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Preparation and characterization of solar light-induced rutile Cu-doped TiO_2 photocatalyst by solid-state molten salt method

Mahsa Madadi[a], Mohammad Ghorbanpour[a,*], Atabak Feizi[b]

[a]*Technical and Engineering Faculty, Department of Chemical Engineering, University of Mohaghegh Ardabili, Ardabil, Iran, email: m.madadi01@gmail.com (M. Madadi), Ghorbanpour@uma.ac.ir (M. Ghorbanpour)*

[b]*Technical and Engineering Faculty, Department of Civil Engineering, University of Mohaghegh Ardabili, Ardabil, Iran, email: a_feizi@uma.ac.ir (A. Feizi)*

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ABSTRACT

This study is the first report on the synthesis of Cu-doped TiO_2 nanoparticles with solid-state molten salt method for solar light-induced photo catalytic applications. Cu-doped TiO_2 nanoparticles were prepared using a precursor of a solid mixture of TiO_2 powder and $CuSO_4$. The effect of copper loading on the micro-structure and photo catalytic properties of TiO_2 particles was discussed. The obtained nanoparticles were characterized by structural X-ray diffraction (XRD), morphological scanning electron microscopy (SEM), optical (UV-Vis diffuse reflectance) and energy dispersive X-ray (EDX) analytical techniques. XRD analysis revealed the anatase crystalline phase for pure nanoparticles and rutile crystalline phase for Cu-doped TiO_2. According to SEM results, doping of TiO_2 nanoparticles with Cu ions changed their spherical shape into new larger structures. The existence of copper ions was confirmed by EDX. Doping process converted the absorption threshold of TiO_2 into visible spectrum range. The photo catalytic activity was also checked. With an appropriate content of Cu (0.1–3%), the Cu-doped TiO_2 nanoparticles exhibit improved photo catalytic performance in photo degradation of methyl orange, and the best performance was achieved by catalyst doped with 0.1% copper.

Keywords: Rutile; Cu-doped TiO_2; Solar light-induced; Photo catalyst

1. Introduction

Nowadays, numerous studies have been conducted on TiO_2 nanoparticles, which have led to many promising applications in different areas such as photo catalysis, antibacterial agents and sensors [1–3]. It is proved that the morphological and structural properties of TiO_2 nanoparticles strongly affect their photo catalytic activity [4]. Therefore, many studies have been focused on the preparation and modification of TiO_2 nanoparticles. Accordingly, many investigations have been carried out on the synthesis and enhancement of the photo catalytic activity in the ultraviolet or visible range [5–9].

TiO_2 nanoparticles could be synthesized by various methods including, molten salt [2,10], sol–gel [5,8], hydrothermal [1], co-precipitation [6] and sonochemical methods [7]. Recently, molten salt method is considered as a versatile and promising technique for generating a variety of novel materials and metal oxide [2,10–13]. In order to improve the photo-efficiency of TiO_2 nanoparticles, their doping with transition metals and preparation of TiO_2 nanoparticles with rutile phase have been widely employed [5,14]. So far, among the various elements used for doping of TiO_2, Cu has been considered important due to the narrow band-gap energies of its oxides and its high light absorption coefficients [6–8]. For instance, Behnajady et al. (2013) prepared Cu doped TiO_2 nanoparticles containing anatase-rutile and pure rutile phases by sol–gel and hydrolysis in acidic solution methods [16]. Colon et al. (2006) investigated photo catalytic oxidation of phenol by copper doped TiO_2 prepared by the sol–gel method. They found that the photo degradation activity can be enhanced by doping an appropriate amount of Cu. They associated this photo catalytic

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*Corresponding author.

improvement to the stabilization of Cu_2O species in doped TiO_2 and consequently, the presence of oxygen vacancies created in the preparation procedure [5]. In another work, Xia et al. (2013) prepared copper-doped rutile TiO_2 with variable Cu/Ti ratios via aqueous-phase method. Their results showed that the sample with 2% copper doping has the best photo catalytic activity vs. brilliant red X-3B [9]. According to their results, The Cu doping replaces certain Ti^{4+} ions in substitution sites of TiO_2, and results in segregation and the incorporation of Cu into the interstitial sites of TiO_2 [6]. Traditionally, the Cu doped TiO_2 has been used in CO_2 photo catalytic reduction processes [5].

According to previous studies, anatase TiO_2 has higher photo catalytic activity than that of rutile TiO_2 [15]. However, rutile TiO_2 has a smaller band gap than anatase TiO_2. Furthermore, the rutile phase of TiO_2 is the most stable phase of TiO_2 even in strongly acidic or alkaline media [9].

Nowadays, various studies are carried on the preparation and modification of rutile TiO_2 [1,15], however, modifying rutileTiO_2 with copper is less addressed [9]. As far as this study is concerned, the synthesis of Cu-doped TiO_2 with molten salt method is absent in the literatures. This study synthesized Cu-doped TiO_2 nanoparticles by a solid-state molten salt method using a precursor of a solid mixture of TiO_2 and $CuSO_4$. The effects of different Cu dopant content on their physical properties and micro structure were investigated.

2. Experiment

Cu-doped TiO_2 powders were prepared by a modified synthetic method of Lotfiman and Ghorbanpour [10]. An appropriate amount of $CuSO_4$ (Merck) and TiO_2 powder (Merck), i.e. 0, 0.1, 0.5,1 and 3 wt% of $CuSO_4$ to the weight of TiO_2, was completely mixed and left in a furnace at 700°C for 60 min. Then, the prepared nanoparticles were washed with distilled water adequately. After dissolution, the nanoparticles were dried in an oven at 25°C.

The morphology of samples was observed with a scanning electron microscope (LEO 1430VP, Germany). UV-Vis diffuse reflectance spectroscopy (DR UV-Vis) was exposed to the wavelength range of 200–800 nm using a spectrophotometer (Scinco S4100, S. Korea). Powder X-ray diffraction analysis was carried out using a PW 1050 diffractometer (Philips, The Netherlands) with a Ni filter and Cu Kα (λ = 1.54 Å) radiation. The particle size was calculated by Scherrer's equation. The average crystallite sizes of the molecules were counted based on the peak width of 101 planes, using the Scherrer's Eq. (1):

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where k is a constant (k = 0.9), is the X-ray wavelength, β is the full-width at the half-maximum (FWHM) and θ is the Bragg diffraction angle.

The photo catalytic activity of the prepared TiO_2 nanoparticles was evaluated by decolonization of methyl orange as a model dye. The radiation source consisted of a 250 W visible light projection (Osram, Germany), positioned on opposite sides of the cabinet interior close to the top. Emission spectrum of the light source used for photo degradation of methyl orange is presented in Fig. 1. A weighed amount of photo catalyst (0.1 g catalyst/100 ml solution) was first dispersed in 50 ml of methyl orange solution (100 ml, 25 ppm). Prior to irradiation, the suspensions were magnetically stirred in the dark for 15 min to ensure the establishment of an adsorption/desorption equilibrium. The solution was then irradiated with a visible light in a photo reactor. After the reaction, the solution was immediately centrifuged and its absorbance was measured to calculate the percentage of degradation using the UV–visible spectrophotometer.

3. Results and discussions

The SEM micro graphs of the pure and Cu-doped TiO_2 powders are shown in Fig. 2. The accumulated spherical shaped particles with less than 100 nm average size are observed in un-doped sample. The morphology of the prepared particles starts to change with doping of Cu. According to Fig. 2b, TiO_2 powders are doped with 0.5% Cu, which is composed of accumulated spherical nanoparticles and a new structure. As the Cu concentration is increased to 1%, the spherical nanoparticles completely disappeared. It seems that the melting point of mixture was reduced and powder was almost sintered or fused by introducing the Cu in the starting precursor. This results in agglomeration of particles and forming larger structures.

Concentration of Cu ions in TiO_2 matrix was checked by EDX instrument. The chemical composition data is summarized in Table 1. The data of this table confirm that Cu concentration gradually increased in TiO_2 with increasing dopant concentration in the starting precursor mixtures. Measurements confirmed that real concentration of Cu in TiO_2 matrix is lower than the targeted values. This is due to copper ions that did not enter into the structure of TiO_2 nanoparticles during the synthesis step, which is washed in the washing step. Another reason is the experimental errors. In the case of 0.1 and 0.5% samples, the analyzer did not show any copper. The reason for this is the detection range of the device, which does not specify values less than 0.2%.

The XRD patterns of pure and doped TiO_2 powders are shown in Fig. 3. A noticeable diffraction peak positioned at 2θ = 25.4°, which is observed on the un-doped sample spectrum is associated with (101) orientation plane of anatase crystalline phase of TiO_2. This result is consistent with the available reports that prepared titanium dioxide nanoparti-

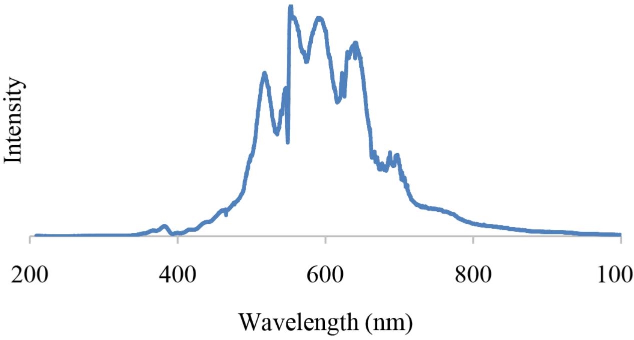
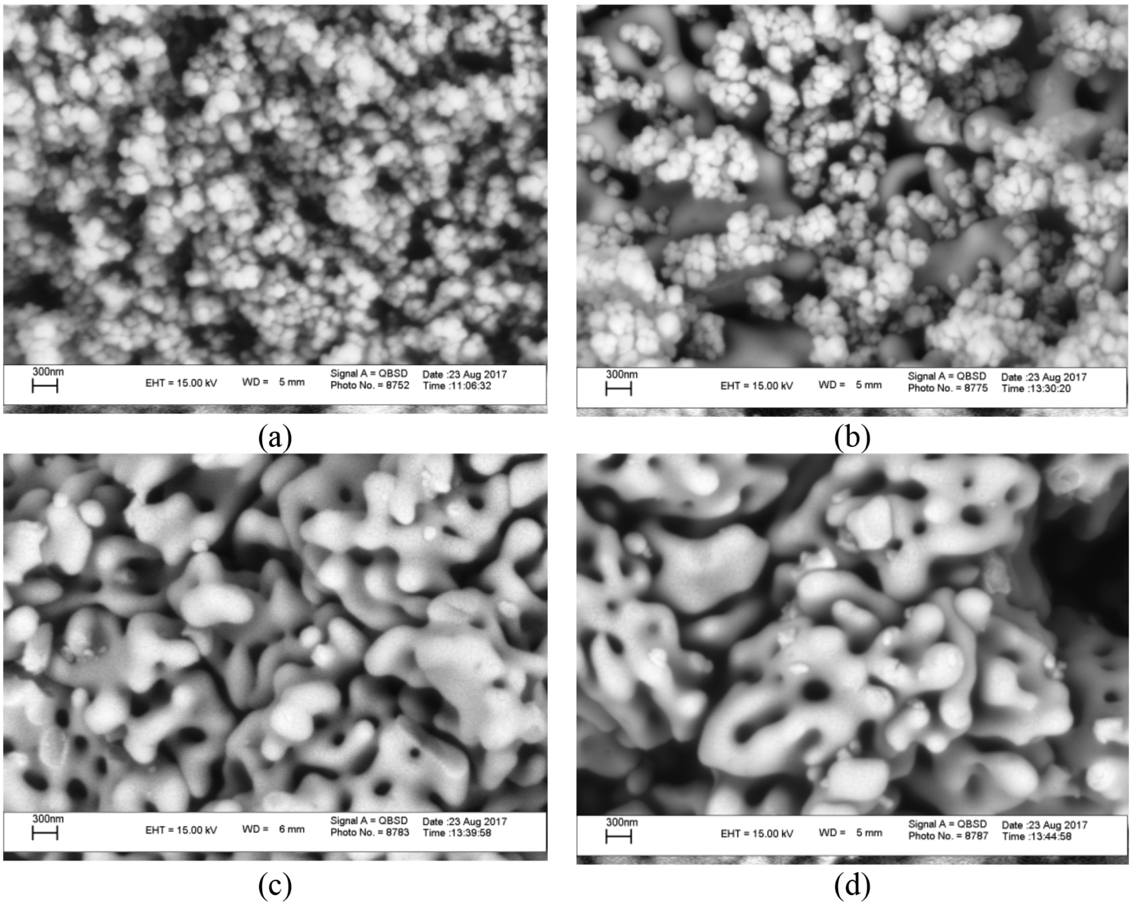


Fig. 1. Emission spectrum of the light source used for photo degradation of methyl orange.



(a) (b)

(c) (d)

Fig. 2. Typical SEM images of TiO_2 powders (a) doped with 0.5 (b), 1 (c) and 3% (d) copper.

cles by the molten salt method [2,10]. After doping of copper, the main anatase peak disappeared, but a new distinct peak at around 27.7° was observed which indexed to rutile phase of TiO_2. It seemed that this change arises from the rapid phase transformation of TiO_2 due to presence of copper ions. According to present reports, rutile TiO_2 has two notable advantages over anatase TiO_2.

First, rutile TiO_2 has smaller band gap than anatase. Second, rutile TiO_2 is the most stable phase of TiO_2 [9]. Bu and Zhuang found that the presence of metallic ion could reduce the phase transition temperature of TiO_2 nanoparticles and accelerate phase transition. Although the ionic radius of Cu^{2+} (0.072 nm) is similar than Ti^{4+} (0.068 nm), copper ion did not enter into the lattice, because of the large difference in valence states. It is also proved that the copper is ionic formation rather than element formation in the Cu doped TiO_2. However, the peak of crystalline CuO was less noticeable. This may be due to the CuO species dispersed on the surface of the TiO_2. The dispersed CuO forms Ti\O\Cu chemical bond, changes the lattice-periodicity, and further affects the transformation of crystalline phase [18].

Table 1
Composition of Cu-doped TiO_2

Element	Dopant concentration (% w/w)				
	0	0.1	0.5	1	3
Oxygen	35.36	32.03	32.93	31.89	30.59
Titanium	64.64	67.97	67.07	67.6	68.19
Copper	0	<0.2	<0.2	0.51	1.22

The crystallite size of prepared particles was 52, 146 and 133 nm for the dopant concentrations of 0, 1, and 3%, respectively. On the other hand, the width of the diffraction increased and the intensity of the peaks decreased with

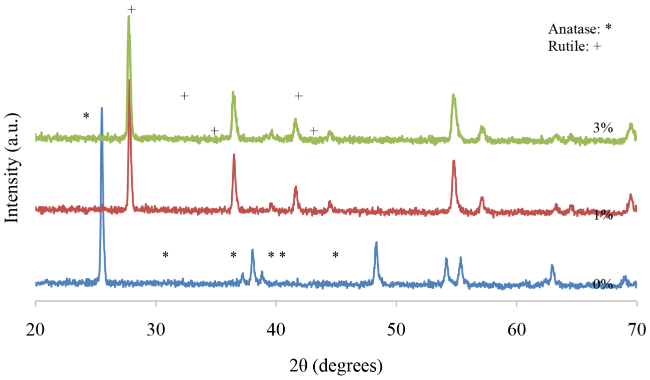


Fig. 3. XRD pattern of nanoparticles with different Cu doping contents and pure TiO_2.

increasing the copper content. It is well accepted that the broadening of the diffraction peaks indicates the reduced particle size, and the intensity of the diffraction peaks reflects the crystallization of the samples [8]. The XRD results suggest that both particle size and the crystallization of TiO_2 decreased with increasing copper content. These results are in agreement with Xia et al. 2008 [9].

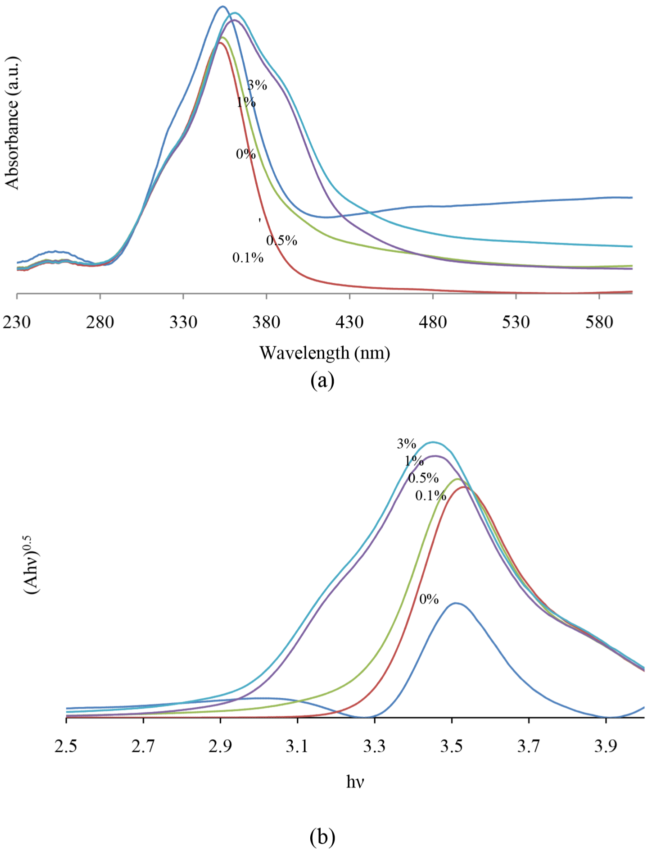
UV-Vis diffuse reflectance spectra of pure and doped TiO_2 particles with different Cu contents are illustrated in Fig. 4. Compared with the absorbance spectrum of pure TiO_2 nanoparticles, Cu-doped TiO_2 nanoparticles have a higher light harvest performance, which is not only due to the widening of its UV absorbance peak, but also the evident enhancement of light absorbance covering the whole visible range. Furthermore, compared to pure sample, due to the convergence of CuO spectra in the UV and visible range, a red shift towards the visible range from 300-700 nm occurred after doping. The absorption value is related to the amount of metal deposition; in other words, higher amount of copper deposition leads to greater absorption in the visible range [7].

The red shift of the band gap can be obtained by $(Ahv)^2$ vs hv plot in Fig. 4b (A is the absorbance; h is the Planck constant; v is the frequency of incident light), which reveals that the band gap shifts from 3.32 eV for the pure TiO_2 to 2.98–3.30 eV for the Cu-doped TiO_2 (Table 2).

Table 2
The band gap energy of doped TiO_2 samples

Doping amount (% w/w)	Band gap (eV)
0	3.32
0.1	3.3
0.5	3.28
1	2.99
3	2.98

Yang et al. [8]. and Colon et al. [5] reported that the band gap shifts from 3.28 eV for the undoped TiO_2 toward 3.02–3.17 and 3.18–3.48 eV for the Cu-doped TiO_2, respectively. It is worth noting that the decreased band gap value is more important than the one observed previously for Cu-doped catalysts [5,6]. As a result, the simple method presented in this study leads to producing nanoparticles with better band gaps or equivalent to nanoparticles prepared by other methods.



(a)

(b)

Fig. 4. UV-Vis reflectance spectra (a) and band gap (b) of pure TiO_2 and TiO_2 doped with 0.1, 0.5, 1, 3 and 7% copper.

Fig. 5 shows the photo catalytic activity of Cu-doped TiO_2 with different Cu contents and pure TiO_2 in the degradation of 20 mg/L methyl orange. In a preliminary study of methyl orange photolysis, less than 5% of its initial concentration was decreased after 2 h of irradiation without photo catalyst. Hence, the photolysis of methyl orange was negligible and degradation could be attributed to the presence of the photo catalyst. The pure TiO_2 nanoparticle only reduce the dye content in the first 15 min which was done in the dark and present no activity afterwards. Therefore, these nanoparticles can only adsorb the dye and show no photo catalytic activity. The reason is that given the obtained band gap, these nanoparticles require to be exposed to UV light to perform photo catalytic activity and they are inactive under the visible light irradiation.

Accordingly, Cu-doped TiO_2 with Cu content of 0.1%–3% showed improved photo catalytic performance, and 0.1% Cu-doped TiO_2 had the best photo catalytic performance. The visible light absorption and the band gap narrowing are the most important factors for the TiO_2 photo catalytic activity enhancement [19]. As discussed earlier, doping of TiO_2 nanoparticles with copper could shift the light absorption of the TiO_2 into the visible spectrum. The presence of metal ions on the surface of the photo catalyst particles improves the rate of electron transfer to O_2 and consequently has a positive effect on the photo oxidation

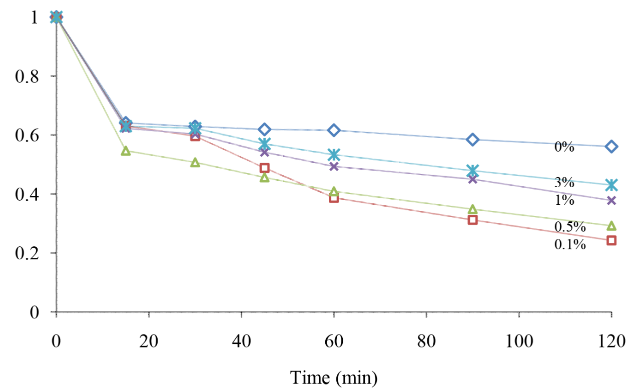


Fig. 5. Photo degradation of methyl orange by Cu-doped TiO_2 with different Cu contents and pure TiO_2.

Table 3
Performance of some photo catalysts

Catalyst	Pollutant	Initial concentration (ppm)	Performance (%)	Source of irradiation	References
Cu-doped TiO_2	Phenol	50	<90	UV	5
Fe doped ZnO	Bisphenol	20	45.3	Visible	17
ZnO@nitrogen-doped carbon sheets	Methylene blue	–	95.0	UV	16
Cu-doped TiO_2	Methyl orange	20	100	UV	8

rate of organic species. This result could also be proved by UV–vis spectrum (Fig. 4a).

As the content of Cu doping reached 3.0%, the photo catalytic performance decreased. Thus higher Cu amount seems to be detrimental to the photo degradation of methyl orange. The increased photo catalytic performance of Cu-doped TiO_2 can be attributed to the following reasons. Firstly, according to Fig. 5a, the absorption spectrum of Cu-doped TiO_2 exhibits the enhanced light harvest in both UV and visible light regions, which provided higher light energy for photo catalysis. Secondly, Cu species (CuO/ Cu_2O/ metallic Cu) have a smaller band gap and higher function than pure TiO_2, so electrons can transfer from TiO_2 conduction band to metallic copper ion. Thus, the photo catalytic performance of TiO_2 is enhanced [8].

Table 3 provides a comparison between the results of the works performed by various photo catalysts and Cu-doped TiO_2 available in the references. By comparing the results of this research with these references, it is observed that the results of this work are acceptable and even better in some cases.

4. Conclusion

Cu-doped TiO_2 photo catalysts were successfully synthesized by a solid-state process. The photo catalytic activity of the prepared materials was investigated by the photo catalytic oxidation of methyl orange in aqueous solution. The sample prepared with 0.1 % copper had the highest photo catalytic activity.

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