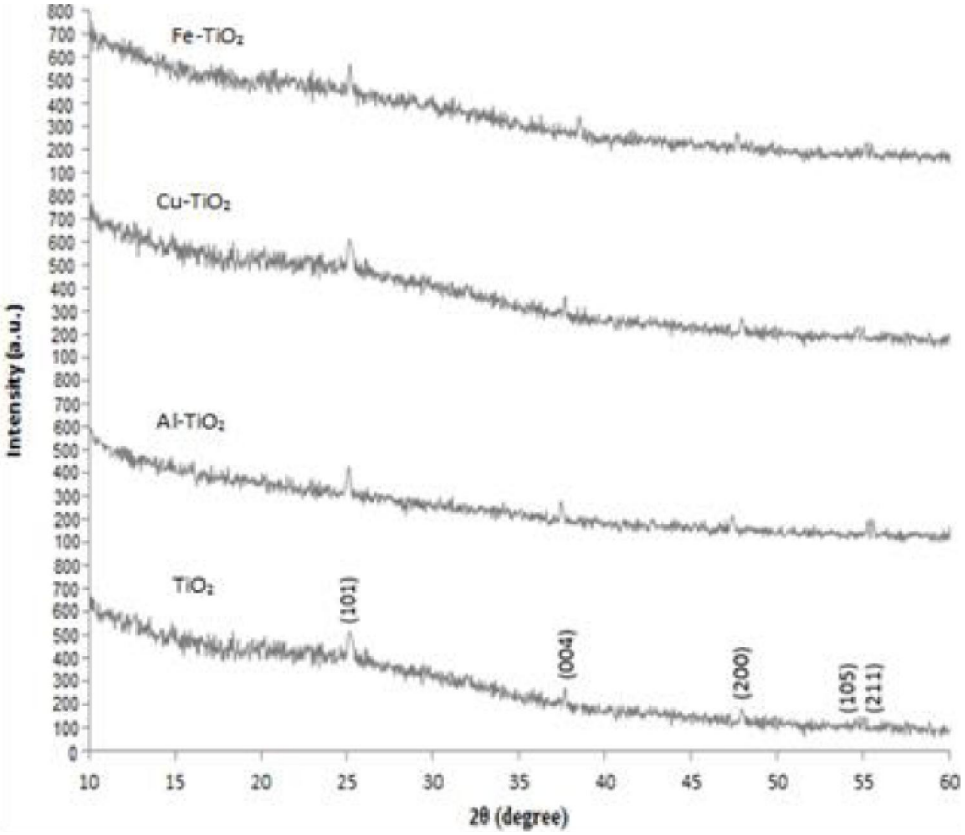

Figure 1 : X-ray patterns for bare TiO2 and metal doped TiO2 samples

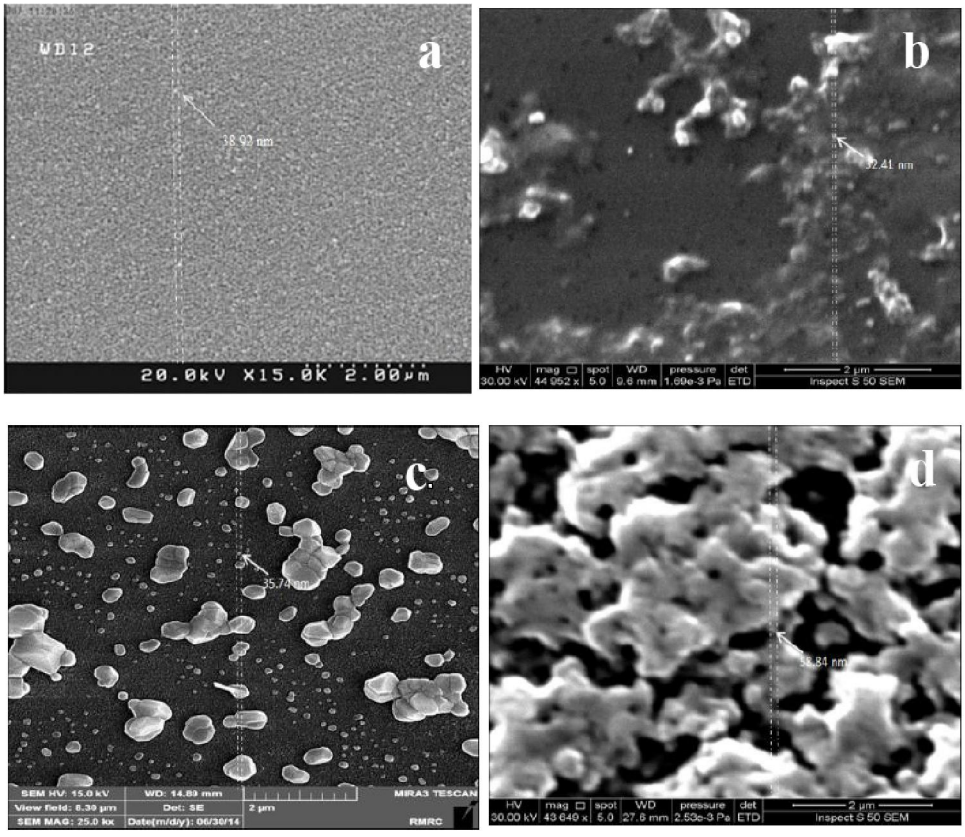

Figure 2 : SEM images of: a) bareTiO_2 sample b) Fe-TiO_2 c) Cu-TiO_2 d) Al-TiO_2

optimize metal doped TiO2 samples are shown in the Figure (4). Subsequently the band gap value is decreases in the direction of the absorption edge shifting.

Contact angle measurements

Bare TiO_2 thin film was irradiated under (3×6W),(UV-C) sources of intensity of (10mW/cm^2) and the (AL, Cu and Fe-doped TiO_2) samples were irradiated under (1×18W); (VIS) source with intensity (10mW/cm^2) for different time intervals.

Contact angle measurements were adopted after stored all samples in dark place for five days. The contact angles were measured for the bare$TiO_2$and optimummetal doped TiO_2samples, theredrop shape before and after irradiation are shown in Figures (5).

The bare sample reached zero contact angle (superhydrophilicity property) after less than 15 minutes of UV-irradiation, while Fe-doped TiO_2. Sample reached about(7.9º)after 15 minutes of VIS-irradiation.

Photocatalytic activity

Methylene blue (MB) dye was chosen as pollutant model for photocatalytic activity test. The photodegradation efficiency of this dye was examined as a function of UV and visible irradiation time for bare and doped samples respectively. The absorbance decays of (MB) dye versus irradiation time are illustrated in the Figure (6).

The measured grain size, contact angle, energy gap and photo-catalyst activity values for the optimized samples were summarized in TABLE (1).

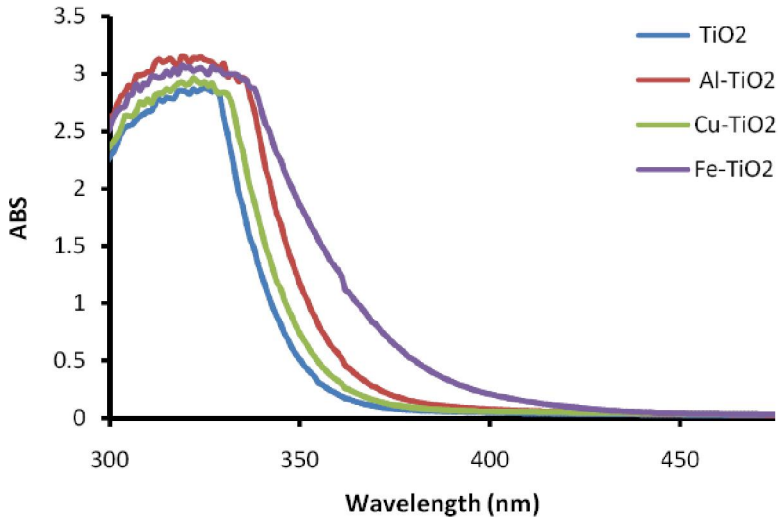

Figure 3 : The Absorption spectrum of bare and materials-doped TiO_2 samples

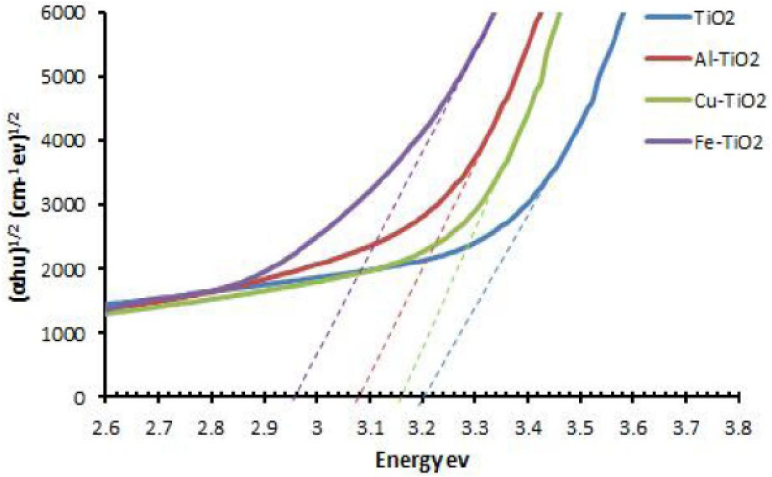

Figure 4 : Band energy gap forbare and metal doped TiO_2 samples

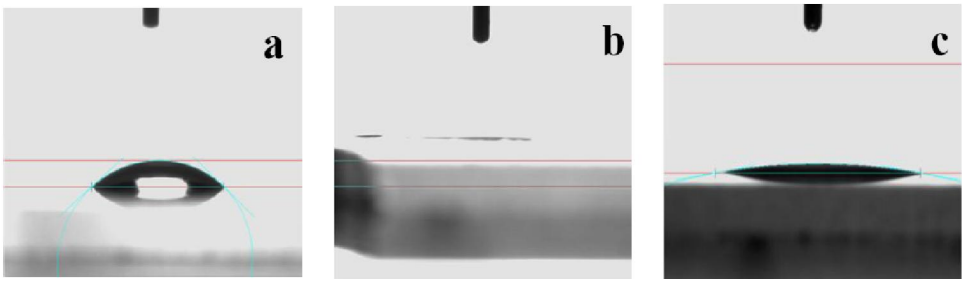

Figure 5 : Image of water droplet on the samples: a) without irradiationb) bare $TiO_2$with UV irradiationc) fe-doped TiO_2 withVISirradiation

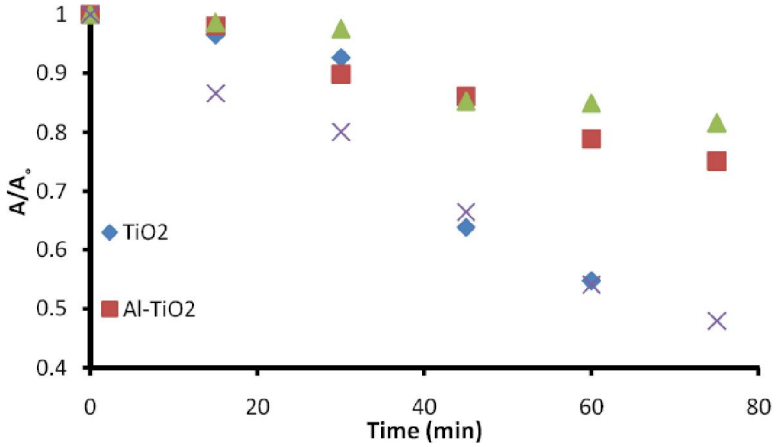

Figure 6 : Absorbance decay of m ethylene blue dyeversus irradiation time in minutes for optimize samples

TABLE 1 : Grain size, contact angle, energy gap and photo-catalyst activity values for the optimized samples.

Samples	Grain size (nm)	CA after 15 minutes	EG(eV) for optimum concentration	Crystalline phase	Photo catalyst activity A/A_0
TiO_2	38.92	0°	3.2	A	0.34
Al-TiO_2	58.84	27.9°	3.08	A	0.75
Cu-TiO_2	35.74	20.1°	3.16	A	0.81
Fe-TiO_2	32.41	7.9°	2.96	A	0.47

DISCUSSION

The TiO_2 is characterized by sharp absorption edges at about 386 nm (Eg ~ 3.2 eV). Most of Fe-TiO_2 samples show extended absorption spectra into the visible region. This can increased the facility of adopted iron doping samples in self-cleaning process at visible light region. The XRD spectrum confirms that the anatase phase is dominated in the pattern, while the rutile phase was vanished providing high photo-catalyst performance, where the excess of anatase phase in TiO_2 film is favourable in photocatalyst applications[13-15]. The contact angle for iron doped film was reduced to its quarter initial value after fifteen minute of visible exposure time. This modification in the film response from UV to the VIS light may extend its facility to theindoor applications. As a result the iron doped samplesare the best in photocatalytic activity in visible light than Aluminium and cooper samples. Thus it can be used in theself-cleaning using normal illumination that actually exists in our houses or institutes.

CONCLUSIONS

Bare TiO_2 and some metallic doped TiO_2 nanoparticles were successfully synthesized via Sol-gel technique using Titanium tetraisopropoxide (TTIP) as a precursor. By using this technique totally anatase phase can exhibited in the thin film that's confirm by XRD measurements. Doping iron

chloride in titanium oxide matrices yields red shift in the TiO_2 absorption edge, thus, subsequently; decreasethe TiO_2 band gap energies. The doping concentration play significant rule in determine the final band gap achieve value. Hydrophilicity in the visible region was accomplished merely by suitable doping concentration of iron dopant.

In conclusion from SEM images; metallic doping in TiO_2 via sol-gel technique, in sol phase, may be reducing the final product particle size, such as in case of iron and Aluminium dopant. Calcination temperature should not exceed 450 ºC to keep anatase phase.

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