Synthesis and Characterization of Copper and Tin Codoped TiO₂ Nanoparticles

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ABSTRACT
Copper and tin co-doped Titania nanophotocatalyst has been prepared by Sol gel method and characterized by XRD, FE-SEM, EDS, FT-IR, HR-TEM and SAED. X-ray diffraction studies of the Cu²⁺-Sn⁴⁺/TiO₂ show the presence of anatase phase TiO₂ and in the sample prepared from 0.05, 0.10, 0.15 and 0.20 mmol have also shown the presence of anatase phase only in which 0.15 mmol of Cu²⁺-Sn⁴⁺/TiO₂ is the optimum concentration. The FE-SEM images of the prepared samples showed the decrease in size and morphological change of the TiO₂ particles when compared to undoped TiO₂. The presence of elements copper, tin, titanium and oxygen were confirmed by Energy Dispersed Spectroscopy (EDS). From TEM images it can be concluded that the addition of dopants to titania hinders the growth of nanoparticles. These results suggested that the simple and cost effective method and shows excellent adsorption removal properties on dyes for industrial applications.

Keywords: copper and tin co-doped TiO₂, Sol-gel.

INTRODUCTION
Large amounts of coloured waste water are generated in industries which use dyes to impart a desired colour to their products (food, paper, rubber, textile, plastics), and are discharged into natural hydric bodies with undesirable consequences to the environment and to human health [1–4]. The potential way to utilize these properties in various applications could be to integrate graphene sheets in composite materials such as in the preparation of highly photoactive composites materials based on TiO₂ and ZnO [5]. Nanomaterials usage is continuously being increased rapidly and widely in areas such as cosmetics, eatables, pharmaceuticals and other industrial applications. [6].

The most widely studied catalyst in this respect is TiO₂ in view of its favorable physicochemical properties, low cost, easy availability, high stability, and low toxicity [7]. However, it is active only in the UV range which constitutes less than 5% of sunlight. Photocatalytic reactions take place when particles of the semiconductor absorb photon of energy equal to or greater than its band gap and the electrons get excited from the valence band to the conduction band. This results in the formation of an electron-hole pair which promotes oxidation/reduction of the adsorbed substrate. In aqueous solution, the reactive OH
radicals can promote the oxidation and eventual mineralization of organic compounds. The photocatalytic activity of TiO$_2$ nanoparticles under ultraviolet light particularly is prominent in the anatase form, but it has been recently found that this oxide, when doped with nitrogen ions, is also a photocatalyst under visible light [8].

Sol-gel process is one of the versatile, simple, and easy means of synthesizing nanosize materials in contrast to the other conventional preparation methods which do not usually produce homogeneous, high-surface-area materials. The main advantage of the sol-gel method in preparing catalytic materials is its excellent control over the properties of the product via a host of parameters that are accessible in all four key processing steps: formation of a gel, aging, drying, and heat treatment. Although titania catalysts have been extensively studied, the procedure of preparing photocatalytic metal-doped titania is still of great interest. Particle size of catalyst is considered one of the most important physical parameters in these reactions, because it can directly furnish the active sites for the reaction to occur [9-11]. The prepared Cu$^{2+}$ and Sn$^{4+}$ co-doped TiO$_2$ photocatalyst was characterized by several analytical techniques such as XRD, FTIR, FE-SEM, EDS, HR-TEM and SAED.

**MATERIALS AND METHODS**

Copper Nitrate and Tin Chloride sources for preparing Cu$^{2+}$ and Sn$^{4+}$ co-doped TiO$_2$ photocatalysts and Titanium tetra-n-butoxide [Ti(O-Bu)$_4$] purchased from Merck, China and anhydrous ethanol were obtained from Hangzhou High-crystal Fine Chemical Co., Ltd., China.

**Preparation of Copper and Tin co-doped TiO$_2$ nanoparticles:** In brief, 0.02 mol tetrabutyl orthotitanate were added drop wise into 50 ml absolute ethanol to give a solution which was then vigorously stirred for 20 min at room temperature and add 3 drops of Conc. HNO$_3$. The desired amounts 0.05, 0.10, 0.15 and 0.20 mmol of copper nitrate and Tin Chloride (the molar ratio of Cu to Sn was 1:1) were then added in the reaction mixture while stirring continuously for 60 min until the Cu and Sn dopants were dissolved. An amount of 2.0 mL of deionized water was then dropped into the above solution. Afterwards, the resultant solution mixture was maintained at room temperature with continuous stirring for 2 h to form a gel which was then aged for 12 h at room temperature. After being dried at 80 °C for 24 h were obtained and then annealed at 400 °C for 3 h to give a light greenish material. An un-doped TiO$_2$ (anatase) sample was also prepared by adopting the above procedure without adding the Copper Nitrate and Tin Chloride which is pure TiO$_2$. The doping concentrations are expressed as mmol of titanium atom.

**Characterization of Cu$^{2+}$ and Sn$^{4+}$ co-doped TiO$_2$ nanoparticles:** The FE-SEM micrographs were obtained by using a JEOL 6335F FE-SEM microscope equipped with a Thermo Noran energy dispersive spectroscopy (EDS) detector. The presence of elemental copper, tin, titanium and oxygen was confirmed through EDAX. The EDAX observations were carried out in STIC, CUSAT, (JOEL Model JED-2300). Crystalline structure and crystallinity were identified by X-ray diffraction (XRD, DX2700, China) operating with Cu Ka radiation (1 ½ 1.5418 Å) at a scan rate (2θ) of 2° min$^{-1}$ with the accelerating voltage of 40 kV and the applied current of 45 mA, ranging from 5° to 80°. Fourier transform infrared (FT-IR) spectra for Cu$^{2+}$ and Sn$^{4+}$ nanoparticles was obtained in the range 4,000 to 400 cm$^{-1}$ with an IR-Prestige-21 Shimadzu FT-IR spectrophotometer, by KBr pellet method. The particle size and morphology of the sample and the corresponding selected area electron diffraction (SAED) were examined by high resolution transmission electron microscopy (HR-TEM) with an accelerating voltage of 200 kV, respectively.

**RESULTS AND DISCUSSION**

**X-ray Diffraction Studies:** Fig. 1 shows the XRD patterns of un-doped TiO$_2$ (curve a), 0.05 mmol Cu-Sn/TiO$_2$ (curve b), 0.10 mmol Cu-Sn/TiO$_2$ (curve c), 0.15 mmol Cu-Sn/TiO$_2$ (curve d) and 0.20 mmol Cu-Sn/TiO$_2$ (curve e) powders. It is found that the majority of the crystal phase is anatase for all of the
samples [12]. No diffraction peak corresponding to Cu and Sn was detected. The reason could be due to the fact that the content of Cu and Sn might be too small to detect. The inset in fig. 1 is the enlarged XRD peaks of crystal plane (101) for all of the samples.

![XRD patterns](image)

**Fig. 1**: XRD patterns of (a) Un-doped TiO$_2$, (b) 0.05, (c) 0.10, (d) 0.15 and (e) 0.20 mmol of Cu$^{2+}$-Sn$^{4+}$/TiO$_2$ nanoparticles. Inset is the enlarged XRD peaks of crystal plane (101).

Compared with the un-doped TiO$_2$, peak shift of the peak position is observed. The intensity of anatase TiO$_2$ peaks increased due to doping, and peaks corresponding to CuNO$_3$ and SnCl$_4$ were not detected. This may be due to the well dispersion of Cu$^{2+}$ and Sn$^{4+}$ content in TiO$_2$ particles. The well-defined diffraction peaks with 20 are at about 25’, 38’, 48’, 54’, 62’, 68’, 70’, 74’, and 82’ which are assigned to the (101), (004), (200), (105), (211), (204) (116), (220), (215) and (224) crystal planes, respectively. This XRD characteristic pattern is consistent with the standard JCPDS values of anatase TiO$_2$ (JCPDS Card No. 21-1272) [13-14] and did not appear in rutile and brookite form.

With increasing amount of Sn$^{4+}$ there is a gradual diminishing of crystallites in all three phases. Concerned the structural properties, the very similar ionic radius of Ti$^{4+}$ (0.605 Å) [15] and Sn$^{4+}$ (0.690 Å) [16] would allow easy substitution of Ti$^{4+}$ by Sn$^{4+}$ in the TiO$_2$ lattice, in comparison to Sn$^{2+}$ that is much larger, 1.22 Å [17]. Therefore, Sn$^{2+}$ can only occupy the interstitial sites in [TiO$_4$] and [TiO$_6$], resulting in a decrease in the lattice distortion energy, while Sn$^{4+}$ can substitute for Ti$^{4+}$ in [TiO$_4$] and [TiO$_6$], resulting in an increase in the distortion energy [18].

Decrease in the particle size of TiO$_2$ might be ascribed to a broadening effect due to incorporation of the metal oxides into TiO$_2$ matrix [19], as can be seen by comparing the (101) reflection plane of pure TiO$_2$ with Cu-Sn/TiO$_2$ (Fig. 1). Moreover, the (101) reflection plane of the Cu-Sn/TiO$_2$ samples shifted to higher diffraction angle relative to pure TiO$_2$ (Fig. 1(Inset)), implying an incorporation effect of copper at the TiO$_2$ lattice as Ti$^{4+}$ position may be substituted by copper due to the similarity of their ionic radii (Ti=0.68 Å and Cu = 0.72 Å) [20].

**Field Emission-Scanning Electron Microscopic study**: Field Emission Scanning Electron Microscopy was used to characterize the surface morphology and size of the particles. The surface morphology of the sample calcined at 400 °C corresponded to a mixture of nanoparticles (Fig. 2).
Fig. 2: FE-SEM image of 0.15 mmol Cu$^{2+}$-Sn$^{4+}$/TiO$_2$ nanoparticles.

The average particle size was ~30 nm. The morphology, structure and particle size of the powder were also further investigated by transmission electron microscopy.

**Fourier Transform Infrared Spectroscopy Study:** The FTIR spectra of the samples in the frequency range of 400–4000 cm$^{-1}$ are shown in fig. 3. Furthermore, the broadening of ~3400 cm$^{-1}$ O-H stretching vibration the formation of a different -OH group, and most probably as Ti-OH surface group. The broad intense band in the range of 450–700 cm$^{-1}$ is due to the Ti–O stretching and Ti–O–Ti bridging stretching modes [21-24].

![FTIR spectra](image)

Fig. 3: FT-IR spectra of (a) Un-doped TiO$_2$, (b) 0.05, (c) 0.10, (d) 0.15 and (e) 0.20 mmol of Cu$^{2+}$-Sn$^{4+}$/TiO$_2$ nanoparticles.

The broad absorption peaks at about 3400 cm$^{-1}$ and the band at 1625 cm$^{-1}$ correspond to the surface adsorbed water and the hydroxyl groups [25]. Since the Ti–O bond is shorter than the Sn–O bond, the doping of Sn$^{4+}$ in TiO$_2$ may lead to a shift of the lower wave number of Ti–O lattice vibration [26]. Copper and tin co-doped TiO$_2$ intensity has reduced compared to un-doped TiO$_2$. No additional peaks are present.
upon Cu and Sn doping, supporting the efficient dispersion of copper and tin, and it indicates the absence of clusters of copper and tin, which is in good agreement with the XRD analysis result.

**Energy Dispersive X-ray (EDX) spectra:** The energy dispersive X-ray (EDX) spectra of cu and sn co-doped TiO$_2$ are shown in fig. 4, respectively. The peaks corresponding to titanium, oxygen and the respective doped metals copper and tin can be clearly seen in these spectra.

![EDS spectra](image)

**Fig. 4:** EDS spectra of 0.15 mmol Cu$^{2+}$-Sn$^{4+}$/TiO$_2$. nanoparticles.

**Transmission Electron Microscopy:** Transmission electron microscopy was used to examine the particle size, crystallinity and morphology of the samples.

![TEM images](image)

**Fig. 5:** TEM images of (a) Undoped TiO$_2$, (b) 0.15 mmol of Cu$^{2+}$-Sn$^{4+}$/TiO$_2$ nanoparticles, (c) HRTEM images of Cu$^{2+}$-Sn$^{4+}$/TiO$_2$ nanoparticles.

The main purpose of TEM is to characterize the object individually, not in the bulk. Fig. 5b shows the bright-field TEM image revealing the high resolution morphology of the nanostructured particles containing anatase TiO$_2$ calcined at 400 °C. It was observed that the titania was almost exclusively composed of small sized nanocrystallites. The anatase TiO$_2$ powder mostly had a spherical morphology.
High-resolution transmission electron microscopy (HR-TEM) was used to elucidate the surface planes of the titanium dioxide particles. Fig. 5c shows the discrete apparent crystallites. The clearly distributed anatase lattice fringe indicates that the titania was highly crystalline. The fringes of the TiO$_2$ nanocrystallites were used to determine the crystallographic spacing’s and their orientation. Anatase nanocrystallites consisting of tetragonal particles with (101) plane surfaces were observed by HR-TEM [27]. The TiO$_2$ nanocrystals had many crystal lattice planes with a d spacing of 0.35 nm being obtained for the (101) plane. The fringes corresponding to the (101) crystallographic planes of anatase were the most prominent.

The particle size was close to 10 to 30 nm, with the observed sizes of the crystallites comparable to those calculated from the XRD patterns. Thus, the presence of nano sized particles was confirmed from the TEM images. The selected area electron diffraction (SAED, Fig. 6) pattern showed distinct and good diffraction rings corresponding to the anatase phase [27]. The intensity of the diffraction rings obtained from the particles indicated the crystalline nature of the particles, with a narrow particle size distribution.

**Selected Area Electron Diffraction:** Fig. 6 shows the crystallinity of titania was confirmed by the SAED pattern of copper and tin co-doped TiO$_2$ nanoparticles.

![SAED Image](image_url)

**Fig. 6:** SAED images of 0.15 mmol of Cu$^{2+}$-Sn$^{4+}$/TiO$_2$ nanoparticles.

The SAED pattern showed distinct and good diffraction rings corresponding to the anatase phase [28]. It shows well resolved bright and intense polymorphic ring patterns without any additional spots or rings of second phases. It revealed the typical diffraction rings for a crystalline powder, due to the absence of an amorphous nature. Image processing analysis of TEM micrographs is a useful method of fine-tuning the microstructure. It can be indexed to the reflection of Tetragonal structure in crystallography, and this result was also investigated by means of X-ray diffraction.

**APPLICATIONS**

The prepared Cu and Sn co-doped TiO$_2$ nanocparticles by Sol-gel method. X-ray diffraction studies of the Cu$^{2+}$-Sn$^{4+}$/TiO$_2$ show the presence of anatase phase TiO$_2$ and in the sample preparation of 0.05, 0.10, 0.15 and 0.20 mmol have also shown the presence of anatase phase only. The FE-SEM images of the prepared samples showed the decrease in size and morphological change of the TiO$_2$ particles. These results suggested that the simple and cost effective method and shows excellent adsorption removal properties on dyes for industrial applications.

**CONCLUSIONS**

We synthesized a sol gel method for preparation of high quality of different concentrations of Cu and Sn co-doped TiO$_2$ with pure anatase phase using copper nitrate and tin chloride as Cu and Sn source. By
tuning the starting molar ratio of Cu and Sn to titanium, different doping level samples were obtained in which 0.15mmol of Cu$^{2+}$-Sn$^{4+}$/TiO$_2$ is optimum concentration. The nanophotocatalyst was characterized using XRD, FT-IR, FE-SEM, EDS, HR-TEM and SAED. The results showed that, the product was in the form of anatase phase. These results suggested that the simple and cost effective method and shows excellent adsorption removal properties on dyes for industrial applications.

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