

# SURFACE MODIFICATION OF ZnO AND TiO<sub>2</sub> NANOPARTICLES UNDER MILD HYDROTHERMAL CONDITIONS

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## ABSTRACT

There are various techniques for synthesizing different Nanoparticles depending upon the desired properties, application, etc. One of these widely applied techniques is Hydrothermal. However, this technique is known for bulky materials and fabrication of nano-scale materials requires adopting some strategies to alter the properties of materials synthesized. We developed surface modification for this drawback. Application of surface modifier, or surfactant, or capping agent, or organic ligands in proper concentration could not only change morphology, reduce particle size, but also change the surface chemistry of the nanoparticles fabricated. The ZnO and TiO<sub>2</sub> nanoparticles were modified using *n*-butylamine and caprylic acid as surface modifier under mild hydrothermal conditions (*p*= autogenous, *T*= 150-250°C, and *t*= 18 h). The nanoparticles modified were systematically characterized using Powder XRD, FTIR, SEM, zeta potential, and BET surface area. The characterization results revealed that nanoparticles have small size range, low agglomeration and highly stable.

**Key words:** surface modification, *n*-butylamine, caprylic acid, ZnO/TiO<sub>2</sub> nanoparticles, hydrothermal conditions

## INTRODUCTION

Surface modification and characterization of nanomaterials is a field of immense research potential for researchers worldwide for nearly half a century. Zinc oxide is a promising group II-VI oxide semiconductor showing quantum confinement effects at room temperature [1-3]. ZnO and TiO<sub>2</sub> nanoparticles have broad applications such as UV absorption [4], deactivation of bacteria [5], photocatalysis of industrial effluents [6-7], etc. Furthermore, they are an environmentally friendly material, which are desirable especially for bio-applications, such as bioimaging, cancer detection, and chemical sensors [8].

The photoactivity of zincite and titanium dioxide is generally detrimental for their application as photocatalyst or filler that oxidatively degrades, leading to embrittlement and chalking when exposed to sunlight or UV irradiation, especially in presence of moisture. Hence, some form of modification is im-

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plemented in order to reduce the surface photoactivity, to alter their hydrophobic/hydrophilic character and improve their dispersibility in various media, to introduce new functional groups, which can react with organic molecules and enhance their compatibility with organics. Therefore, caprylic acid and *n*-butylamine were selected as surface modifiers to resolve the abovementioned problems. The present authors have modified ZnO and TiO<sub>2</sub> nanoparticles with these surfactants because they have low toxicity, eco-friendly, low density and low melting temperature.

Most of the ZnO/TiO<sub>2</sub> crystals have been synthesized by traditional high temperature solid-state method, which is energy consuming and difficult to control the particle properties. ZnO/TiO<sub>2</sub> nanoparticles can be prepared on a large scale at low cost by simple solution-based methods, such as chemical precipitation [9], sol-gel synthesis [10], and solvothermal/hydrothermal reaction [11, 12]. Hydrothermal technique is a promising alternative synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process has several advantages over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazardous [13].

#### **EXPERIMENTAL PREPARATION OF SURFACE MODIFIED ZNO/TIO<sub>2</sub> NANOPARTICLES**

ZnO and TiO<sub>2</sub> nanoparticles were modified under mild hydrothermal conditions ( $T=150 - 250^{\circ}\text{C}$ ,  $P = \text{autogeneous}$ ). 1M of reagent grade ZnO/TiO<sub>2</sub> (Loba Chemie, India) were taken as starting material. A certain amount of 1 N NaOH and HCl was added as mineralizer to the precursors respectively. Caprylic acid and *n*-butylamine (Sisco Research Lab PVT, Ltd., Mumbai, India) with different concentration (0.8, 1.0, 1.2, 1.4 and 1.6 ml) was added into the above-mentioned mixtures separately and it was stirred vigorously for a few minutes. The final mixture was then transferred to the Teflon liner ( $V_{\text{fill}}=15 \text{ ml}$ ), which was later placed inside a General-Purpose autoclaves. The autoclaves were provided with Teflon liners of 30 ml capacity. Then the assembled autoclave was kept in an oven with a temperature programmer-controller. The temperature was programmed and kept at  $150-250^{\circ}\text{C}$  for 18 hr. After the experimental run, the autoclaves were cooled to the room temperature. The resultant product in the Teflon liner was then transferred in to a clean beaker and the product was washed with double distilled water. The surplus solution was removed using a syringe and the remnants were centrifuged for 20 minutes at 3000 rpm. The product was recovered and dried in a hot air oven at  $50^{\circ}\text{C}$  for a few hours. The dried particles were subjected to a systematic characterization using powder XRD, FTIR, SEM, Zeta potential and BET surface area measurement.

### CHARACTERIZATION OF THE SURFACE MODIFIED ZnO/TiO<sub>2</sub> NANOPARTICLES

The Powder X-ray diffraction patterns were recorded using Bruker, D8 Advance, Germany, with Cu K $\alpha$ ,  $\lambda$  1.542 Å radiation, Voltage = 30 kV, Current 15 mA, Scan speed ~ 5° min<sup>-1</sup>. The data were collected in the 2 $\theta$  range 10–80°. The Fourier transform infrared (FTIR) spectra were recorded using FTIR, JASCO-460 PLUS, Japan, at resolution of 4 cm<sup>-1</sup>. SEM images of surface modified ZnO hybrid nanoparticles were recorded using Hitachi, S-4200, Japan. Zeta potential and BET surface area was measured using Zetasizer 2000 instrument (Malvern instruments), UK

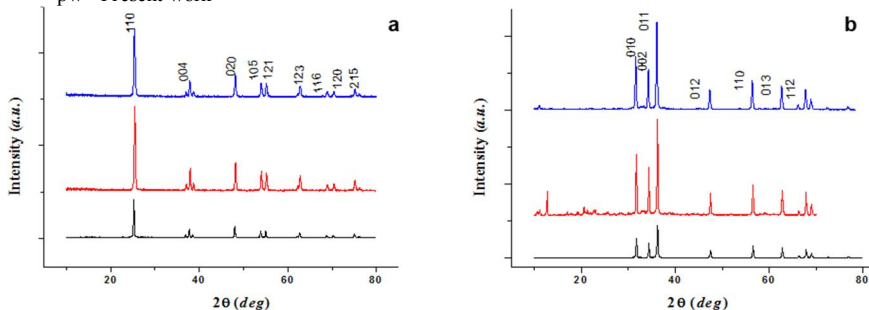
### RESULTS AND DISCUSSION

The powder XRD data reveals a highly crystallized wurtzite and anatase structures and there is a small new peak, which may be corresponded to caprylic acid (Fig. 1). There is a slight change in the lattice parameters of surface modified ZnO/TiO<sub>2</sub> nanoparticles at a-axis and c-axis when compared to pure one (Table 1); this confirms the existence of surface modifier in ZnO/TiO<sub>2</sub> hybrid nanoparticles.

**Table 1** – Cell parameters of modified ZnO and TiO<sub>2</sub> nanoparticles

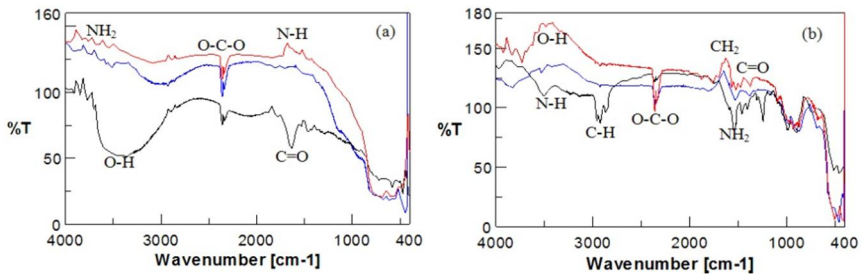
Nanoparticles	Surface modifier	<i>a</i> (Å)	<i>c</i> (Å)	<i>a c</i> ratio	<i>V</i> (Å <sup>3</sup> )	Ref
Pure ZnO	NIL	3.249	5.207	0.6239	47.60	[17]
Used ZnO	NIL	3.2556	5.2166	0.6241	47.88	pw <sup>a</sup>
ZnO	Caprylic acid	3.2567	5.2021	0.6260	47.78	pw
ZnO	<i>n</i> -butylamine	3.2435	5.1996	0.6238	47.37	pw
Pure TiO <sub>2</sub>	NIL	3.7845	9.5143	0.3977	136.30	pw
Used TiO <sub>2</sub>	NIL	3.7918	9.5296	0.3979	137.02	pw
TiO <sub>2</sub>	Caprylic acid	3.7881	9.5230	0.3978	136.65	pw
TiO <sub>2</sub>	<i>n</i> -butylamine	3.7837	9.4983	0.3983	135.98	pw

<sup>a</sup>pw = Present work



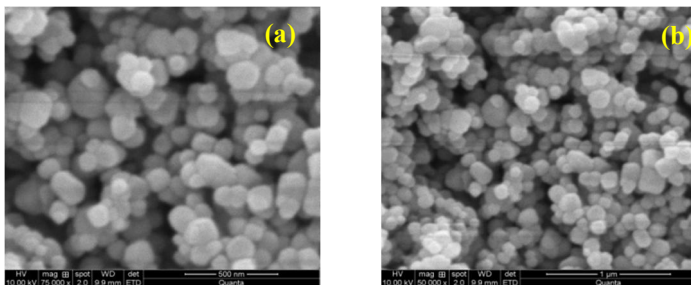
**Fig. 1** – Powder XRD patterns of — pure nanoparticles without surfactant, surface modified using — *n*-butylamine and — caprylic acid as surface modifier: a) TiO<sub>2</sub>, b) ZnO

As Fig. 1 indicates, the presence of new peaks is more in the case of using HCl as solvent for surface modification of ZnO nanoparticles; these new peaks can be contributed to the presence of mixed phases of ZnO and ZnCl<sub>2</sub>. The modification with caprylic acid resulted in changing the crystal structure (Fig. 1). The functional groups present in the modified nanoparticles can be studied using FTIR spectroscopy. Fig. 2 shows the FTIR spectra of the reagent grade ZnO/TiO<sub>2</sub>, surface modified ZnO/TiO<sub>2</sub> nanoparticles modified with *n*-butylamine and caprylic acid as surface modifier respectively. The intensity of the peaks was more when concentration of surface modifier was increased. The FTIR spectra of the modified nanoparticles show the presence of new peaks imply that the reagents were chemically immobilized on the surface of nanoparticles. Thus, it can be concluded that the ZnO/TiO<sub>2</sub> nanoparticles modified with the above said modifiers, have organic coverage on their surfaces, which has changed surface property of the nanoparticles. The absorption peaks corresponding to the presence of CH<sub>3</sub>, N-H, O-H, C=O, etc. have been identified and illustrated in Fig. 2 [15].

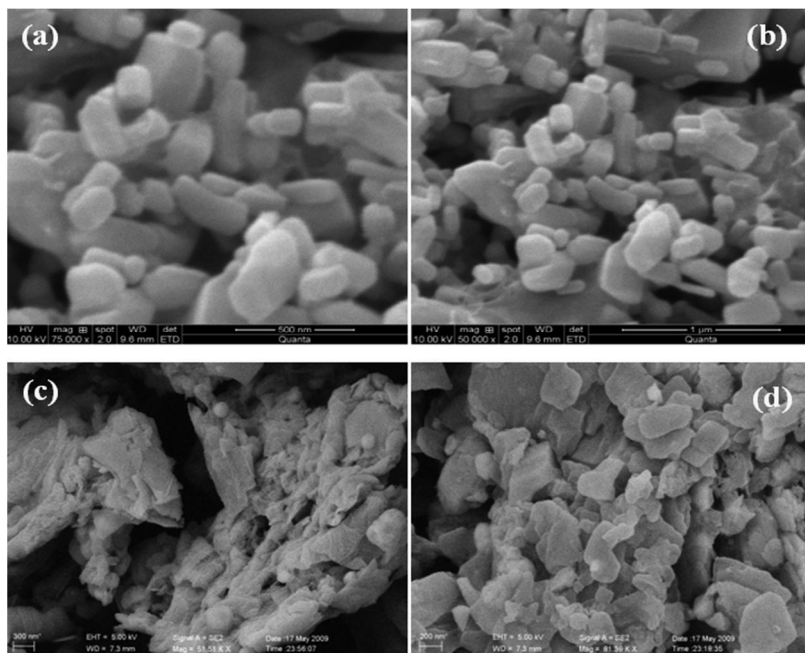


**Fig. 2** – FTIR spectra of — reagent grade surface modified undoped hybrid nanoparticles using — caprylic acid, and — *n*-butylamine: a) TiO<sub>2</sub>, b) ZnO.

Fig. 3 and Fig. 4 show characteristic SEM and HRSEM images of ZnO/TiO<sub>2</sub> nanoparticles modified with (0.8 and 1.4 ml) *n*-butylamine and caprylic acid using 0.1 N NaOH and HCl as solvent.



**Fig. 3** – Characteristic SEM images of surface modified TiO<sub>2</sub> nanoparticles using NaOH as solvent: a) *n*-butylamine, and b) caprylic acid as surface modifier



**Fig. 4** – Characteristic SEM and HRSEM images of surface modified ZnO hybrid nanoparticles using: a) NaOH and n-butylamine as solvent and surface modifier respectively, b) NaOH and caprylic acid as solvent and surface modifier respectively, c) HCl and n-butylamine as solvent and surface modifier respectively, and d) HCl and caprylic acid as solvent and surface modifier respectively.

These figures show effect of the surface modifiers on the nanoparticles morphology. The agglomeration was less when a higher concentration of the surface modifier was used. The surface modification has led to the controlling of growth direction, also particle size and preventing agglomeration. It was found that the surface modifier could not only affect the dispersibility of the modified ZnO nanoparticles, but also change their morphology and size of the particles. The achieved morphology is quite suitable for the photodegradation purposes, since the ZnO/TiO<sub>2</sub> nanoparticles are rounded, they can be more active in photodegradation of the organic pollutants presenting in the municipal and industrial effluents

#### **ZETA POTENTIAL OF SURFACE MODIFIED ZnO/TiO<sub>2</sub> NANOPARTICLES**

Zeta ( $\zeta$ ) potential measurement was performed for ZnO/TiO<sub>2</sub> nanoparticles in order to characterize the surface charge of nanoparticles and Fig. 5 shows the result as a function of pH. The obtained  $\zeta$  potential of the nanoparti-

cles was found to decrease with increase of pH as is expected for a surface with acid-base group. The iso-electric point or point of zero charge (PZC) for ZnO nanoparticles was found to be 4.0 and 4.2 for modification by caprylic acid and *n*-butylamine respectively. For small enough nanoparticles, a high  $\zeta$  potential will confer stability, i.e. the solution or dispersion will resist aggregation. When the potential is low attraction exceeds repulsion and the dispersion will break and flocculate [16,17]. Therefore, colloids with high  $\zeta$  potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate. Our results indicate that the both surface modified nanoparticles are stable and highly negatively charged (at pH > 4.0 -4.2) and this negative charge intensity is proportional to the increasing pH. On the other hand, the particles modified are positively charged at pH < 4.0. The modified nanoparticles synthesized had low agglomeration, which prevents their flocculation or coagulation tendency.

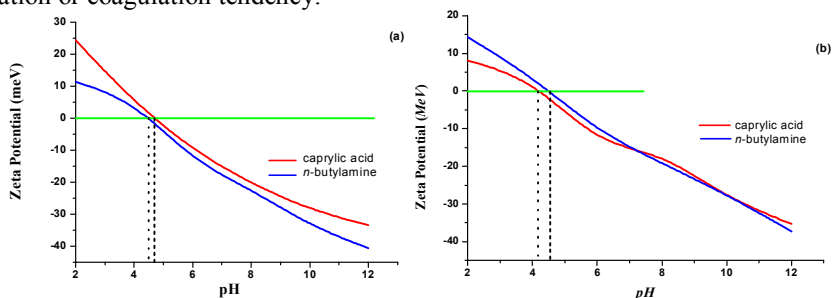


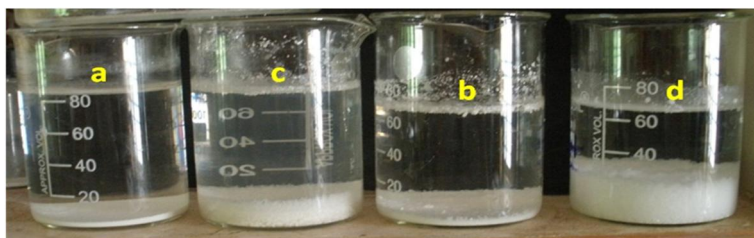
Fig. 5 – Zeta potential of surface modified a) TiO<sub>2</sub> and b) ZnO nanoparticles

### BET SURFACE AREA OF SURFACE MODIFIED ZnO/TiO<sub>2</sub> NANOPARTICLES

BET surface area was measured for the surface modified hybrid ZnO nanoparticles using Malvern 2000. It was found that the BET surface area is 5.630 and 4.513 m<sup>2</sup>/g for surface modified ZnO hybrid nanoparticles using and *n*-butylamine and caprylic acid as surface modifier respectively. The BET surface area was found to be 15.928, 14.140 m<sup>2</sup>/g for surface modified TiO<sub>2</sub> hybrid nanoparticles using *n*-butylamine and caprylic acid respectively. In both cases, NaOH was used as solvent. The results reveal that *n*-butylamine makes the surface area more; the reason for having such low surface area can be contributed to the complex formation of ZnO nanoparticles with caprylic acid. It is known that surface modifiers are used to reduce agglomeration and hence reducing the particle size by controlling its growth direction. However, it was found that the affinity of ZnO nanoparticles to give bigger particles is proportional to the increasing concentration of the surfactant. Such phenomenon was not observed in the case of TiO<sub>2</sub>.

### EFFECT OF SOLVENT ON HYDROPHILICITY AND HYDROPHOBICITY

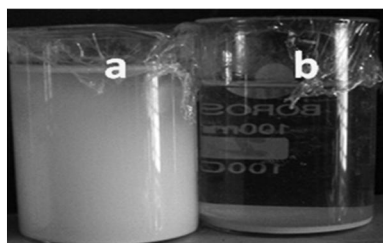
One of the most important effects of surfactant on nanomaterials is changing their hydrophilicity property. Density of ZnO is high (about  $7.0 \text{ g/m}^3$ ) so that they are getting settle down quickly. We observed that *n*-butylamine could make the nanoparticles highly hydrophilic, which is very favorable for photo-degradation purposes. The reason is controlling the crystal growth, reducing agglomeration, and reducing density of the nanomaterials modified. The surface modification of the nanoparticles gives them an organic-inorganic hybrid so that the nanoparticles with desired properties can be fabricated. It was also observed that when HCl was used as solvent in modification of ZnO in presence of caprylic acid, it made the nanoparticles highly hydrophobic while using NaOH as solvent in presence of caprylic acid made the ZnO hybrid nanoparticles hydrophilic and reduced density of the nanoparticles modified. However, both surfactants gave hydrophilic property to  $\text{TiO}_2$  nanoparticles. Reduction of density was directly proportional to the concentration of the surface modifier (i.e. caprylic acid) added. Such interesting hydrophobic and hydrophilic properties of the ZnO nanoparticles have been shown in Figs. 6-8.



**Fig. 6** – Effect of caprylic acid concentration on density and in turn hydrophilicity of the ZnO nanoparticles using NaOH as solvent a) 0.6 mL, b) 0.8 mL, c) 1.0 mL, and d) 1.2 mL caprylic acid



**Fig. 7** – Effect of caprylic acid concentration on density and in turn hydrophobicity of the ZnO nanoparticles using HCl as solvent and caprylic acid as surface modifier



**Fig. 8** – Effect of surfactant on hydrophilicity property of  $\text{TiO}_2$  nanoparticles: a) using *n*-butylamine as surface modifier and b) without surface modifier

It seems HCl reacts with ZnO and give highly low dense mixed phases of  $\text{ZnCl}_2$  and ZnO, which their density is less than water, which made them float at the surface of the water as a separate supernatant powder.

### CONCLUSIONS

Surface modified ZnO/TiO<sub>2</sub> nanoparticles were successfully carried out under mild hydrothermal conditions. Caprylic acid and n-butylamine were used as surface modifier separately. Surface modification changed morphology and size of the ZnO/TiO<sub>2</sub> hybrid nanoparticles modified. In addition, it changed the surface charges and increased stability of the nanoparticles, which is necessary to achieve higher photodegradation efficiency. Using suitable solvent with respect to the precursors is an important factor in obtaining desired properties. Surface modifier along with solvent could give hydrophilic or hydrophobic property to the in situ surface modified ZnO hybrid nanoparticles. The results revealed that both caprylic acid and n-butylamine could be used for surface modification of ZnO particles. The strategy applied for surface modification could not only reduce agglomeration but also enhance the ZnO nanoparticles dispersibility.

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