Single-step processing of copper-doped titania nanomaterials in a flame aerosol reactor

Manoranjan Sahu and Pratim Biswas*

Abstract

Synthesis and characterization of long wavelength visible-light absorption Cu-doped TiO$_2$ nanomaterials with well-controlled properties such as size, composition, morphology, and crystal phase have been demonstrated in a single-step flame aerosol reactor. This has been feasible by a detailed understanding of the formation and growth of nanoparticles in the high-temperature flame region. The important process parameters controlled were: molar feed ratios of precursors, temperature, and residence time in the high-temperature flame region. The ability to vary the crystal phase of the doped nanomaterials while keeping the primary particle size constant has been demonstrated. Results indicate that increasing the copper dopant concentration promotes an anatase to rutile phase transformation, decreased crystalline nature and primary particle size, and better suspension stability. Annealing the Cu-doped TiO$_2$ nanoparticles increased the crystalline nature and changed the morphology from spherical to hexagonal structure. Measurements indicate a band gap narrowing by 0.8 eV (2.51 eV) was achieved at 15-wt.% copper dopant concentration compared to pristine TiO$_2$ (3.31 eV) synthesized under the same flame conditions. The change in the crystal phase, size, and band gap is attributed to replacement of titanium atoms by copper atoms in the TiO$_2$ crystal.

Introduction

Nanosized TiO$_2$ has been widely used because of its stability in aqueous environments and low production cost. However, its light absorption range is limited to the ultraviolet (UV) spectrum of light due to its wide band gap (approximately 3.2 eV). To shift the absorption range to the visible spectrum, various approaches have been pursued in the past involving size optimization [1], compositional variation to make sub-oxides [2], surface modification [3], and doping [4-6] to modify the TiO$_2$ structure. Among these methods, tailoring the band structures by incorporating a dopant into the host nanomaterial is a promising approach [6-8]. Several studies have reported enhancement of absorption in the visible range and photocatalytic activity on doping TiO$_2$ by transition metal ions like Cu, Co, V, Fe, Nb, and non-metal like N, S, F [4,5,9-11]. However, a major challenge is to process low-cost, and stable doped nanomaterials with well-controlled properties that can effectively absorb visible light.

Recently, copper has been increasingly investigated as a dopant for titania [12]. Copper oxide is a narrow band gap (cupric oxide, 1.4 eV; cuprous oxide, 2.2 eV) material which has a high-absorption coefficient, but suffers from UV-induced photocorrosion [12]. However, copper oxide coupled with TiO$_2$ has been demonstrated to be stable with improved photocatalytic degradation properties [9,13,14], effective CO$_2$ photoreduction [15,16], improved gas sensing, and enhanced H$_2$ production [17,18]. It has been shown that Cu-doped TiO$_2$ induces more toxicity compared to TiO$_2$ [19]. Though a large number of studies on Cu-doped TiO$_2$ nanomaterials have been reported, there is little information available on the effect of dopant concentration on TiO$_2$ properties. Dopants can replace Ti in the substitutional sites or be incorporated in the interstitial sites. In some cases, they may segregate on the surface [20]. The creation of new energy states due to the incorporation of the dopant in the host TiO$_2$ alters the particle properties, electronic structure, and light absorption properties. These affect their functionality, and hence can be used in different applications [3,8,20,21]. In summary, there is a need to synthesize Cu-doped nanomaterials with controlled properties (independently) which will help understand in detail the role

* Correspondence: pbiswas@wustl.edu
Aerosol and Air Quality Research Laboratory, Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130, USA

© 2011 Sahu and Biswas; licensee Springer. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/2.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
of the dopant in altering TiO$_2$ properties. It is essential to have samples wherein one characteristic is varied, keeping the others the same. For example, samples of varying crystal phases while maintaining the size the same will allow to establish the dependence of biological activity with the crystal phase.

Studies have reported the preparation of various doped TiO$_2$ nanomaterials by multi-step liquid-phase synthesis [5], gas-phase spray pyrolysis, and flame synthesis methods [22-24]. Flame aerosol synthesis is a single-step process and allows independent control of the material properties such as particle size, crystallinity, homogeneity, and degree of aggregation [25,26]. At elevated temperatures encountered in the flame synthesis process, most dopants can diffuse rapidly [27] and be uniformly distributed due to excellent precursor vapor mixing at the molecular level [22,20]. Furthermore, flame aerosol processing is a scalable technique that is commercially used to manufacture large quantities of nanomaterials [28].

The synthesis of Cu-doped TiO$_2$ in a single-step flame aerosol process is reported in this paper. A detailed characterization of the as-produced samples to understand the influence of process parameters on material properties is done. The role of key process parameters such as molar feed ratio of precursors and dopant concentration on TiO$_2$ nanomaterial properties such as size, composition, crystallinity, stability in suspension, and morphology are thoroughly investigated. A method to control the crystal phase of the Cu-doped TiO$_2$ nanomaterial has been discussed. The effect of annealing temperature on crystal phase and microstructure of the Cu-doped TiO$_2$ material is reported. A formation mechanism of Cu-doped TiO$_2$ nanomaterial in the flame aerosol reactor is elucidated.

**Experimental**

**Nanomaterial synthesis**

Figure 1 shows the schematic diagram of the flame aerosol reactor system used for the synthesis of the Cu-doped TiO$_2$ nanomaterials. The main components of the flame aerosol reactor system are: a diffusion burner, a precursor feeding system, and a quenching and collection system. The design details of the diffusion burner used for this study is given in Jiang et al. [26]. Nitrogen was passed through titanium tetra-isopropoxide (TTIP, 99.7%, Aldrich, Steinheim, Germany) in a bubbler, and the saturated vapor was introduced into the central port of the burner. The bubbler containing the liquid TTIP precursor was placed in an oil bath and was maintained at a temperature of 98°C. The precursor delivery tube was maintained at a temperature of 210°C by a heating tape. This avoided the condensation of the precursor TTIP vapor in the delivery tube. Copper nitrate trihydrate (99.5%, VWR International, Radnor, PA, USA) was used as the dopant precursor. The dopant precursor solution was prepared by dissolving a known amount of copper nitrate in distilled water. A stainless steel collision nebulizer was used to generate fine spray droplets (less than 2 μm), which were then carried by nitrogen gas into the high-temperature zone of the flame. The doping percentage was varied by introducing different molar ratios of both the precursors. The overall doping concentration was varied from 0 to 15 wt.%. Methane and oxygen were introduced into the second and third ports of the burner respectively to create a diffusion flame zone. The volumetric flow rates of N$_2$ through the TTIP bubbler and the O$_2$ were precisely controlled by mass flow controllers at 2 and 7.5 lpm, respectively. The methane flow rate was maintained at 1.8 lpm, and varied for few of the tests. A 20-lpm flow of compressed air was supplied in a radial direction to the quenching ring for cooling. The entrained air diluted the aerosol stream and suppressed particle growth. The synthesized materials were collected using a glass microfiber filter paper (Whatman) for further characterization.

**Material characterization**

The size, morphology, and microstructure of the nanoparticles were determined by a transmission electron microscope (TEM; Model: JEOL 2100F FE-(S) TEM, JEOL Ltd., Tokyo, Japan) with an accelerating voltage of 200 kV and by a field emission scanning electron microscope (SEM) (Model: JEOL 7001LVF FE-SEM, JEOL Ltd.). The elemental analysis of the doped nanomaterial was done using energy dispersive spectroscopy (EDS) analysis integrated with a SEM. Phase structures of the material were determined using an X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 A) (Rigaku D-MAX/A9). Zeta potential, an indicator of the stability of nanoparticles in suspensions, was measured by using a ZetaSizer Nano ZS (Malvern Instruments Ltd., Worcestershire, UK) dynamic light scattering instrument. Nanoparticles were dispersed in de-ionized water at a concentration of 30 μg/ml and sonicated for 25 min using a bath sonicator (40 W, 50 kHz, 5 Fisher Scientific, Fairlawn, New Jersey, USA) before zeta potential measurements. UV-visible absorption spectroscopy (Perkin Elmer Lambda 2S, Perkin Elmer, Waldham, MA, USA) was used to analyze the absorbance spectrum of the nanomaterials over wavelengths ranging from 200 to 800 nm at room temperature. From the absorption spectrum, the band gap was estimated. The absorption edge was estimated to be the point where the absorption was 30% of the maximum, corresponding to where 50% of the photons were absorbed. This approach was used because of the difficulty in finding the linear region of the absorption spectrum according to conventional methods of band gap estimation [21].
The list of experiments performed is outlined in Table 1. The flow rates were controlled to maintain the same residence time in the high-temperature flame (test 1). TiO\textsubscript{2} was synthesized under the same experimental conditions using only TTIP as the precursor (test 1A). Addition of dopant influences nanomaterial properties such as size, crystal structure, stability in suspension, and optical properties. The copper dopant concentration was varied from 0 to 15 wt.% to process Cu-doped TiO\textsubscript{2}.

**Table 1** Summary of the experimental test plan

| Test no. | Dopant concentration (wt %) | CH\textsubscript{4} (lpm) | Objective |
|----------|-----------------------------|---------------------------|-----------|
| 1        | A 0                         | 1.8                       | Study the influence of dopant concentration on TiO\textsubscript{2} material properties such as size, crystal phase, suspension stability, and light absorption. |
|          | B 0.5                       |                           |           |
|          | C 1                         |                           |           |
|          | D 3                         |                           |           |
|          | E 5                         |                           |           |
|          | F 15                        |                           |           |
| 2        | A 3                         | 0.8                       | Study the effect of methane flow rate on size and crystal phase of the material. |
|          | B 1.2                       |                           |           |
|          | C 1.5                       |                           |           |
|          | D 1.8                       |                           |           |
| 3        | A 1                         | Annealing temperature, 400°C, 600°C | Examine the effect of annealing on phase and microstructure characteristics of Cu-doped TiO\textsubscript{2} nanoparticles |
|          | B 15                        | Duration of annealing under air, 4 h |

All the particles were synthesized by diffusion flame aerosol reactor. Annealing was done in a furnace under air atmosphere.
nanomaterials (test 1(B-F)) to investigate the impact on properties. The copper dopant concentration was estimated based on the precursors feed rate to the flame. The temperature-time history in the flame impacts the particle formation and growth rates. This was varied by altering the methane flow rate from 0.8 to 1.8 lpm at a constant dopant level of 3 wt.% (test 2). Annealing of the 1 and 15-wt.% Cu-doped TiO₂ was conducted for 4 h at 400 and 600°C in an atmosphere of air to examine property alterations (test 3).

Results and discussion

Doping TiO₂ with other atoms changes properties such as particle size, crystal structure, stability in suspension, and light absorption. The mechanism of Cu-doped TiO₂ nanoparticle formation in the flame aerosol reactor is discussed first. The effect of copper dopant on TiO₂ particle properties are discussed followed by crystal structure control of the doped TiO₂ nanomaterials. Finally, microstructure changes of Cu-doped TiO₂ are discussed under different annealing conditions.

Particle formation mechanism

The proposed Cu-doped TiO₂ particle formation mechanism is illustrated in Figure 2. This is similar to the pathways proposed by Basak [24] for multi-component nanomaterial systems. To understand the formation mechanism of the Cu-doped TiO₂ nanoparticles in the flame aerosol reactor, pristine TiO₂ was synthesized first using TTIP only as the precursor. TTIP decomposes to form TiO₂ monomers, which then undergo subsequent growth by collision followed by sintering to form nanoparticles (test 1A). For synthesizing Cu-doped TiO₂ particles, both the TTIP and copper nitrate precursor are fed to the high-temperature flame. The nanoparticle properties such as size and composition depend on the relative decomposition kinetics and molar feed ratios of the precursors (see Figure 2). The decomposition rate of TTIP is given by, $k_a = 3.96 \times 10^5 \exp((-7.05 \times 10^4)/RTs^{-1}$ [29]. Since the kinetic data for copper nitrate precursor is not available, the decomposition rate reported for copper acetyl acetonate was assumed ($k_b = 3.02 \times 10^7 \exp((-1.15 \times 10^3)/RT)s^{-1}$) [30]. The two precursors form TiO₂ (formed from TTIP molecular decomposition) and CuO (formed by decomposition of copper nitrate followed by evaporation) monomers at similar time instants as their decomposition rates are similar ($k_{Cu}/k_{Ti}$ to approximately 5, at 2,200°C). Depending on the molar feed ratio of the precursors, a variety of morphologies can be formed, ranging from particles consisting of only copper oxide, particles of only TiO₂, and the particles of mixed TiO₂ and CuO. At low copper concentrations (1-5 wt.%), CuO monomers are readily incorporated into the higher concentration TiO₂ clusters by a scavenging process.

This is similar to the phenomenon demonstrated by Wang et al. [22]. Subsequent collisional growth and sintering result in a homogenous mix of Cu-doped TiO₂ particles. However, at higher Cu feed concentration (approximately 15wt%), apart from the collision and sintering of the CuO monomers and TiO₂ clusters, some of the CuO oxide monomers also condense onto the formed Cu-doped TiO₂ particles. The HR-TEM image of the synthesized 15-wt.% Cu-TiO₂ nanoparticles indicates regions of amorphous CuO on the particle surface. The explanation of CuO monomer condensation on the particle surface is thus corroborated (test 1F). The nanomaterials synthesized at various dopant concentration were verified by single particle EDS analysis to be comprised of both copper and titania. No particles were found consisting of only Ti or only copper species.

Effect of copper dopant concentration on TiO₂ properties

Particle size analysis

Figure 3 shows the TEM, HR-TEM images, and primary particle size distribution of 1 wt.% Cu-TiO₂ (test 1B) and 15 wt.% Cu-TiO₂ (test 1F) samples. The particle size distribution was obtained by measuring the diameter of 200 particles from representative TEM images. As shown in the size distribution of these samples (see Figure 3), the particles were spherical and size decreased with increasing doping concentration. The geometric mean primary particle size obtained at 1 wt.% doping was approximately 47 nm compared to approximately 33 nm obtained at 15 wt.% doping. The peak broadening observed in XRD pattern (see Figure 4) also qualitatively explained the change in particle size and lattice expansion with doping. The crystallite size was estimated from the XRD pattern obtained using Scherrer formula. The crystallite size obtained at 1 wt.% doping was 33 nm compared to 25 and 23 nm at 5 and 15-wt.% doping concentration. It is important to note that crystallite size estimation from XRD is different from the particle size observed from the microscopic analysis. XRD measures the size of the small domains within the grains and one particle may consist of several crystallites based on the preparation methods [31]. The decreased particle size with increasing doping concentration is due to the inhibition of the grain growth. As evident from the HR-TEM images of the 15 wt.% Cu-TiO₂ (see Figure 3), an enhanced amorphous layer is observed on the surface. The excess CuO monomers condense on to the existing Cu-doped TiO₂ particles. Thus, particle crystallinity decreases and also prevents grain growth. Wang et al. [22] observed an amorphous crystal structure and decreased grain size with an increasing Fe³⁺/Ti⁴⁺ ratios consistent with our Cu-doped TiO₂ materials. Reduction in size was also observed when Li et al. [3] synthesized Zn-doped SnO₂ nanomaterials. Norris et al. [27] proposed a process...
called self-purification by which dopants diffuse from inside to the surface sites of TiO₂ nanocrystals. This change in particle size with doping concentration is fundamentally a very important phenomenon for electronic structure modification. These results indicate that the particle size of the Cu-doped TiO₂ can be controlled by manipulating the dopant concentration in addition to the methods demonstrated by other researchers by controlling the precursor feed concentration and residence time of the particle in the high-temperature flame [26,32].

Crystal phase
The functionality of TiO₂ nanomaterials for various applications depends on its crystal phase. The anatase phase of TiO₂ is preferred for photocatalytic applications, whereas rutile phase is preferred for applications in pigments [1]. It is, therefore, necessary to understand the modifications in the crystal structure by incorporation of the dopants in TiO₂. The XRD diffraction pattern of the Cu-doped TiO₂ nanomaterials synthesized at various concentrations is shown in Figure 4. The pristine and Cu-doped TiO₂ nanoparticles were prepared at the same flame conditions for comparison. The pristine TiO₂ was primarily anatase under the chosen processing conditions. However, with increasing dopant concentration, the transformation from anatase to rutile phase occurred, as shown in Figure 4a from the (110) rutile peak, consistent with other studies [18,33]. The anatase and rutile fraction were calculated according to the formula proposed by Spurr and Myers [34]. The pristine TiO₂ had 1.2% rutile content, but with increasing doping concentration to 15 wt.%, the rutile phase increased to 21.8%. Even at high dopant concentration (15 wt.%), no pure dopant-related crystal phase was observed within the XRD detection limit. The same anatase to rutile phase transformation was observed for synthesis of Cu-doped TiO₂ by other methods [9,35].

The similarity in ionic radius of Cu²⁺ (0.73 Å) to that of Ti⁴⁺ (0.64 Å) enable copper to substitutionally replaces Ti in the titanium lattice in the flame environment, where particles are formed from the atomistic state. In the high-temperature flame synthesis of Cu-doped TiO₂ nanomaterial, the copper dopant creates a higher number
of defects inside the anatase phase, resulting in a faster formation and growth of a higher number of rutile nuclei [36]. At elevated temperatures, the substitution of Ti$^{4+}$ by Cu$^{2+}$ increases the oxygen vacancy concentration and decreases the free electron concentration. The excess of oxygen vacancies created in the TiO$_2$ crystal lattice is the responsible for anatase to rutile phase transition [36,37]. Nair et al. [36] found that a dopant with an oxidation state above 4+ will reduce the oxygen vacancy concentration in the titania lattice as an interstitial impurity. Dopants with an oxidation state of 3+ or lower when placed in the titania lattice points create a charge-compensating anion vacancy [36] and cause a transformation to the rutile phase as also found in this study. At higher dopant concentration (15 wt.%), amorphous phase was also observed on the surface as well as in the bulk. The TEM and HR-TEM images and 15-wt.% Cu-doped TiO$_2$ nanoparticles (see Figure 3) shows that particles at lower doping concentrations are fully crystallized, and the crystal lattice spacing corresponds to the anatase phase of TiO$_2$ (0.331 ± 0.03 nm), whereas the particle synthesized at 15-wt.% copper concentration shows both crystalline and amorphous phases of the material. The HR-TEM images confirm that Cu$^{2+}$ doping retards the grain growth of TiO$_2$ nanoparticles. Similar results of decreasing crystalline nature of material were observed when Fe$^{2+}$- and Zn$^{2+}$-doped TiO$_2$ were synthesized [3,22]. In a similar doping study, Wang et al. [22] found that at higher Fe$^{2+}$/Ti$^{4+}$ ratios of 0.12, more rutile and amorphous crystal structure was observed, consistent with our Cu-doped TiO$_2$ materials.

Figure 4b and 4c represent the XRD spectra for (101) and (201) anatase peaks scanned at a very small steps of 0.004 degree for pristine and doped TiO$_2$ nanomaterials. It is important to note that with increasing dopant concentration, broadening of the major anatase peaks (101) and (201) was observed, which indicates a decrease in crystallite size. The shift in peak position to the right [8] with increasing dopant concentration indicates that Cu$^{2+}$ ions replaced some Ti$^{4+}$ ions along with the lattice expansion. The results clearly indicate that addition of dopant alters the crystal phase of the host nanomaterial and the degree of phase transition depends on dopant types and their concentrations.

Zeta potential and suspension stability
The dispersion characteristics of nanoparticles in aqueous suspensions influence the fate and transport, catalytic reactivity in the environmental system as well as critical in understanding for toxicological applications [38,39]. The stability of the synthesized Cu-doped TiO$_2$
nanoparticles was analyzed through the measurement of zeta potential in aqueous system using de-ionized water suspension (Figure 5) and compared with pure TiO$_2$ (test 1A) and commercial CuO. When metal oxide nanoparticles are dispersed in water, the hydration of the nanoparticle surface followed by protonation and deprotonation of the surface groups from the oxide surface results in a surface charge. The effective surface charge on the particle depends on the isoelectric point (IEP) in the suspension [39,40]. The zeta potential observed for pure TiO$_2$ particle was +3.4 mV in the suspension, as the measured pH of the suspension was 5.06, which is less than the IEP of the TiO$_2$(pH approximately 6.0) and consistent with other studies [40]. However, for Cu-doped TiO$_2$ nanoparticles, the zeta potential value decreased to -3.4 mV and -25.6 mV at 1-wt.% (test 1B) and 15-wt.% (test 1F) copper dopant concentration. The zeta potential measured for the
commercial CuO was -27.3 mV which is close to the zeta potential value observed for 15-wt.% Cu-TiO₂ samples (test 1F). The high surface charge on the 15 wt.% Cu-TiO₂ indicates better stability of these particles over pristine TiO₂ nanoparticles in aqueous suspension. The higher zeta potential value and suspension stability of the doped nanoparticles compared to TiO₂ is attributed to charge imbalance created due to substitution of Ti⁴⁺ atoms by Cu²⁺ in the TiO₂ structure resulting in a more negatively charged surface. Furthermore, zeta potential values for 15-wt.% Cu-TiO₂ samples being similar to pure CuO supports the presence of a copper oxide layer on the outer surface of the particles.

**Light absorption properties**

The absorption spectra of the resulting Cu-doped TiO₂ nanomaterials was determined by a diffusive reflectance spectroscopy measurement. The absorption spectrum of Cu-doped TiO₂ nanomaterials prepared at various dopant concentrations are shown in Figure 6. With increasing dopant concentration, an increased absorbance in the visible spectrum is observed. The estimated Eg for pristine TiO₂ was 3.31 eV which is consistent with the reported value for anatase TiO₂ [21]. With increasing dopant concentration, the band gap energy decreased and was estimated to be 2.51 eV at the highest dopant concentration of 15 wt.%. This change of approximately 0.8 eV was due to the incorporation of Cu²⁺ ions into TiO₂ crystal structure, and CuO forming a layer on the particle surface. From an experimental and theoretical study of band structure estimation of metal oxides, The results are consistent with findings of Thimsen et al. [21] that the band gap energy decreases with increasing Fe concentration in anatase-based TiO₂ materials.

Change in the optical absorption is due to the defect centers created by the substitution of Ti⁴⁺ by Cu²⁺ atoms in the TiO₂ crystal lattice. Earlier studies indicated that doping with aliovalent ions changes the local lattice symmetry and defect characteristics, which could change the absorption properties and the material properties. In Cu-doped TiO₂, when copper ions are either located inside the bulk TiO₂ or on the surface sites, a rearrangement of the neighbor atoms take place to compensate the charge deficiency, resulting in lattice deformation. The lattice deformation affects the electronic structure causing the band gap shift [3]. Furthermore, small amounts of Cu²⁺ dopant in the lattice sites of TiO₂ introduce oxygen vacancies due to the charge compensation effect [36,41]. Increasing the copper doping concentration increases the oxygen vacancies and probably form a newly doubly occupied oxygen vacancy as discussed in Li et al. [3]. Therefore absorption of the doped nanomaterial and band gap shift may be controlled by surface effects, doping-induced vacancies, and lattice strain. It can be said that the copper modified TiO₂ structure extends its absorption to the visible spectrum of sunlight (400-700 nm) effectively. Hence, these copper-
doped materials can be utilized for various visible-light photocatalytic applications, which have been demonstrated in several other studies [9,18].

**Crystal phase control of Cu-doped TiO$_2$ nanoparticle**

The functionality of the nanomaterials depends on their properties such as particle size, crystal phase, morphology, and agglomeration [38,40]. A recent study by Braydich-Stolle et al. [42] showed that cytotoxicity in the cells is both size and crystal structure dependent. They demonstrated that mechanism of cell death varied with different crystal structure; the anatase phase of TiO$_2$ being more toxic than the rutile phase. To understand the role of crystal phase of the doped nanomaterials on its functionality, it is important to independently control the crystal phase without varying the other material properties such as size. Previous studies have demonstrated that crystal phase of
the TiO$_2$ nanoparticle can be controlled by varying the temperature in the flame (changing the methane flow rates) and quenching rate downstream of the flame [25,26]. A similar methodology was adopted to control the crystal phase of the Cu-doped TiO$_2$ materials. The dopant concentration was kept constant at 3 wt.% and methane flow was varied from 0.8 to 1.8 lpm (test 2, Figure 7a). The anatase phase varied from 39% to 95%, when the methane flow was increased from 0.8 to 1.2 lpm, whereas the primary particle sizes for all the cases were similar. The representative TEM micrographs and corresponding size distribution of the particles synthesized at 0.8 and 1.8 lpm are shown in Figure 7b, c. The geometric mean size of 31.5 and 32.3 nm were nearly the same for the two flow

![Figure 7](https://example.com/figure7.png)

**Figure 7** Dopant concentration, representative TEM micrographs and corresponding size distribution of the particles. (a) XRD spectra at different methane flow rates (A anatase, R rutile) and particle size distributions at (b) 0.8 lpm, (c) 1.2 lpm methane flow rates for 3-wt.% Cu-TiO$_2$ nanoparticles (test 2).
rate conditions. The size remained similar due to the balance between temperature profile and residence time in the flame at different methane flow rates. For a fixed flame operating parameters, increasing the methane flow rate increases the flame temperature but at the same time reduces the residence time in the flame. For lower methane flow rate the temperature decreases and residence time increases. Thus the crystal phase of the Cu-doped TiO₂ nanoparticles was independently varied while keeping the primary particle size the same. These well-controlled Cu-doped TiO₂ samples will be of significant importance in biological studies to elucidate the role of crystal phases without interferences from the other particle properties such as size.

**Effect of annealing on Cu-doped TiO₂ nanoparticle properties**

The morphological and structural transformation of the doped nanoparticles plays important role in photocatalytic activity by modifying the surface chemistry, crystal and electronic structure [43]. Since both amorphous and crystalline phases were observed in HR-TEM images at higher dopant concentration, the as-prepared Cu-doped TiO₂ samples were annealed at different temperatures to investigate the effect on crystal structure and morphology. The 1 and 15-wt.% Cu-doped TiO₂ samples were annealed at temperatures of 400°C and 600°C for 6 h. No phase transformation was observed at 400°C. At 600°C, the transformation from anatase to rutile phase was observed as shown in Figure 8, which is consistent with other studies [18,44]. The anatase weight fraction decreased from 75% to 21% for the 15-wt.% Cu-doped TiO₂ sample. However, the morphology of the particles changed from spherical to hexagonal structure for nanoparticles prepared at both the dopant concentrations. The crystallite size increased with annealing. For 15-wt.% Cu-doped TiO₂ sample, the phase related to CuO was observed based on the peaks recorded at Bragg angle of 35.5 and 39 from the XRD pattern (Figure 8). The amorphous CuO present in the outer layers were annealed to form the crystalline phase in the presence of air.

The HR-TEM images of samples annealed at 600°C are shown in Figure 9. The figure indicates that the annealed 1-wt.% Cu-doped TiO₂ particle was completely crystallized with no discontinuity in the crystal fringes as observed from HR-TEM images, similar to the as-prepared 1-wt.% Cu-doped TiO₂ particles. However, for the 15-wt.% dopant sample, some amorphous regions were still detected as shown in Figure 9 (highlighted with the white squares). More detailed investigations are needed to understand the effect of dopant concentration and reaction environments on morphology change during post-synthesis treatment of the initially synthesized spherical particles. The UV-vis measurements of absorption spectra of 1- and 15-wt.% Cu-doped TiO₂ annealed samples are shown in Figure 10 and compared with the commercially available CuO nanoparticles. Annealing of the 15 wt.% Cu-TiO₂ increased the absorption compared to the as prepared samples in the visible spectrum mainly because of enhanced crystalline CuO formation. It is clear from the results that post-synthesis annealing can alter the doped TiO₂ nanomaterial properties such as size, crystal structures as well as absorption properties, thus influencing eventual functionality and performance.

**Conclusions**

Cu-doped TiO₂ nanoparticles were synthesized in a diffusion flame aerosol reactor and the properties were
Figure 9 TEM images of annealed Cu-doped TiO$_2$ samples (a) 1 wt.% Cu-TiO$_2$ and (b) 15 wt.% Cu-TiO$_2$. Annealing temperature, 600°C; duration of annealing, 4 h (test 3).

Figure 10 Normalized UV-visible absorption spectra measured by diffuse reflectance spectroscopy of the annealed Cu-doped TiO$_2$ nanomaterials. Samples were annealed for 4 h at 600°C (test 3).
readily varied by controlling the processing conditions. The increase in dopant concentration caused the transformation from anatase to rutile phase of TiO₂ due to replacement of Ti⁴⁺ by Cu²⁺ in the crystal structure of TiO₂. A decrease in primary particle size was also observed. The doped nanomaterials exhibited better aqueous suspension stability compared to pristine TiO₂ due to charge imbalance created. The annealing of the doped samples resulted in the phase segregation and crystallization of CuO for the higher dopant concentration samples. Spectroscopy measurements confirm a shift in the absorption to visible frequencies, due to crystal structure modification.

Acknowledgements
This work was partially supported by a grant from the NIEHS, Grant No. 100003N. The authors thank the McDonnell International Scholars Academy and the McDonnell Academy Global Energy and Environment Partnership (http://imagep.wustl.edu) for providing partial support for this work.

Authors’ contributions
PB and MS both participated in the design of the study. MS carried out all the experiments. MS and PB participated in results analysis. MS drafted the manuscript and PB provided comments/suggestions to revise it.

Competing interests
The authors declare that they have no competing interests.

Received: 10 October 2010 Accepted: 6 July 2011 Published: 6 July 2011

References
1. Almquist CB, Biswas P. Role of synthesis method and particle size of nanostructured TiO₂ on its photocatalytic activity. J Catal 2002, 212:145-156.
2. Dhurnal SY, Daulton TL, Jiang J, Khomami B, Biswas P. Synthesis of visible light-active nanostructured TiO₂ (x < 2) photocatalysts in a flame aerosol reactor. Appl Catal B 2009, 86:145-151.
3. Li LP, Liu JJ, Su YG, Li GS, Chen XB, Qiu XQ, Yan TJ. Surface doping for photocatalytic purposes: relations between particle size, surface modifications, and photocatalytic activity of SnO₂/Zn⁺ nanocrystals. Nanotechnol 2009, 20:155706.
4. Asahi R, Monikawa T, Ohwaki T, Aoki K, Taga Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. Science 2001, 293:269-271.
5. Choi WY, Termin A, Hoffmann R. The role of metal-ion dopants in quantum-sized TiO₂ - correlation between photoreactivity and charge-carrier recombination dynamics. J Phys Chem 1994, 98:13669-13679.
6. Li W, Wang Y, Lin H, Shah SI, Huang CP, Doren DJ, Rykov SA, Chen JG, Barrete MA. Band gap tailoring of Nd³⁺ doped TiO₂ nanoparticles. Appl Phys Lett 2003, 83:4143-4145.
7. Bhattacharya K, Varma S, Tripathi AK, Bharadwaj SR, Tyagi AK. Effect of vanadia doping and its oxidation state on the photocatalytic activity of TiO₂ for gas-phase oxidation of ethene. J Phys Chem C 2008, 112:19012-19112.
8. Lu W, Frenkel AJ, Woccik JC, N C, Shah SH. Dopant location identification in Nd³⁺ doped TiO₂ nanoparticles. Phys Rev B 2005, 72:155315-155316.
9. Arana J, Dona-Rodriguez JM, Gonzalez-Diaz O, Rendon ET, Melian JAH, Colon G, Navio JA, Pena JP. Gas-phase ethanol photocatalytic degradation study with TiO₂ doped with Fe, Pd and Cu. J Mol Catal A Chem 2009, 215:133-160.
10. Rane KS, Mhalikar R, Yin S, Sato T, Cho K, Dunbar E, Biswas P. Visible light-sensitive yellow TiO₂-xNex and Fe-N co doped Ti1-yFe₂O₃-xNex anatase photocatalyst. J Solid State Chem 2006, 179:3033-3044.
11. Asahi R, Monikawa T. Nitrogen complex species and its chemical nature in TiO₂ for visible-light sensitized photocatalysis. Chem Phys Lett 2007, 339:57-63.
12. Mor GK, Varghese OR, Wilke RHT, Sharma S, Shankar K, Latempa TJ, Choi KS, Grimes CA. p-Type Cu-Ti-O nanotube arrays and their use in self-biased heterojunction photoelectrochemical diodes for hydrogen generation. Nano Lett 2008, 8:3555-3555.
13. Park HS, Kim DH, Kim SJ, Lee KS. The photocatalytic activity of 2.5% Cu-doped TiO₂ nanopowders synthesized by mechanical alloying. J Alloys Compd 2006, 415:51-55.
14. Xu YH, Liang DH, Liu ML, Liu DZ. Preparation and characterization of Cu₂O-TiO₂: Efficient photocatalytic degradation of methylene blue. Mater Res Bull 2008, 43:3474-3482.
15. Tseng IH, Wu JCS, Chou HY. Effects of sol-gel procedures on the photocatalysis of Cu/ TiO₂ in CO₂ photo reduction. J Catal 2004, 221:432-440.
16. Li Y, Wang WN, Zhan Z, Woo MH, Wu CY, Biswas P. Photocatalytic reduction of CO₂ with H₂O on mesoporous silica supported Cu/ TiO₂ catalysts. Appl Catal B 2011, 100:386-392.
17. Sakata Y, Yamamoto T, Okazaki T, Imamura H, Tsuchiya S. Generation of visible light response on the photocatalyst of a copper ion containing TiO₂. Chem Lett 1998, 129:1264.
18. Teleki A, Bellobiró N, Pratsinis SE. Flame-made Nb- and Cu-doped TiO₂ sensors for CO and ethanol. Sens Actuators, B 2008, 130:449-457.
19. Wu B, Huang R, Sahu M, Feng X, Biswas P, Tang YJ. Bacterial responses to Cu-doped TiO₂ nanoparticles. Sci Total Environ 2010, 408:1755-1858.
20. Nowotny MR, Sheppard LR, Bak T, Nowotny J. Defect chemistry of titanium dioxide. Application of defect engineering in processing of TiO₂-based photocatalysts. J Phys Chem B 2009, 112:5275-5300.
21. Thimsen E, Biswas S, Lo CS, Biswas P. Predicting the band Structure of mixed transition metal oxides: theory and experiment. J Phys Chem B 2009, 113:2014-2021.
22. Wang ZM, Yang GX, Biswas P, Bresser W, Boolchand P. Processing of iron-doped titania powders in flame aerosol reactors. Powder Technol 2001, 114:197-204.
23. McMillin BK, Biswas P, Zacharias MR. In situ characterization of vapor phase growth of iron oxide-silica nanocomposites. 1. D-Planar laser-induced fluorescence and Mie imaging. J Mater Res 1996, 11:1552-1561.
24. Basak S. Synthesis and characterization of magentic iron oxide for nanomaterial and nanosystem fabrication. Ph.D Dissertation, Washington University in St. Louis, Saint Louis, MO, USA, 2008.
25. Tiwari V, Jiang J, Sethi V, Biswas P. One-step synthesis of noble metal-titium dioxide nanocomposites in a flame aerosol reactor. Appl Catal A, 2008, 345:241-246.
26. Jiang J, Chen DR, Biswas P. Synthesis of nanoparticles in a flame aerosol reactor with independent and strict control of their size, crystal phase and morphology. Nanotechnol 2007, 18:256036.
27. Norris DJ, Efros AL, Envin SC. Doped nanocrystals. Science 2008, 319:1776-1777.
28. Swihart MT. Vapor-phase synthesis of nanoparticles. Curr Opin Colloid Interface Sci 2003, 8:127-133.
29. Farfelis S, Pratsinis SE. Soft- and hard-agglomerate aerosols made at high temperatures. Langmuir 2004, 20:5933-5939.
30. Tsyanova E, Mazurenko GA, Drobotenko VN, D'yagileva LM, Aleksandrov YA. Kinetic principles of the thermolysis of yttrium, barium and copper acetylacetonates. Zh Obshch Khim 1992, 62:499-504.
31. Narayen H, Alemu H, Machelli L, Thakurdesai M, Rao TK. Synthesis and characterization of Y₃-doped TiO₂ nanocomposites for photocatalytic applications. Nanotechnol 2009, 20:255007.
32. Thimsen E, Biswas P. Nanstructured photocative films synthesized by a flame aerosol reactor. AIChE J 2007, 53:1727-1735.
33. Francisco MSP, Mastelaro VR. Inhibition of the anatase-rutile phase transformation with addition of CeO₂ to CuO-TiO₂ system: Raman spectroscopy, X-ray diffraction, and texture studies. Chem Mater 2002, 14:2513-2518.
34. Spurr RA, Myers H. Quantitative analysis of anatase-rutile mixtures with an X-Ray diffractometer. Anal Chem 1957, 29:760-762.
35. Colon G, Maicu M, Hidalgo MC, Navio JA. Cu-doped TiO₂ systems with improved photocatalytic activity. Appl Catal, B 2008, 67:41-51.
36. Nair J, Nair P, Mizukami F, Oosawa Y, Okubo T. Microstructural and phase transformation behavior of doped nanocrystalline titania. Mater Res Bull 1999, 34:1275-1290.
37. Yuan SB, Menaudeau P, Perrichon V. Catalytic combustion of diesel soot particles on copper-catalysts supported on TiO₂ - effect of potassium promoter on the activity. Appl Catal, B 1994, 3:319-333.
38. Jiang J, Oberdorster G, Elder A, Gelein R, Mercer P, Biswas P: Does nanoparticle activity depend upon size and crystal phase? Nanotoxicology 2008, 2:33-42.

39. Suttiponparnit K, Jiang J, Sahu M, Suvachittanant S, Charinpanitkul T, Biswas P: Role of surface area, primary particle size, and crystal phase on titanium dioxide nanoparticle dispersion properties. Nanoscale Res Lett 2011, 6:1-8.

40. Jiang JK, Oberdorster G, Biswas P: Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. J Nanopart Res 2009, 11:77-89.

41. Liu G, Sun CH, Yan XX, Cheng L, Chen ZG, Wang YW, Wang LZ, Smith SC, Lu GQ, Cheng HM: Iodine doped anatase TiO2 photocatalyst with ultra-long visible light response: correlation between geometric/electronic structures and mechanisms. J Mater Chem 2009, 19:2822-2829.

42. Braydich-Stolle LK, Schaeublin NM, Murdock RC, Jiang J, Biswas P, Schlager JJ, Hussain SM: Crystal structure mediates mode of cell death in TiO2 nanotoxicity. J Nanopart Res 2009, 11:1361-1374.

43. Zhao YX, Qiu XF, Burda C: The effects of sintering on the photocatalytic activity of N-doped TiO2 nanoparticles. Chemistry of Materials 2008, 20:2629-2636.

44. Xin BF, Wang P, Ding DD, Liu J, Ren ZY, Fu HG: Effect of surface species on Cu-TiO2 photocatalytic activity. Appl Surf Sci 2008, 254:2569-2574.

doi:10.1186/1556-276X-6-441

Cite this article as: Sahu and Biswas: Single-step processing of copper-doped titania nanomaterials in a flame aerosol reactor. Nanoscale Research Letters 2011 6:441.