

# One-step flame synthesis of SnO<sub>2</sub>/TiO<sub>2</sub> composite nanoparticles for photocatalytic applications

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**ABSTRACT.** SnO<sub>2</sub>/TiO<sub>2</sub> composite nanoparticles have been synthesized in a single-step by feeding evaporated precursor mixtures into an atmospheric pressure diffusion flame. Particles with controlled Ti : Sn ratios were produced at various flow rates of oxygen, and the resulting powders were characterized by BET surface area analysis, XRD, TEM, EDAX and UV-Vis spectroscopy. For the lowest concentration (3.4 mol%) of SnO<sub>2</sub> employed in this study anatase phase of TiO<sub>2</sub> is stabilized, while segregation of SnO<sub>2</sub> is seen at medium (6.9 to 12.4 mol%) and high concentrations (20.3 mol%). Though the equilibrium phase diagram predicts complete solubility of one oxide in another at all compositions, segregation of SnO<sub>2</sub> phase is observed which is explained by the usage of diffusion flame in the present study. The particle formation mechanism of SnO<sub>2</sub>/TiO<sub>2</sub> composites is proposed basing on the single component aerosol formation. Photocatalytic activity of the composite particles is tested for the degradation of methylene blue and is compared with pure TiO<sub>2</sub> synthesized under similar conditions. Improved photocatalytic activity of the composite particles is attributed to the stabilized anatase phase and better charge separation due to the coupling of TiO<sub>2</sub> and SnO<sub>2</sub> within the composite nanoparticles.

## 1. INTRODUCTION

Interest in the study of TiO<sub>2</sub> as photocatalyst was triggered in 1972 by Fujishima and Honda, who first demonstrated its use for photo-oxidation of water [1]. Since then considerable research has been done from both fundamental and an applied perspective. Although a few studies have explored the photocatalytic activity of other semiconductors such as SnO<sub>2</sub> [2], ZnO [3], Nb<sub>2</sub>O<sub>5</sub> [4], CeO<sub>2</sub> [5], SrTiO<sub>3</sub> [6], CdS, HgS, ZnS, CdSe, Ga<sub>2</sub>S<sub>3</sub> [7] and CdTe [8], the preponderance of work has focused on TiO<sub>2</sub> due to its suitable thermodynamic positions of valence and conduction band edges for redox reactions, long term stability, low cost, non-toxicity, resistance to photo and chemical corrosion [9, 10]. In spite of its numerous advantages, widespread commercial application of TiO<sub>2</sub> is hindered because of low efficiency [11]. Quantum efficiency of the photocatalytic process, that is, the rate at which the desired oxidation products are formed divided by the absorbed photon flux, is determined by the competition for carriers between the reactions of oxidation and reduction on one hand and processes of recombination on the other hand. Riegel and co-workers [12] studied the variations in rate constants related to recombination and/or oxidation which varies the steady-state photocatalytic efficiency and concluded, based on a simple kinetic model, that the observed variability arises specially from variations in the rate constant for recombination. So suppression of recombination of the

photogenerated charge carriers is essential for improving the efficiency. Several researches proved that the recombination is prevented by semiconductor-metal composites or by employing two different semiconductors. Modification of TiO<sub>2</sub> by noble metal deposition i.e. Au [13–15], Ag [16], Pt [17] increases photocatalytic efficiency. When the deposited metal particle interacts with the photoexcited TiO<sub>2</sub>, the two particles undergo charge equilibration. The shift in the Fermi level towards the conduction band energy enhances the catalytic efficiency of the composite system. However, the associated processes and reagents are expensive which makes it difficult to scale-up the process.

Efficiency can also be increased by coupling two semiconductors which have suitable conduction and valence band potentials. In the past years, a number of studies related to TiO<sub>2</sub> coupled with other semiconductors like SnO<sub>2</sub> [18, 19], WO<sub>3</sub> [20, 21], Fe<sub>2</sub>O<sub>3</sub> [22, 23], ZnO [24], CdS [25], Cd<sub>3</sub>P<sub>2</sub> [26] were performed. Among them, coupling TiO<sub>2</sub> with SnO<sub>2</sub> attracts much attention. The band gaps of SnO<sub>2</sub> and TiO<sub>2</sub> are 3.88 and 3.2 eV, respectively, and the conduction band of SnO<sub>2</sub> is approximately 0.5 V more positive than that of TiO<sub>2</sub> [27]. When the two semiconductor particles are coupled, the conduction band of SnO<sub>2</sub> acts as a sink for photogenerated electrons. Since the photogenerated holes move in the opposite direction, they accumulate in the valence band of the TiO<sub>2</sub> particle, thereby increasing the efficiency of charge separation [27, 28]. Two variants of SnO<sub>2</sub>/TiO<sub>2</sub> system has been studied for the improvement of photoactivity i.e. composite SnO<sub>2</sub>/TiO<sub>2</sub>

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particles/films [29–31] and mixed oxides of  $\text{SnO}_2/\text{TiO}_2$  (substitution of Sn for Ti in  $\text{TiO}_2$  lattice) [32]. Increase of the photoactivity with the mixed oxides is due to the increased band gap of the solid solution which necessitates the use of light of much higher energy (lower wavelengths). Sensato and co-workers [33] reported that increase in the band gap with the Sn content in the  $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$  system is in large part due to an increase in its conduction band. Since the conduction band shifts toward higher potential, the energy of the electrons on the conduction band have sufficient over-potential to efficiently reduce oxygen. Thus, the photoexcited electrons and holes in the  $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$  can be separated effectively and have a longer life time which increases the photocatalytic activity. On the other hand, theoretical band gaps of the  $\text{SnO}_2$  and  $\text{TiO}_2$  are preserved in the particles/films and due to this composite particles/films are interesting systems to study in more detail. Some authors reported the synthesis of  $\text{SnO}_2/\text{TiO}_2$  particulate films and particles by using mixed suspensions of separate  $\text{TiO}_2$ ,  $\text{SnO}_2$  particles and calcining finally [29–31]. Shi and co-workers [34] reported the synthesis of  $\text{SnO}_2/\text{TiO}_2$  coupled nanoparticles by homogenous solution precipitation method which includes multiple steps of adding  $\text{SnCl}_4$  precursor to  $\text{TiO}_2$  powder externally and subjecting the resultant powder to calcination. Resultant composite particles showed better photoactivity than pure ultrafine and commercial  $\text{TiO}_2$  particles, and the optimum loading of  $\text{SnO}_2$  on  $\text{TiO}_2$  is reported as 18.4 wt%. Tai [35] reported the synthesis of particulate films by sol-gel method and maximum incident photon-to-current efficiency (IPCE) was obtained at an optimum film thickness of 3.5 and 7  $\mu\text{m}$  for  $\text{SnO}_2$  and  $\text{TiO}_2$  respectively. By employing an optimum concentration [34, 35] of both species ( $\text{SnO}_2$  and  $\text{TiO}_2$ ) it is seen that better charge separation can be achieved to improve the efficiency of the photocatalytic process. However, coupled semiconductor particles prepared above were randomly distributed as they are prepared from a mixture of  $\text{TiO}_2$  and  $\text{SnO}_2$  colloidal solutions or of the colloidal  $\text{SnO}_2$  with slurry of  $\text{TiO}_2$  powder. Though Sn substitution enhances the transformation of anatase to rutile, Yang and co-workers [36] reported the synthesis of  $\text{SnO}_2/\text{TiO}_2$  binary oxides by a novel stearic acid method (SAM) which stabilizes the anatase phase and showed better photocatalytic activity than P25. Above method is also a wet chemical synthesis route which needs calcination steps to improve the crystallinity of the resultant powder. Vemury and co-workers [37] synthesized the Sn doped  $\text{TiO}_2$  nanoparticles by flame aerosol process, but didn't investigated the photocatalytic activity of the same.

In this paper we report the photocatalytic activity of the flame synthesized  $\text{SnO}_2/\text{TiO}_2$  composite nanoparticles. Powders of high crystallinity have been produced which do not need any further calcination. Gas phase process employed in this study enables the mixing of

the constituents at a molecular level to achieve better chemical homogeneity. To obtain this coupled nanoparticles, a stream of  $\text{N}_2$  containing evaporated tetramethyl tin (TMT) and titanium-tetraisopropoxide (TTIP) was brought into a methane-oxygen diffusion flame. Upon condensation, highly crystalline  $\text{SnO}_2/\text{TiO}_2$  coupled nanoparticles were formed. In contrast to the equilibrium phase diagram of  $\text{SnO}_2/\text{TiO}_2$ , segregated phase of  $\text{SnO}_2$  is observed. Composite particles are produced at various flow rates of oxidant and  $\text{SnO}_2$  contents. Photocatalytic activity of the resultant particles is tested for decomposition of methylene blue and is found to vary with  $\text{SnO}_2$  content.

## 2. EXPERIMENTAL PROCEDURE AND MATERIALS

**2.1. Flame aerosol plant.** Figure 1a shows the experimental set-up of the aerosol flame reactor schematically, the reactant dosing and delivery system and the particle collection unit. A co-flow diffusion burner consisting of three concentric tubes was used (Figure 1b).

Methane ( $\text{CH}_4$ , purity > 99.95%, Carbagas, Switzerland) was employed as fuel, and oxygen ( $\text{O}_2$ , purity > 99.95%, Carbagas, Switzerland) as oxidant. Titanium-tetraisopropoxide (TTIP,  $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$ , purity > 99%, VWR International, Switzerland) and tetramethyl tin (TMT,  $\text{Sn}(\text{CH}_3)_4$ , purity > 99%, Fluka, Switzerland) were used as precursors for  $\text{TiO}_2$  and  $\text{SnO}_2$  respectively. Controlled amounts of precursors totalling 46 g/h were fed to the evaporator (Hovacal, IAS, Germany) through independent mass flow controllers (Bronkhorst HI-TEC, Netherlands) and 120 l/h of nitrogen ( $\text{N}_2$ , purity > 99.995%, Carbagas, Switzerland) was used as carrier gas to transport the vaporized precursor mixture to the central tube of the burner. Oxygen was fed through the outer annulus, nitrogen (33 l/h) as a lift gas (to lift the flame from the burner face) through the inner annulus and methane (120 l/h) through the centre tube, resulting in a single diffusion flame. Experiments were performed with oxygen flow rates of 720 to 1200 l/h. The flow rates of the precursors were varied to produce the precursor concentrations in the flame as given in Table 1. All gas flow rates were controlled by mass flow controllers (Bronkhorst HI-TEC, Netherlands). The evaporator, the gas delivery tubes to the burner and the burner itself were kept at 175 °C to prevent condensation of precursor vapours. The product particles were collected on borosilicate glass fiber filters (Type GF50, Schleicher and Schuell, Germany) placed inside an open-faced, stainless steel filter holder connected to a vacuum pump (Trivac A-D16A, Leybold, Switzerland). The filter (150 mm diameter) was fixed 55 cm vertically above the tip of the burner in all experiments.

**2.2. Photochemical reactor and reaction vessel.** Details of photochemical reactor have been reported

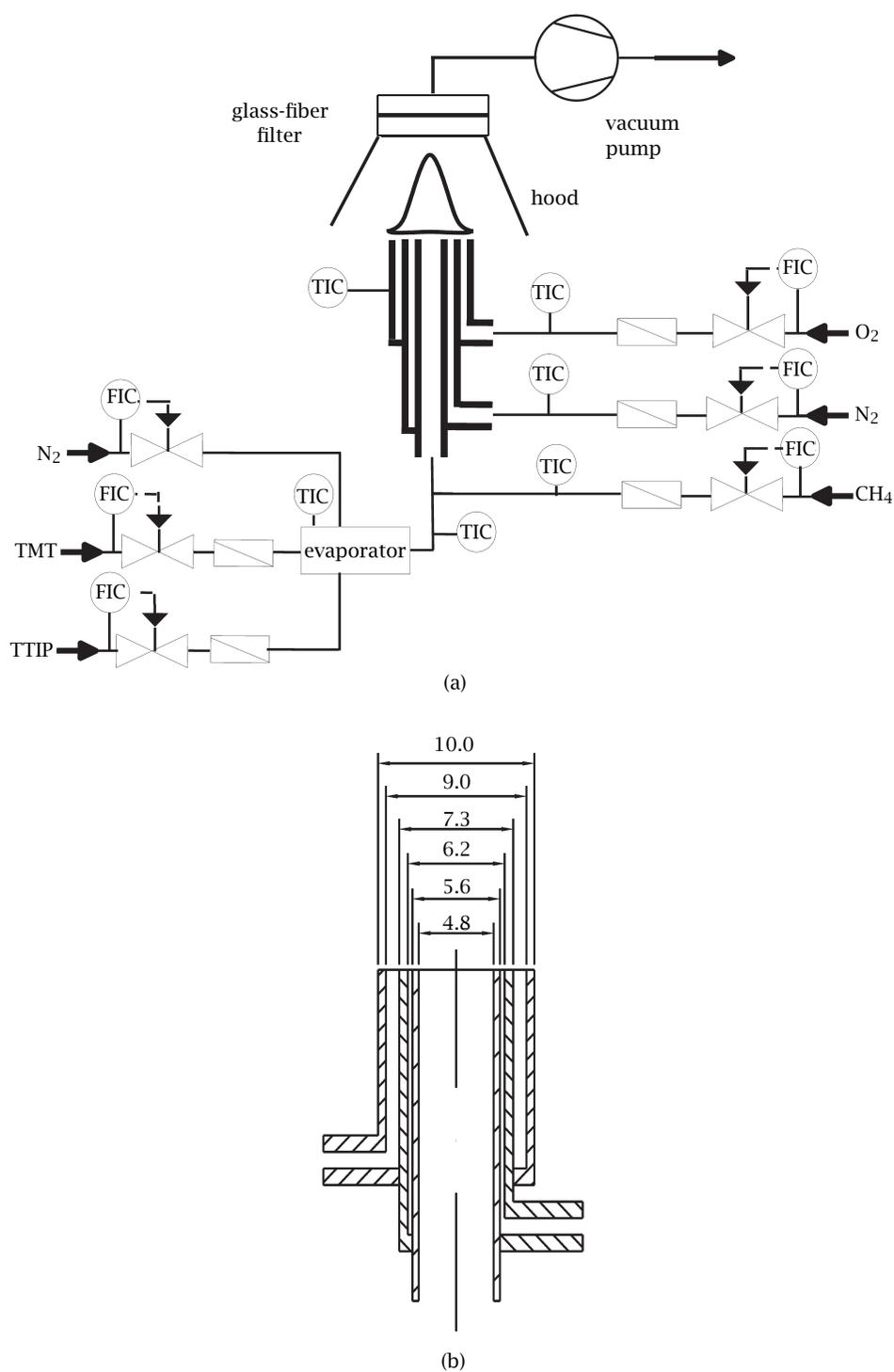


Figure 1. (a) Experimental set-up for the synthesis of SnO<sub>2</sub>/TiO<sub>2</sub> nanopowders by atmospheric pressure flame aerosol process; (b) cross section and tube dimensions (in mm) of the diffusion burner used.

Table 1. Vapour flow rates and resulting mole ratios of precursor species.

Flow rate at STP (l/min)	TiP	TMT	28.3 : 1 Ti : Sn	13.3 : 1 Ti : Sn	9 : 1 Ti : Sn	7 : 1 Ti : Sn	3.9 : 1 Ti : Sn
TiP	0.0604		0.0591	0.0576	0.0564	0.0554	0.0533
TMT		0.0960	0.0020	0.0043	0.0062	0.0078	0.0112

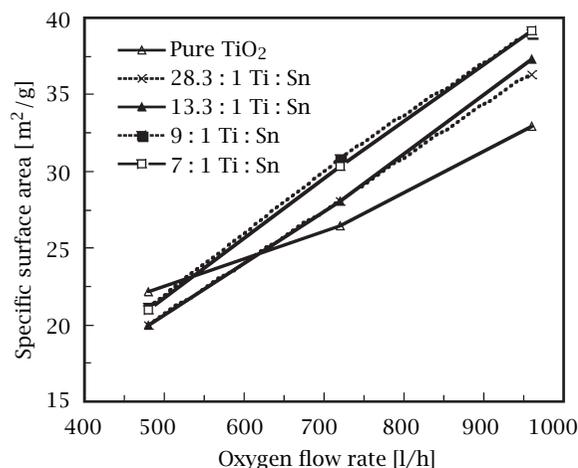


Figure 2. Specific surface area of pure  $\text{TiO}_2$  and  $\text{SnO}_2/\text{TiO}_2$  composite powders synthesized as a function of oxygen flow rate and Ti : Sn ratio at 120 l/h  $\text{CH}_4$  and  $\text{N}_2$ .

elsewhere in detail [38, 39]. In brief, the photochemical reactor comprised two half-cylinders, each of which contained  $6 \times 8$  W Coastwave Blacklight UVA lamps (Coast-AirR®; radiation  $\lambda$  (max.) = 355–360 nm; length = 28.7 cm) set against a half-cylinder aluminium reflector. The reaction vessel comprised a 125 cm<sup>3</sup> quartz Dreschel bottle fitted with a rubber septum, to allow samples from the reaction solution to be withdrawn online. Thermostatted water (30°C) was pumped continuously through the outer jacket of the reaction vessel.

A typical reaction solution placed in the photochemical reaction vessel comprised of  $5.35 \times 10^{-5}$  mol l<sup>-1</sup> MB (methylene blue ( $\geq 82\%$ ), Acros Organics) dissolved in 125 cm<sup>3</sup> of deionized water containing 50 mg of photocatalyst. Degradation experiments were carried out at 303 K and at neutral pH. The reaction solution was continuously purged with air (160 ml/min) and magnetically stirred (300 rpm) throughout irradiation. Samples of the reaction solution were taken regularly as a function of time for the determination of MB concentration to follow its kinetics of disappearance by UV-Vis spectroscopy.

### 3. CHARACTERIZATION OF PHOTOCATALYST

The specific surface area (SSA) of the product powder was determined from a five point  $\text{N}_2$  adsorption isotherm obtained from BET (Brunauer-Emmett-

Teller) measurements using a Beckman-Coulter SA3100 (Beckman-Coulter, Switzerland). Prior to BET analysis, the powder samples were degassed at 200°C for 180 min under flowing  $\text{N}_2$  atmosphere to remove adsorbed  $\text{H}_2\text{O}$  from the surface.

The primary particle size, shape and morphology of the particles were investigated by transmission electron microscopy (TEM). Powder samples were dispersed in isopropanol (purity > 99.5%, Fluka, Switzerland) and a few drops of the dispersion were allowed to dry on carbon-coated copper grids (Plano GmbH, Germany). The TEM analysis was performed on a Philips CM30 electron microscope operating at 200 kV. EDAX (Energy Dispersive X-ray Analysis) was performed using a Noran explorer X-ray detector, allowing the cross checking of chemical analysis of the particles.

X-ray diffraction (XRD) was used for identification of the crystal phases and determination of the average crystallite size. Diffraction measurements were performed with a PANalytical PW 3040/60 X'Pert PRO instrument using Ni-filtered  $\text{Cu-K}\alpha$  radiation of wavelength 1.5418 Å. A  $2\theta$  scan range from 5 to 80°, a scanning step size of 0.01° and a scintillation counter detector was used. Curve fitting and integration was carried out using proprietary software from Philips X'Pert high score plus.

Samples for UV-Vis spectroscopy were filtered through 0.2  $\mu\text{m}$  Whatman Anotop 10 membrane filters to remove the catalyst particles before analysis. A Beer-Lambert diagram was established to correlate the absorbance at 660 nm to MB concentration.

## 4. RESULTS AND DISCUSSION

**4.1. Catalyst characterization: BET, TEM and XRD.** Figure 2 shows the specific surface area of the mixed  $\text{SnO}_2/\text{TiO}_2$  aerosols at various concentrations of  $\text{SnO}_2$  and as a function of oxygen flow rate. Increasing oxygen flow rate reduces the flame temperature [40] as additional  $\text{O}_2$  flow dissipates the generated heat very quickly and shortens the flame length [41] as the combustion rate is enhanced [42]. Consequently, particle residence time at high temperatures is reduced and less growth species are generated by precursor oxidation [43]. Furthermore, the additional  $\text{O}_2$  greatly dilutes the aerosol, and reduces the particle number concentration. Therefore, the collision rate of newly formed  $\text{SnO}_2/\text{TiO}_2$  particles as well as the effective sintering time decreases, and this favours the formation and

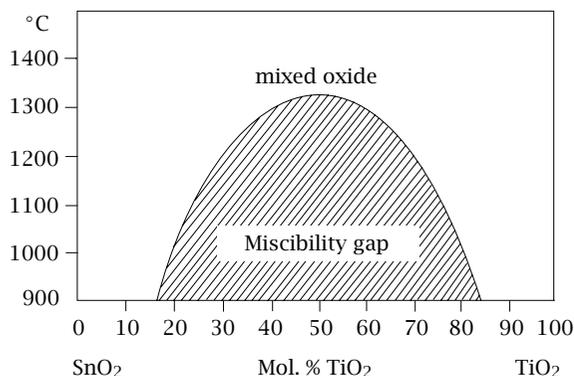


Figure 3. Phase diagram of the SnO<sub>2</sub>/TiO<sub>2</sub> system, adapted and modified from Padurow and co-workers [49].

retention of small primary particles resulting in powders with high specific surface area. In contrast, the surface area of the mixed SnO<sub>2</sub>/TiO<sub>2</sub> powders do not show much variation compared to the pure TiO<sub>2</sub>. SnO<sub>2</sub> forms as a segregated phase within the TiO<sub>2</sub> particle (up to Ti : Sn of 13.3 : 1) though there is a complete solubility of one oxide in another in the solid phase (Figure 3). Because of the above reason, presence of SnO<sub>2</sub> didn't contribute to any significant changes in the surface area. Vemury and co-workers [37] synthesized the Sn doped TiO<sub>2</sub> and draw the same conclusion that the presence of SnO<sub>2</sub> does not affect the primary particle size or the surface area of the TiO<sub>2</sub> particles. Presence of SnO<sub>2</sub> as distinct primary particles is not seen until its concentration exceeds 13.3 : 1 mole ratio of Ti : Sn (Figures 4b and 4c). This is confirmed by the TEM pictures (Figure 5a) as the SnO<sub>2</sub> particles can be easily distinguished from TiO<sub>2</sub> because of its faceted morphology when compared to the spherical form of later (Figure 5b). Several authors reported that this difference in morphology stems from the difference in the particle formation and sintering mechanism. SnO<sub>2</sub> has a low melting point (1625°C) and sinters by evaporation-condensation mechanism [40], while titania sinters by grain boundary diffusion [44].

Figure 6 shows X-ray diffraction patterns of the mixed SnO<sub>2</sub>/TiO<sub>2</sub> aerosols at various concentrations of SnO<sub>2</sub>. In the 28.3 : 1 Ti : Sn sample neither reflections corresponding to cassiterite phase characteristic of segregated SnO<sub>2</sub> nor a shift of rutile reflection towards lower  $2\theta$  angle (characteristic of increased lattice parameter due to the solid solution of SnO<sub>2</sub> and TiO<sub>2</sub> [32]) is observed. For 13.3 : 1 Ti : Sn sample, reflections corresponding to segregated SnO<sub>2</sub> phase is observed and is confirmed by TEM and EDAX analysis that SnO<sub>2</sub> segregates within the TiO<sub>2</sub> particle. From 9 : 1 Ti : Sn samples, SnO<sub>2</sub> forms as distinct primary particles along with segregation within the TiO<sub>2</sub> particles (Figures 4b and 4c).

Addition of dopants is an effective way of controlling the phase composition of titania particles. Akhtar and co-workers [45] showed that adding SiCl<sub>4</sub>, POCl<sub>3</sub> and BCl<sub>3</sub> during TiCl<sub>4</sub> oxidation inhibits the transformation of anatase to rutile, while adding SnCl<sub>4</sub> [37] and AlCl<sub>3</sub> [46] results in a substitutional solid solution that enhances the transformation to rutile. Vemury and co-workers [37] also synthesized SnO<sub>2</sub> doped TiO<sub>2</sub> particles in flame reactor and observed the decrease of intensity of anatase reflection even with the low concentration of SnO<sub>2</sub>. In contrast, for the 28.3 : 1 of Ti : Sn sample, anatase phase is stabilized and its intensity increased consistent with the results obtained by Yang co-workers [36] during the synthesis of SnO<sub>2</sub>/TiO<sub>2</sub> particles by stearic acid method. The ionic radius of Sn<sup>4+</sup> is 0.69Å and is likely to substitute for Ti<sup>4+</sup> (with an ionic radius of 0.61Å) in the titania lattice. Further, tin is in octahedral coordination with oxygen, with lattice parameters very close to those of rutile titania, (for SnO<sub>2</sub>,  $a = 0.4737$  nm and  $c = 0.3186$  nm; for rutile TiO<sub>2</sub>,  $a = 0.4539$  nm and  $c = 0.2958$  nm). The reason for this stabilization of anatase phase in 28.3 : 1 Ti : Sn sample is not understood well though Sn is reported as rutile stabilizer. The results obtained here cannot be directly compared with Vemury and co-workers [37] as they used different sources of precursors for SnO<sub>2</sub> and TiO<sub>2</sub> which can affect the particle nucleation and growth mechanism [47].

SnO<sub>2</sub> forms as segregated phase within the TiO<sub>2</sub> particle in 13.3 : 1 Ti to Sn sample. Dissolution of SnO<sub>2</sub> in TiO<sub>2</sub> is ruled out as there is no change in the lattice parameter of the later. Change of lattice parameter of Sn<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> is systematically studied by Sensato and co-workers [33] and reported that lattice parameters vary non-linearly with composition supporting positive deviations from Vegard's law. Segregation of SnO<sub>2</sub> phase within the TiO<sub>2</sub> particle is seen by the atomic number contrast in the TEM images (Figure 4) [48]. The orientation of the crystalline region with respect to the electron beam (scattering contrast of TiO<sub>2</sub>) may also affect contrast which can be falsely interpreted as the segregated SnO<sub>2</sub>. In addition, if two particles are overlapping, the overlapped area will appear darker than the remainder of the particles. To cross check the contrast as segregated SnO<sub>2</sub>, EDAX analysis was performed and confirmed that individual TiO<sub>2</sub> particles contain Sn as the other constituent. As the TEM pictures didn't show any separate SnO<sub>2</sub> particles (Figure 4a), and XRD pattern didn't show any shift of rutile peak towards lower  $2\theta$  angle (characteristic of solid solution of SnO<sub>2</sub>/TiO<sub>2</sub>) (Figure 6), this Sn signals should only come from segregated SnO<sub>2</sub> phase within the TiO<sub>2</sub> particle.

Examination of the equilibrium phase diagram (Figure 3) of SnO<sub>2</sub>/TiO<sub>2</sub> [49] shows that the two oxides exhibit solid solubility at all compositions provided the processing temperature is more than 1300°C. As the temperatures of the flame reactors exceeds well above

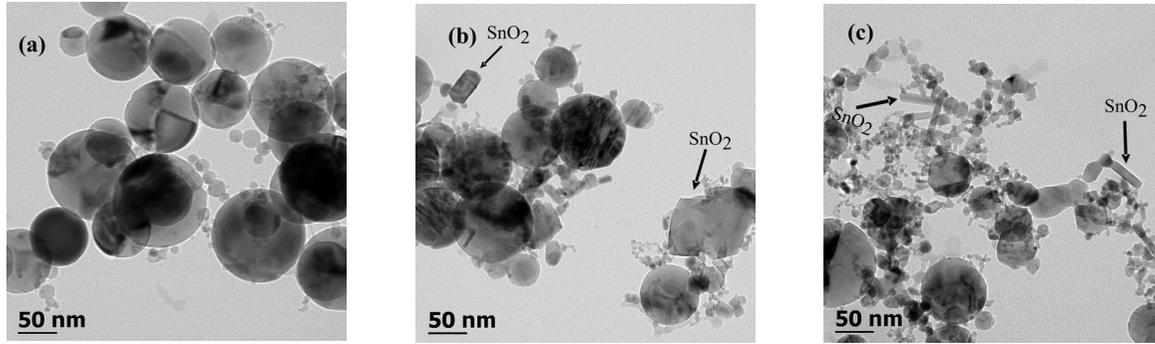


Figure 4. TEM images of  $\text{SnO}_2/\text{TiO}_2$  nanocomposites produced at various mole concentrations of TMT/TTIP precursors: (a) Ti : Sn ratio 28.3 : 1, (b) Ti : Sn ratio 9 : 1 and (c) Ti : Sn ratio 7 : 1.

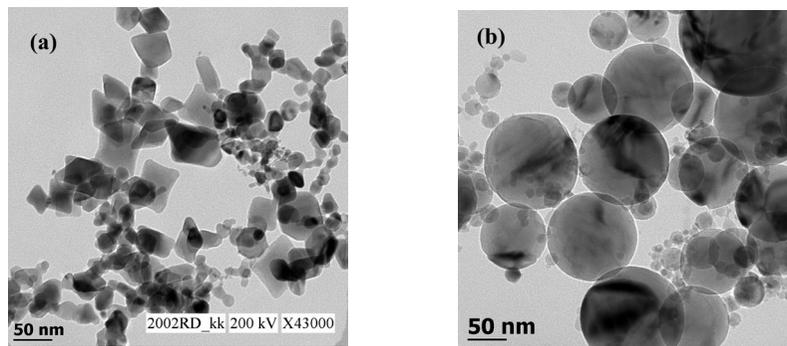


Figure 5. TEM images of pure oxide particles synthesized at flow rates of 4801/h  $\text{O}_2$ , 1201/h  $\text{CH}_4$  and  $\text{N}_2$ : (a)  $\text{SnO}_2$  and (b)  $\text{TiO}_2$ .

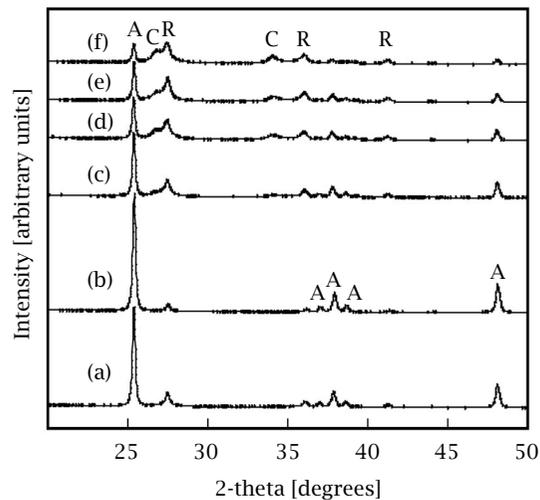


Figure 6. XRD patterns of pure  $\text{TiO}_2$  and  $\text{SnO}_2/\text{TiO}_2$  powders produced at 4801/h  $\text{O}_2$ , 1201/h  $\text{CH}_4$  and  $\text{N}_2$  and at various concentrations of TMT/TTIP; (a) Pure  $\text{TiO}_2$ , (b) 28.3 : 1 Ti : Sn, (c) 13.3 : 1 Ti : Sn, (d) 9 : 1 Ti : Sn, (e) 7 : 1 Ti : Sn and (f) 3.9 : 1 Ti : Sn; A- $\text{TiO}_2$  anatase phase, R- $\text{TiO}_2$  rutile phase and C- $\text{SnO}_2$  cassiterite phase.

1300°C [41], it is expected that  $\text{SnO}_2$  and  $\text{TiO}_2$  will form solid solutions at all compositions. Presence of segregated  $\text{SnO}_2$  phase is related to the usage of diffu-

sion flame instead of a premixed type. Premixed flame is characterized by a very different time-temperature history than the diffusion flame used in the present

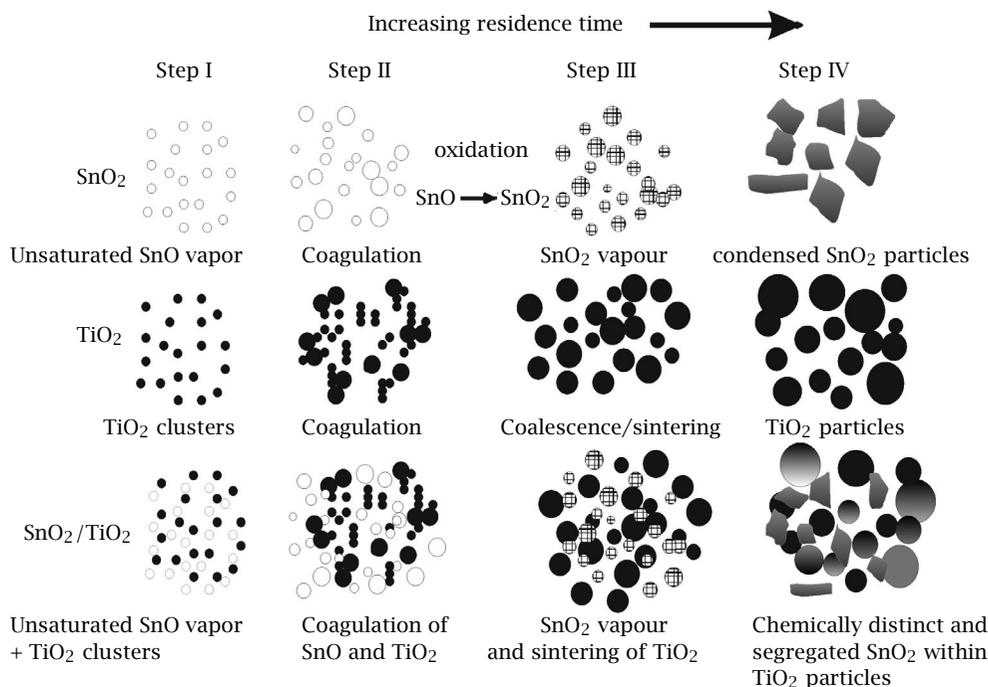


Figure 7. Scheme of the particle growth processes for SnO<sub>2</sub>, TiO<sub>2</sub> and SnO<sub>2</sub>/TiO<sub>2</sub> composite particles.

study [47]. The reaction zone of the premixed flame is characterized by high concentrations of radical species such as O, OH and H. As a result, precursor decomposition chemistry is driven by low activation energy radical abstraction reactions. Because of the fast radical driven decomposition of precursors, it is reasonable to expect that there will be little difference between precursor reaction rates i.e. both the precursors will decompose at the same time, in which case particles of uniform interparticle composition are formed. In contrast, for the diffusion flame, precursor decomposition chemistry is governed by thermal decomposition reactions. In addition, in the precursor decomposition/particle formation region of the burner, temperature increases with increasing residence time which means that the precursor with lowest activation energy for decomposition reacts first and chemical segregation/chemically distinct primary particles are expected to form [47]. TMT has low activation energy [50] for decomposition compared to TTIP [47] and due to this segregation of SnO<sub>2</sub> phase is seen within the TiO<sub>2</sub> particle at low mole ratios of Ti : Sn and chemically distinct SnO<sub>2</sub> primary particles at high mole ratios. Further more residence time of the particles in the flame is only few ms which may not facilitate to reach the equilibrium.

The processes occurring during multicomponent aerosol formation from the gas-phase precursors are the same as for the single component aerosol formation: Chemical reaction, nucleation and aerosol growth. Particle formation mechanism of individual SnO<sub>2</sub> [51]

and TiO<sub>2</sub> [44] is reported by several authors. Basing on that we propose a mechanism for the SnO<sub>2</sub>/TiO<sub>2</sub> system and is shown in (Figure 7). Initially, the TMT precursor is oxidized to form SnO vapor as the activation energy for decomposition of TMT is low. When TiO<sub>2</sub> particles start to nucleate, they form within the precursor vapour of SnO which subsequently oxidizes and condenses onto the existing TiO<sub>2</sub> particles (step III). SnO<sub>2</sub> condensed TiO<sub>2</sub> particles start to grow and retains the segregated phase. With increased concentration of TMT precursor in the mixed aerosol, SnO<sub>2</sub> forms as distinct primary particles along with the segregation within the TiO<sub>2</sub> particles (Figures 4b and 4c).

**4.2. Photocatalytic degradation of MB.** Photocatalytic activity of the pure TiO<sub>2</sub> and SnO<sub>2</sub>/TiO<sub>2</sub> nanocomposites synthesized under similar conditions (7201/h O<sub>2</sub> flow rate) are tested for the degradation of MB after checking that there is no degradation with TiO<sub>2</sub> (no irradiation) or UV irradiation alone (no photocatalyst). Figure 8 shows the kinetics of disappearance of MB for pure TiO<sub>2</sub> and SnO<sub>2</sub>/TiO<sub>2</sub> powder. It can be seen from the figure that SnO<sub>2</sub>/TiO<sub>2</sub> composites (up to 7 : 1 Ti : Sn) shows better activity compared to pure TiO<sub>2</sub>. In slurry based photocatalytic reactor systems, the rate-determining step in the degradation process is considered to be the reduction of oxygen (which is circulated in the reactor vessel) by the conduction band electrons [52]. Excited conduction band electrons must be separated spatially from the holes, because the

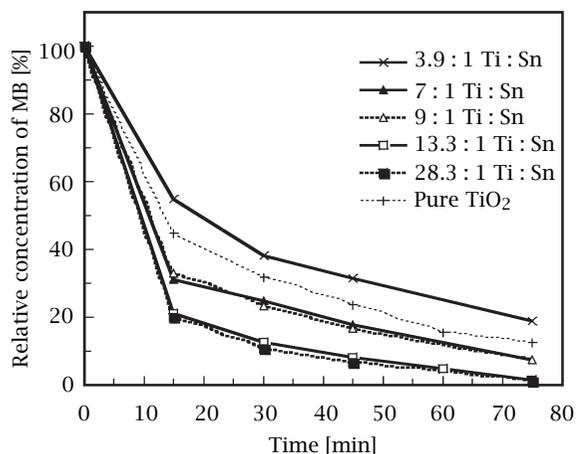


Figure 8. Degradation profile of MB for pure  $\text{TiO}_2$  and  $\text{SnO}_2/\text{TiO}_2$  composite particles.

characteristic time required for reduction ( $\sim \mu\text{s}$ ) is generally much greater than that for oxidation ( $\sim 100\text{ ns}$ ) [53]. The potential of the conduction band electrons should be high in order to get scavenged by the oxygen and unless otherwise will recombine with the valence band hole. The potential of the conduction band is more negative for anatase compared to rutile and due to this anatase is considered as more beneficial for photocatalytic activity [54]. In the 28.3 : 1 Ti to Sn sample, anatase phase is stabilized and its intensity of reflection increased compared to pure  $\text{TiO}_2$ . This might be the reason for the increased photocatalytic activity of the sample mentioned above.

Alternatively photogenerated electrons can be separated from holes by coupling  $\text{TiO}_2$  with  $\text{SnO}_2$ . Gerischer and co-workers [55] proposed a model regarding the role of oxygen in photo-oxidation of organic molecules which states that a sufficiently fast  $\text{O}_2$  reduction rate for attaining high quantum efficiency is achieved only when catalytic sites are incorporated on the  $\text{TiO}_2$  surface and is supported by several researches [13–17]. The 13.3 : 1 Ti to Sn sample showed similar activity like the 28.3 : 1 Ti to Sn sample for the MB decomposition, even though addition of  $\text{SnO}_2$  extensively decreased the X-ray intensity of anatase phase. Increased photocatalytic activity of the 13.3 : 1 Ti to Sn sample is correlated to the segregated  $\text{SnO}_2$  which acts as electron scavenger. The conduction band (CB) edges of  $\text{TiO}_2$  and  $\text{SnO}_2$  are situated at  $-0.34$  and  $+0.07$  eV versus normal hydrogen electrode (NHE) at pH 7, respectively. The valence band (VB) edge of  $\text{SnO}_2$  ( $+3.67$  eV) is much lower than that of  $\text{TiO}_2$  ( $+2.87$  eV) [56]. In terms of the energetics, electrons flow into the  $\text{SnO}_2$ , while holes oppositely diffuse into the  $\text{TiO}_2$ . Consequently, more holes reach the  $\text{TiO}_2$  surface to cause oxidation reaction, whereas electrons withdrawing from the surface are probably consumed for reduction of  $\text{O}_2$  at the

edge of the segregated  $\text{SnO}_2$ . Thus the interfacial electron transfer from  $\text{TiO}_2$  to  $\text{SnO}_2$  can explain the higher photocatalytic activity of the composite particles.

Photocatalytic activity of the composites starts to decrease from 9 : 1 and 7 : 1 Ti : Sn samples but still better than the activity of pure  $\text{TiO}_2$ . The 3.9 : 1 Ti to Sn sample shows further decrease in activity and is inferior compared to pure  $\text{TiO}_2$ . Increasing the  $\text{SnO}_2$  content means that there is a decrease in the active photocatalyst ( $\text{TiO}_2$ ) content, as the former shows poor activity to decompose MB. So, 7 : 1 Ti to Sn (21 wt%  $\text{SnO}_2$ ) sample is the maximum  $\text{SnO}_2$  content up to which composites show better activity than pure  $\text{TiO}_2$ . Shi and co-workers [34] reported in the study of  $\text{SnO}_2$ - $\text{TiO}_2$  coupled particles that an optimum loading of 18.4 wt%  $\text{SnO}_2$  is essential for improving the photoactivity, which agrees well with the results we got.

## 5. CONCLUSION

Formation of  $\text{SnO}_2/\text{TiO}_2$  composite nanoparticles in atmospheric pressure diffusion flames has been investigated. Usage of diffusion flame configuration has been shown to influence the formation of multicomponent aerosols and non-equilibrium phases, making flame aerosol process a unique and inexpensive route to synthesize wide spectrum of new materials. The photocatalytic activity of the composite particles is higher than the pure  $\text{TiO}_2$  synthesized under similar conditions and the maximum content of the  $\text{SnO}_2$  for increased activity is 21 wt%. Improved photocatalytic activity is due to the nanocomposite structure of the particles and as a result thereof the low recombination rate of photoexcited electrons and holes facilitated by coupling of  $\text{TiO}_2$  with  $\text{SnO}_2$ .

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