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# Synthesis, characterization, and photocatalytic properties of surface-modified, silver-doped ZnO

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**Abstract** Hydrothermal synthesis of silver-doped modified ZnO was carried out in the presence of a surface modifier. The experimental conditions were maintained constant (ZnO = 4 M; $T = 250$ °C; P = autogenous; Solvent = 1 N HCl; Duration = 24 h). Caprylic acid was used as a surface modifier with varying concentration from 0.1 to 2 mL. The experiments were carried out with Ag doping from 1 to 5 wt%. Hydrophobic silver-doped ZnO modified with caprylic acid was subjected to a systematic characterization using powder XRD, SEM, FTIR, and photocatalytic properties using Indigo Carmine dye.

**Keywords** Hydrothermal synthesis · ZnO nanoparticulates · Silver doping · Photocatalytic degradation of Indigo Carmine

## Introduction

Zinc oxide (ZnO) has tremendous application potential such as piezoelectric, UV detectors, photocatalysts, varistors that are used to prevent voltage surges in devices like mobile phones, pigments in paints, and sunscreens and sunblocks for the prevention of sunburns due to its abilities to absorbs UV light. It shows high credibility as a potential electronic and photonic material with a wide band gap (3.37 eV), large exciton-binding energy (60 meV), biocompatibility, and high melting temperature (2,248 K) [1–4]. ZnO has stimulated great interest due to its

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dual semiconducting and piezoelectric properties, and also as room-temperature ultraviolet lasers, field effect transistors, and field emission arrays based on ZnO nanorods in the fabrication of functional nanodevices [5, 6]. Several preparative methods have been adopted in the synthesis of ZnO both as bulk and nanosize crystals. So also in the synthesis of various nanostructures of ZnO, both physical and chemical methods like physical vapor deposition, metallorganic vapor phase epitaxy, thermal reduction route, template-based method, pyrolysis method, chemical bath deposition, novel solution methods like hydrothermal, solvothermal, and supercritical hydrothermal methods have been employed regularly. However, physical methods require expensive equipment, extreme operating conditions, and complex procedures and have limited their applications in the synthesis of ZnO. In comparison to the physical methods, chemical methods have some advantages, especially the sol–gel, chemical bath, electrochemistry and novel solution routes like hydrothermal, solvothermal, and supercritical hydrothermal processes [7–9]. However, the hydrothermal method has been proven to be the most favorable method due to homogenous or heterogeneous chemical reaction through a highly controlled diffusion leading to the formation of designer nanoparticulates having the desired size, shape, and properties. It is well known in the literature that the physical properties of materials can be significantly altered by the addition of selected dopants and also by changing the grain size (physical properties of nanomaterials are significantly different from their bulk size counter parts, due to the quantization effect) [10–12]. In the present work, selective doping has been chosen in order to study the effect of doping on the photocatalytic property of ZnO. As it is well known, silver is a strong catalyst, and the present authors have attempted to introduce silver into the ZnO system, such that the photocatalytic activity could be significantly enhanced owing to the synergetic effect of silver and ZnO in the system. Further, the authors have studied the amount of silver doping, surplus ZnO (4 M) in the raw material, and the role of surfactants like caprylic acid on the hydrothermal synthesis of the resultant ZnO product.

## Experimental

Hydrothermal experiments were carried out using general purpose autoclaves made of stainless-steel (SS316) provided with Teflon liners of a capacity of 30 mL. The experimental temperature was kept at 250 °C with an autogenous pressure, and the experimental duration was maintained at 24 h in all experiments. The molarity of ZnO in the raw material was kept at 4 M in order to study the effect of surplus ZnO in the hydrothermal reaction on the resultant product, and in turn the photocatalytic properties. A required amount of ZnO (LR grade, Loba Chemie, India) was taken in a Teflon liner and 1 N HCl (AR grade, Qualigens, India) was added into it. Further, a required amount of silver metal powder (1–5 wt%, LR grade, SLR, India) was added into this mixture. The mixture was stirred well and a required amount of caprylic acid was added into this. In the present work, the surface modifier such as caprylic acid (AR grade, Ranbaxy, India) was added from 0.1 to 2 mL. The mixture then becomes a highly viscous and colorless transparent solution. The pH was measured before the hydrothermal experimental treatment. Later, the liner was kept inside the autoclave and sealed firmly. The autoclave assembly was then placed inside a furnace provided with a temperature programmer. The temperature of the autoclave was slowly raised to 250 °C and held for 24 h. Table 1 gives only some of the characteristic experiments carried out in the synthesis of surface-modified silver-doped ZnO, although the authors have actually carried out a larger number of experiments with varying concentrations of surfactant and percent fills. After the experimental run, the autoclave was quenched to the room temperature and the liner assembly was taken out. pH of the final product in the liner was then measured. The products were first washed with doubled-distilled water and centrifuged repeatedly to remove all the excess acid in the resultant products. The products were then dried at 40 °C in a dust-proof hot-air oven. The resultant products were then subjected to a systematic characterization using powder XRD, FTIR, SEM, and photocatalytic properties.

## Characterization

Silver-doped ZnO particles were characterized using various analytical techniques. The powder X-ray diffraction patterns were recorded using the RIGAKU Miniflex X-ray diffractometer, Japan with a scanning range of 10–80° (2Θ) and a scanning speed of 2° $\text{min}^{-1}$ with $\text{CuK}_{\alpha}$, $\lambda = 1.542$ Å, radiation voltage = 40 kV, and current = 40 mA. The FTIR spectra were recorded in the range 4,000–400 $\text{cm}^{-1}$ using the JASCO-460 Plus, Japan, at a resolution of 4 $\text{cm}^{-1}$. The sample was dispersed in KBr at the ratio 100:1 = KBr: Sample. SEM images were taken for the resultant products using the JEOL analytical scanning electron microscope, Model: JSM-6610A/JSM-6610LA, Japan.

## Results and discussion

The powder X-ray diffraction data for the resultant products of surface-modified pure ZnO and silver-added surface-modified ZnO reveal very interesting results (Fig. 1). On the whole, the resultant products had both homogeneous and mixed phases. The X-ray pattern of surface-modified pure ZnO shows homogeneous phases belonging to the wurtzite structure with all the X-ray peaks matching the standard JCPDS file and *hkl* values was refined using check cell. The crystalline phase of ZnO matches with PDF:800075 with space group $P6_3mc$ of the dihexagonal pyramidal class. Although surplus ZnO (4 M) was taken in the starting material, the hydrothermal experiment has resulted in the formation of pure ZnO, but the quality of the products in terms of size and shape control was poor, and also the product was highly agglomerated. With the introduction of silver metal into the ZnO system, the homogeneity of the products slightly vary with the amount of silver metal added. All these experiments carrying silver as an additive or dopant in the ZnO system were carried out in the presence of a surface modifier viz., caprylic acid in varying amount from 0.1 to 2 mL. Thus, the amount of both silver metal and

**Table 1** Characteristic experimental conditions in the hydrothermal synthesis of silver-doped ZnO particles

| S. no. | Starting precursors | Surfactant | T, °C | % Fill | Remarks |
|---|---|---|---|---|---|
| 1. | ZnO = 3.29 g, 1 N HCl = 10 mL, Ag = 1 wt%, IpH = 5.8, FpH = 5.4 | 0.2 mL caprylic acid | 250 | 40 | White crystalline powder |
| 2. | ZnO = 3.29 g, 1 N HCl = 10 mL, Ag = 2 wt%, IpH = 6, FpH = 5.2 | 0.5 mL caprylic acid | 250 | 50 | White crystalline powder |
| 3. | ZnO = 3.29 g, 1 N HCl = 10 mL, Ag = 3 wt%, IpH = 6.4, FpH = 5.8 | 2 mL caprylic acid | 250 | 50 | White crystalline powder |
| 4. | ZnO = 3.29 g, 1 N HCl = 10 mL, Ag = 4 wt%, IpH = 6, FpH = 5.8 | 1 mL caprylic acid | 250 | 50 | White crystalline powder |
| 5. | ZnO = 3.29 g, 1 N HCl = 10 mL, Ag = 5 wt%, IpH = 6, FpH = 6.1 | 1.5 mL caprylic acid | 250 | 50 | White crystalline powder |
| 6. | ZnO = 3.29 g, 1 N HCl = 10 mL, Ag = 5 wt%, IpH = 6, FpH = 5.9 | 0.5 mL caprylic acid | 250 | 40 | White crystalline powder |

*IpH* initial pH; *FpH* final pH

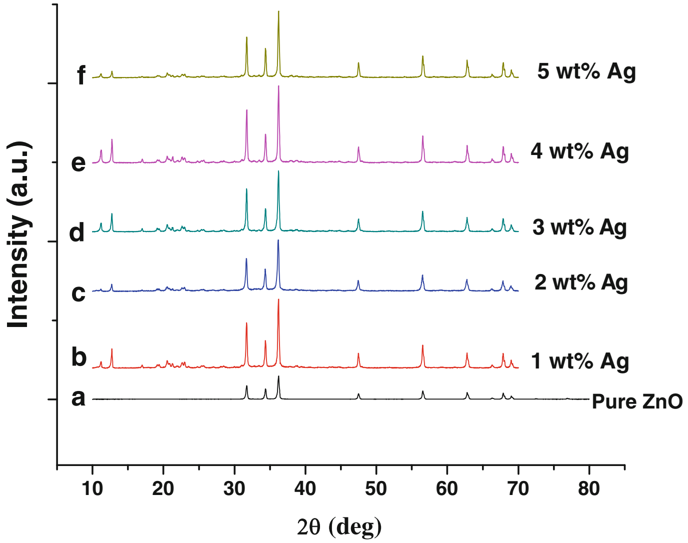

**Fig. 1** **a** Powder X-ray diffraction patterns of surface-modified ZnO: Pure ZnO; **b** 1 wt% Ag-doped ZnO; **c** 2 wt% Ag-doped ZnO; **d** 3 wt% Ag-doped ZnO; **e** 4 wt% Ag doped ZnO; **f** 5 wt% Ag doped ZnO

caprylic acid was varied, and the quality of the resultant products was studied in detail with respect to the size, shape, agglomeration, phase purity, and also the photocatalytic efficiency. When 1 wt% of silver was added, there was not much change in the powder X-ray diffraction pattern from that of the powder X-ray pattern for pure ZnO. However, with an increase in the concentration of silver metal from 2 wt% onwards, the appearance of some additional peaks were observed in addition to the X-ray patterns of pure ZnO. This clearly indicates that the silver has not entered into the crystal structure, but instead it has formed silver chloride (AgCl), since silver and hydrochloric acid react readily to form silver chloride [13] as observed from Fig. 1c–e. Thus, it is doubtful that the silver metal can enter into the internal structure of ZnO, but it has either formed silver chloride or exists as silver metal attached to the surface of ZnO particles. Even the presence of a surface modifier did not influence the incorporation of silver into the structure of ZnO, except in modifying the surface charge of ZnO and accordingly the hydrophobic nature was observed for the resultant products obtained in the presence of caprylic acid as a modifier.

Figure 2a–f shows SEM images of the representative samples of modified ZnO particles with silver added into the system. The SEM images show very interesting results depending on the amount of silver and caprylic acid present in the nutrient. The presence of surplus ZnO (4 M) has introduced large agglomeration and with the presence of higher amount of surfactant has simply led to the formation of bulk aggregates without any specific morphology and faceting of the particles. Instead, the particles have an irregular shape and also vary in size (Fig. 2a). However, with the addition of silver (1 wt%), the agglomeration did not stop, but the particles are finer and irregular (Fig. 2b). When 2 wt% silver was added into the system, this

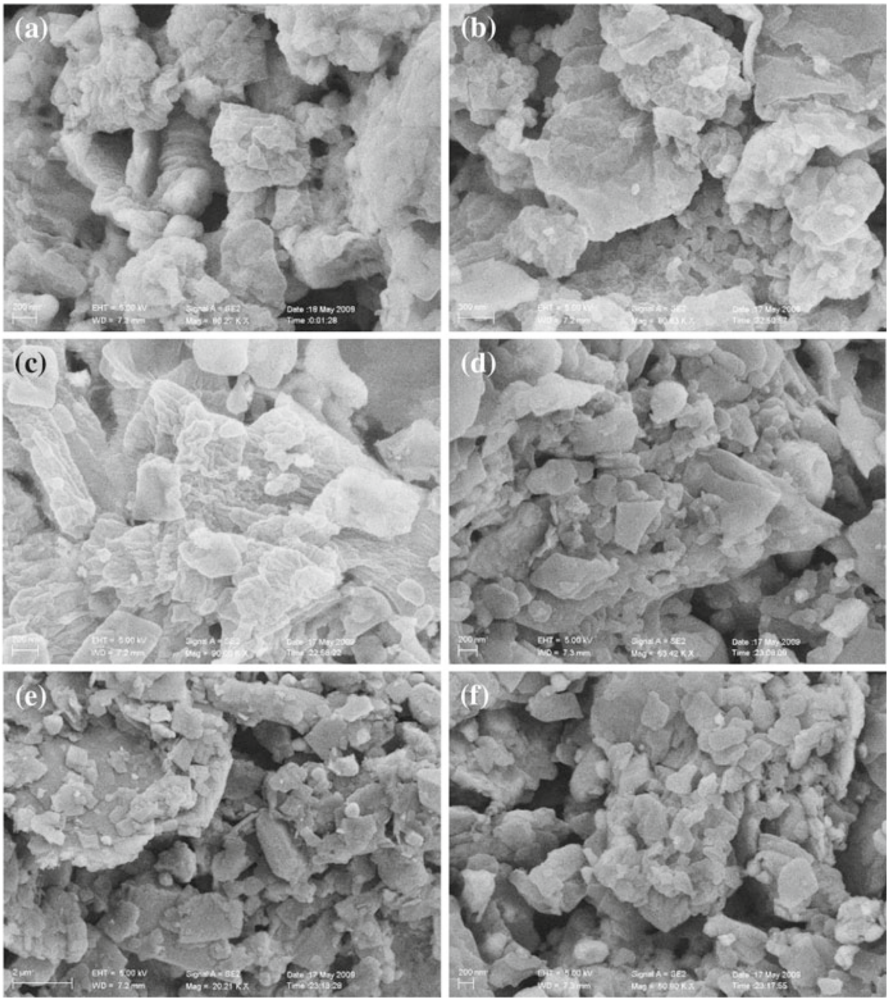

**Fig. 2** Surface-modified silver-doped ZnO particles: **a** undoped ZnO; **b** 1 wt% Ag-doped ZnO; **c** 2 wt% Ag-doped ZnO; **d** 3 wt% Ag-doped ZnO; **e** 4 wt% Ag-doped ZnO; **f** 5 wt% Ag-doped ZnO

resulted in the formation of a very interesting structure for the particles. Although the agglomeration continues, the particles look more tubular, and higher magnification reveals the formation of nanotube-like structures (Fig. 2c). This clearly indicates that silver has acted here in the system during the hydrothermal reaction more as a catalyst than as an additive or dopant. When 3 wt% silver was added into the system, the formation of nanostructure-like ZnO disappears and again larger particles of ZnO with smaller particles of silver chloride was observed (Fig. 2d). When the concentration of silver was increased to 4 and 5 wt%, the formation of larger and elongated particles of ZnO along with small particles of silver chloride attached over the surface of ZnO was observed (Fig. 2e, f). The agglomeration of

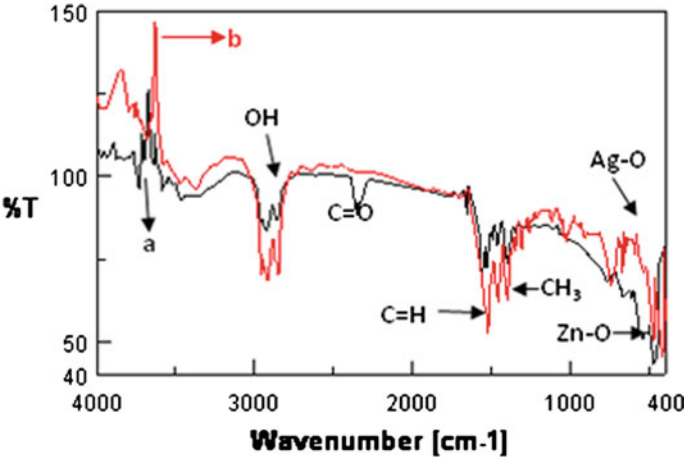

**Fig. 3** FTIR spectra of surface-modified pure ZnO (**a**); surface modified silver-doped ZnO (**b**)

the particles continues in spite of the presence of a surface modifier in the system. In fact, a surplus of the surface modifier reduces the quality of the particles and introduces more agglomeration. The observations made using the SEM images match well with the powder XRD results for these materials.

The FTIR spectra for the representative samples of modified ZnO particles with silver added into the system are shown in Fig. 3a–b. The new absorption bands around 1,400–1,600 and 2,450 cm$^{-1}$ could correspond to the presence of CH$_3$–Cl, C–H, and N–H stretching bands, which exist as organic coverage over the ZnO particles in the modified nanoparticles. The Ag–O bands were also observed at around 530 and 650 cm$^{-1}$ [14]. Since the amount of Ag in the starting mixture was less, the peaks are not very strong. The O–H stretching band appears at 3,450 cm$^{-1}$. The absorption bands around 1,200–1,500 cm$^{-1}$ belong to carboxyl group and 2,950 cm$^{-1}$ belong to C=O and O–H stretching band because of the caprylic acid as surface modifiers [15].

The photocatalytic study of modified silver-added ZnO was studied through the degradation of Indigo Carmine dye, as it is well known that a real-time textile effluent usually contains Indigo Carmine dye as a major constituent along with other dyes. Here, the authors have studied the reduction in the chemical oxygen demand (COD) values of the degraded Indigo Carmine solution, which reveals that only a partial destruction of the organic molecules along with the color removal occurs, since the modified silver added ZnO is highly hydrophobic in nature, and a complete dispersion of these ZnO particles is impossible to achieve a greater photodegradation efficiency. It is interesting to note that as observed from the SEM images that smaller particles of AgCl are directly attached to the surface of the ZnO particle aggregates, and are sparsely dispersed along with ZnO particles. Hence, the hydrophobic nature for the resultant product is maintained in spite of the presence of 5 wt% silver in the raw material. Otherwise, the silver particles would have dispersed in the effluent solution, or in water. Also, it is possible that caprylic acid might have assisted in the binding of silver chloride particles over the ZnO particle aggregates. Hence, the resultant product is highly hydrophobic and floats on the surface of water or effluent. In spite of continuous stirring, these silver particles do not peel off and disperse in the effluent. It is well known that the organic surface modifiers provide a very thin coating around the inorganics during in situ surface modification under hydrothermal conditions [16]. However, in the present case, this organic coating is not uniform owing to the presence of surplus ZnO and also in some cases surplus caprylic acid, and hence the coating is found to be irregular and non-uniform. The silver chloride particles are dispersed within this organic matrix. This is why the silver particles do not peel off during stirring in the photocatalytic degradation process. The amount of catalyst loaded was −50 mg/50 mL, and the concentration of the Indigo Carmine dye solution was 0.00001 M. The pH of the photocatalytic degradation was maintained at 8.6, and the standard UV light source was used. The final COD value was 1,200 after the photocatalytic treatment for about 4 h, which is far above the permissible range. Also, the solution was constantly stirred to disperse the particles, but the photocatalytic efficiency is also due to the presence of silver particles. The photocatalytic degradation of Indigo Carmine dye using modified silver-doped ZnO increased to some extent in samples containing 5 wt% silver in the nutrient. It is around 1.2–1.3 times higher than for the pure ZnO. The COD values dropped to about 930, indicating better photocatalytic efficiency. Hence, the photocatalytic degradation is due to the synergetic processes of both silver metal and photocatalyst. However, there are several other applications for the hydrophobic silver-added modified ZnO particles and such studies are under investigation.

## Conclusions

Hydrothermal synthesis of modified silver-added ZnO under mild PT conditions in the presence of surplus ZnO (4 M) and caprylic acid as surface modifier resulted in the highly agglomerated particles. As the concentration of silver was varied, the resultant products lose the phase homogeneity. Also, the products do not show any control over the size and morphology owing to surplus ZnO. Even the variation in the concentration of surface modifier did not have an influence on the product quality. Caprylic acid resulted in the synthesis of hydrophobic ZnO particles. FTIR spectroscopy data indicated the presence of organic molecules. SEM images showed poorly developed morphology for the silver-doped ZnO particles. Modified ZnO particles show lower photodegradation efficiency under UV light in the degradation of Indigo Carmine dye.

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