

X-ray absorption spectroscopy study and photocatalyst application of CuO and Cu_{0.9}Ti_{0.1}O nanoparticles



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ABSTRACT

We report detailed investigations on the electronic structure and photocatalyst application of CuO and Cu_{0.9}Ti_{0.1}O nanoparticles (NPs). The NPs were prepared by co-precipitation method and subsequent annealing. Crystal structure and morphology of the NPs were investigated by synchrotron X-ray diffraction and high resolution transmission electron microscope, respectively. The local atomic structure around the Cu atoms was investigated by the extended X-ray absorption fine structure (EXAFS) at the Cu K-edge. Electronic structure determination was done using near edge X-ray absorption fine structure (NEXAFS) at the O K-edge, Cu L-edge, Cu K-edge and Ti L-edge. From the structural and electronic structure investigations, it is inferred that the Ti substitutes the Cu in CuO lattice without forming any secondary phases and the valence state of Cu is not affected by the Ti substitution; however the Cu – O bond length is found to be shorten in the Ti doped sample. As prepared NPs exhibit excellent photocatalyst application toward the degradation of methyl orange (MO) and potassium dichromate (PD) pollutant dyes under the visible light irradiation. The mechanism of the photodegradation of MO and PD pollutants, by the smaller sized CuO and larger sized Cu_{0.9}Ti_{0.1}O NPs, is briefly discussed.

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1. Introduction

Organic pollutant dyes from the research laboratories, pharmaceutical, printing and textile industries cause a major source of water contamination. Therefore, in the recent years, much attention has been paid to degrade the water pollutants by using the various nanostructures of oxide materials under the ultra-violet or visible light irradiation. In this regard, nano-composites of CuO@zeolite, CuO@CeO₂, CuO@TiO₂, and CuO@ZnO have been reported for their photocatalyst application [1–5]. Besides this, unusual morphologies of CuO and Cu₂O have also been found to degrade the various azo dyes (i.e., methyl orange (MO) and methyl blue etc.) and metal toxic dyes (i.e., potassium dichromate (PD)) under the UV light irradiation [6,7].

CuO is a p-type semiconductor and has been used in the field-emission devices, gas sensing, magnetic storage media, and

battery applications [8–10]. There are several advantages of CuO to be used as an excellent photocatalyst material. Firstly; its low synthesis cost and nontoxic nature make it easy available for the sensible applications. Secondly; the high optical absorption and low energy band energy gap (1.2 eV), which can be tuned either the particle size variation or foreign element doping, not only advantageous for its application in the visible light photocatalyst but also can be used in the solar cell applications [11]. Thirdly; it exhibits strong adsorption characteristic for the molecular oxygen, which can scavenge photo-electrons to control the $e^- - h^+$ recombination in the photocatalysis reaction [6,7]. Fourthly; dissimilar to the Cu₂O, the CuO does not deactivate by the photo-corrosion in the photocatalyst reaction [12]. There are several reports available on the synthesis of CuO NPs using; (i) soft template assisted method (polymers, surfactants and capping agents were used) [13], reverse microemulsion-impregnation method (cyclohexane, triton-X-100 and n-hexanol solutions were used) [2] and solution combustion technique (citric acid, urea and nitric acid were used) [14]. These techniques, however, offer synthesis of CuO NPs but the use of hazardous chemicals and precarious experimental conditions (high operating temperature etc.) may not favorable for the health and

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environment. Besides this, Cu metallic phases also formed in other synthesis methods which also affect the photocatalyst performance of the products [15]. Among the available solution-chemistry routes, hydrothermal and/or co-precipitation methods are of special interest because they are safe and environmental-friendly process, performed at moderate temperatures and capable in producing pure and doped nanostructures of oxide ceramics [16,17]. These methods are low cost synthesis procedures and, importantly, the hazardous effects can also be minimized by choosing appropriate reagents [16]. Therefore, high quality catalyst production with low cost and high efficiency can be achieved by employing the co-precipitation technique.

In most of the previous reports, X-ray photoelectron spectroscopy (XPS) has been employed to determine the oxidation state of copper in the copper oxide catalyst samples [18–21]. X-ray absorption spectroscopy (XAS), on the other hand, is also an element specific technique and capable to investigate the local atomic structure, coordination number, valence state and hybridization of the probed atoms has not been extensively reported for such catalyst samples. The differences between XAS and XPS are twofold. First, in XAS the core-electron can be excited into an efficient screening orbital so that the perturbation on the remaining ground-state is small, where as in XPS the initial ground-state valence electrons experience the full potential of an unscreened core hole. Second, in XPS various components of the spectrum are broadened rather than exhibiting specific multiplets, because all of the many final-states can be reached. On the other hand, in XAS technique, quite separate spectral features appear in the XAS spectrum because the dipole selection rules allow only a limited number of states to accessible [22]. Although XPS technique often provides information regarding the oxidation state of copper in copper oxides but, (i) it is mainly a surface probing technique (ii) experience charging effects in case of powder sample measurements and (iii) it generally involves cumbersome fitting procedures because the Cu2p XPS peaks of Cu⁺, Cu⁺² and metallic Cu all appear within a very narrow energy range [18,19]. Therefore, an alternative of XPS, here we took advantage of the X-ray absorption spectroscopy, within the low and high energy range, to investigate the valence state of Cu and local atomic structure around the Cu (i.e., bond distances and coordination number) in the copper oxide photocatalyst nanoparticles.

In our previous study [23], small sized (~3 nm–8 nm) CuO nanoparticles and CuO/Cu₂O nanocomposites have shown photocatalyst properties towards the degradation of water pollutant dyes. To enhance our understanding on the photocatalyst behavior and electronic structure properties of copper oxide based catalyst materials, here we explore the catalyst property of larger sized and electronic-structure modified CuO NPs by Ti doping. The 10 M % Ti doping was employed as a test doping concentration to enhance the optical absorbance and electron density of host CuO. Our experimental results reveal that the single phase CuO and Cu_{0.9}Ti_{0.1}O NPs with modified electronic structure properties can serve as effective photocatalyst materials toward the degradation of MO and PD aqueous dyes under the visible light irradiation. The smaller sized CuO NPs show superior photo-degradation rates of MO and PD over the larger sized Cu_{0.9}Ti_{0.1}O NPs.

2. Experimental details

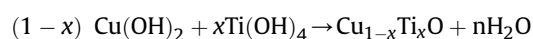
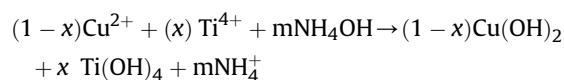
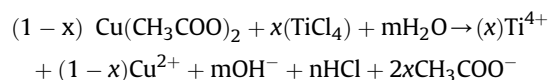
CuO and Cu_{0.9}Ti_{0.1}O NPs were synthesized by using previously stabilized co-precipitation method [23–26]. First of all, Cu(CH₃COO)₂·5H₂O and TiCl₄·5H₂O were dissolved, separately, into deionized (DI) water with magnetic stirring to form the aqueous solutions. To prepare pure CuO NPs, diluted NH₄OH solution was added (drop-wise) into the previously prepared solution of copper

acetate with constant stirring and then aging for 45 min. Similarly, to prepare Cu_{0.9}Ti_{0.1}O NPs the solutions of copper acetate and titanium chloride were added together with the addition of NH₄OH solution. Ti doping ratio was the molar ratio of Ti to Ti + Cu, namely *x*. Both of the samples were prepared at pH ~9. The brown-blue colored precipitates, so formed, were washed several times with DI water and then dried at 100 °C in air to remove the hydroxyl component, Cl⁻ ions and other ionic impurities. Further, in order to establish solid state reactions in the compounds, high temperature annealing in air was done using a thermal cycle corresponding to a temperature upward and downward slope of 100 °C/hour with a plateau of 2 h at maximum temperature (500 °C). The dark brown/blue colored samples were fairly crushed in the mortar-pestle and the fine powdered samples were collected carefully. As-prepared samples were characterized using the synchrotron X-ray diffraction ($\lambda = 1.240 \text{ \AA}$), performed at X-ray scattering beam line (3D beam line of Pohang Accelerator laboratory (PAL), South Korea). To collect high resolution transmission electron microscopy (HR-TEM) images of the samples, the powder samples were sonicated in the ethanol solution and then loaded on the carbon coated Cu grids. The morphology and crystallite sizes were analyzed using JOEL-JEM-2200FS HR-TEM accompanied with selected area electron diffraction (SAED) facility. Near edge X-ray absorption fine structure (NEXAFS) spectra at the O K-edge, Cu L-edge and Ti L-edge were collected in the total electron yield (TEY) mode at 10D (PAL-KIST) beam line. The photon energy resolution of this beam line was better than 0.6 eV (at O K-edge). The extended X-ray absorption fine structure (EXAFS) measurements at Cu Kedge were performed at 1D (PAL-KIST) beam line. To perform the adsorption reactions of the CuO and Cu_{0.9}Ti_{0.1}O NPs, with the MO and PD pollutants the aqueous solutions, (0.2 g/L) of MO and PD were prepared and the 0.1 g of the catalyst samples were fairly dispersed in the previously prepared 50 ml MO and PD aqueous solutions by using magnetic stirring for 45 min in dark. To evaluate the photocatalytic properties of the NPs, a commercial 150 W tungsten-filament bulb was used as a light irradiation source. To avoid the thermal effects from light source; the bulb was kept ~20 inches above from the beaker, beaker was placed in the cold water plate and the water was changed after each 15 min. At the regular intervals (30 min), 10 ml of the suspensions were sampled and the NPs were separated by centrifugation for 10 min. The photo-degradation of MO and PD aqueous pollutants, under the presence of CuO and Cu_{0.9}Ti_{0.1}O NPs, was examined by collecting the UV–visible absorption spectra at the different light irradiation time. The UV–visible absorption spectra of catalyst samples were collected by using Varian Cary-300 UV–visible spectrophotometer. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Synthesis of nanoparticles

From the nature of synthesis and experimental findings, formation of Cu_{1-x}Ti_xO (*x* = 0 and 0.1) nanoparticles in colloidal medium may occur via the following chemical reactions;



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