Research Article

Synthesis of TiO2@ZnO–Ag Nanocomposites and their Anti-inflammatory Activity

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ABSTRACT

Titanium dioxide (TiO2) is used for water purification, because many chemical compounds and microorganism can be decomposed by oxidation and reduction processes. In this study, the composite of TiO2 nanoparticles (NPs) @ mesoporous silica nanoparticles (MSNPs) (TiO2@ZnO) were prepared by the sol–gel method. The prepared TiO2@ZnO nanocomposite was modified by decorating silver nanoparticles (Ag NPs) (TiO2@ZnO–Ag) using a hydrothermal method. The composite was investigated for anti- inflammation of protein denaturation and proteinase inhibitory activity.

Keywords: Nanocomposite, anti-inflammation, denaturation, inhibitory activity.

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INTRODUCTION

In recent years among the technologies used for the degradation of the environmental pollutants the photocatalytic technique gained interest moreover, it is regarded as the most innovative technique. The strongly oxidizing power of titanium dioxide nanoparticles (TiO_2 NPs) leads to pave its potential energy and environmental applications, such as solar cells, water splitting, super capacitor, sensors, biosensors, water purification and anti-inflammatory activity. TiO_2 is considered as one of the most promising and challenge materials low toxicity, less chemical inert and high photo chemically stability[1]. The TiO_2 nanoparticles mesoporous structure, highly surface area and porous nature higher photocatalytic activity in order to adsorption capacity for TiO_2 nanoparticles. [2-4] The TiO_2 nanoparticles noble metal doping (Au, Pt, Ag) for certain subtracting metal oxide, carbon, polymer enhancing catalytic performance of photo induced reaction under the illumination of UV light[5-7]. In this route employed for sensitizing TiO_2 and have proved in significantly enhancing the photo activity of TiO_2. The underlying mechanism being that the Fermi level of the metal is lower than TiO_2 and hence there can be an electron transfer from the conduction band of the semiconductor to the metal. The TiO_2 hollow microspheres, the results confirmed that the as-prepared products exhibited enhanced photocatalytic and microbial activity [8]. At once few researchers TiO_2 structure modifications of nanotube, nanorods, nanowires, nanosphere for further adapted 1D structure and 2D structure was more catalytic activity.

MATERIALS AND METHODS

Materials

The analytical grade were purchased from in Sigma Aldrich, Mumbai, India, were as Titanium (IV) chloride, ($TiCl_4$, 99.99 %), Cityl trimethyl ammonium bromide (CTAB, 99.98%), Tetra ethyl orthosilicate (TEOS, 99.99 %), Silver nitrate ($AgNO_3$, 99.98 %), absolute methanol, ethanol, ammonium hydroxide (NH_4OH, 99.99 %), sodium hydroxide (NaOH, 99.98 %), Hydrochloric acid (HCl, 99.98 %) were received from Merck.. All different chemicals employed in this work were of analytical grade. Unless otherwise specified, deionized double distilled water was used for the preparation of aqueous solutions.

Synthesis of TiO_2 nanoparticles (TiO_2 NPs)

$TiCl_4$ (9 ml) was slowly introduced into deionized double distilled water in an ice bath (0°C) under constant stirring until it was completely dissolved and then 18 ml of 30 % NH_4OH was added to this suspension. The white titanium hydroxide ($Ti(OH)_4$) was allowed to stand for 1 h. Then, the obtained TiO_2 NPs were filtered, washed with deionized double distilled water and dried at 100°C in a vacuum oven for 3 h.

Synthesis of TiO2@ZnO–Ag nanocomposite

1 g of TiO_2 and 50 ml of 1.0 M $ZnSO_4$ solution was added drop wise into 30 ml of 2.0 M NH_4CO_3 solution under vigorous stirring at 60°C in water bath for 1 h. The white precipitate was isolated by filter and washed for three times with double distilled water and ethanol, dried in a

vacuum oven at 60°C for 24 h. Finally, the product was calcined at 600°C for 1 h to obtain powder of TiO_2/ZnO. The Ag NPs were deposited on the surface of TiO_2@ZnO nanocomposite through a chemical reduction method, in which Ag^+ ions were converted into Ag NPs. In the typical synthesis, 1 g of the preformed TiO_2@ ZnO nanocomposite was dispersed in 250 ml of deionized double distilled water with continuous stirring for 30 min to get a homogeneous distribution of TiO_2@ZnO nanocomposite. The $AgNO_3$ (5 wt%) was added and stirred towards the reduction of Ag^+ ions upon the drop wise addition of $NaBH_4$ until the colour changed to greenish yellow. The appearance of the greenish yellow colour indicated the formation of TiO_2@ZnO–Ag nanocomposite and the solution was continuously stirred for another 30 min. The TiO_2@ZnO–Ag nanocomposite was filtered washed thoroughly with deionized double distilled water, dried at 60°C for 3 h and finally calcination at 450°C for 3 h.

Surface morphology analysis (FE-SEM)

The surface morphology analysis of the TiO_2 NPs, TiO_2@ZnO and TiO_2@ZnO–Ag nanocomposite were analyzed using FE-SEM and the corresponding images are shown in Fig.1.

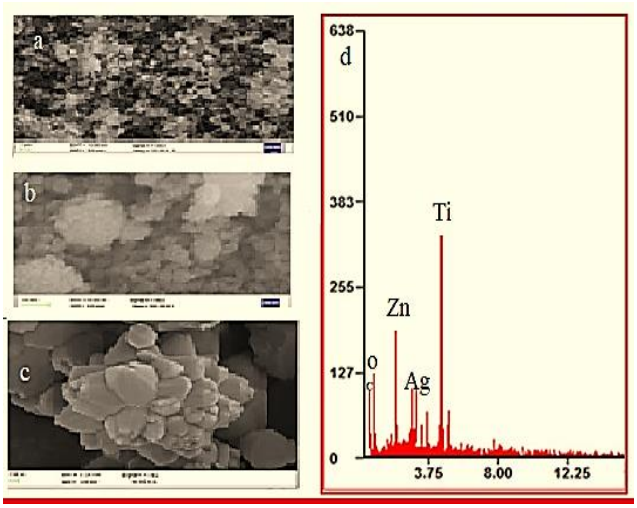

Figure 1: FE-SEM image of (a) TiO_2 NPs (b) TiO_2/ZnO(c) TiO_2/ZnO–Ag (d) EDX- spectrum

The nature of the FE-SEM images revealed that all the TiO_2 NPs, TiO_2@ZnO and TiO_2@ ZnO–Ag nanocomposite are spherical in shape with uniform structure as shown in Fig.1a–c.[5-6] On the surface structure was the characterization and carried out the importance of the preparation of nanoparticle and the maintaining the surface nanostructure. When the nanoparticle growth after the materialized for the nanoparticles affected to the solvent used during the hydrothermal method due to the dielectric constant led to the nature of particles spherical shapes is formed which are shown in the same figures. The Ag NPs are uniformly is deposited on the surface of spherical TiO_2@ZnO nanocomposite. This TiO_2@ZnO–Ag composite material was element analyzed by the EDAX spectrum. Ti, Si, and Ag are apparently present in Fig.1d. The FE-SEM image of TiO_2@ZnO–Ag nanocomposite has the various nanoparticles of Ag present in the catalysis on the surface.

Methodology for anti-inflammatory process

Albumin denaturation

About 0.2 ml of eggs albumin (from hensegg) was comprised 5 ml of reaction mixture, 2 ml of varying concentrations of sample (20-100 µg/ml), and 2.8 phosphate- buffered saline (PBS pH 6.4). The control was served as similar volume of double distilled water. Then the mixture was incubated at 37ºC in biochemical oxygen demand incubator for 15 min and then heated at 70º C for 5 min. After cooling their absorbance were measured at 660 nm at pure blank. Diclofenac sodium (standard drug) was used as reference drug and treated as such for the determination of absorbance. The percentage inhibition of protein denaturation was calculated as below.[9]

$$\text{Percent inhibition} = \frac{\text{Abs control/ Abs treated}}{\text{Abs treated}} \times 100$$

Antiproteinase

The test was performed according to the modified method. The reaction mixture (2 ml) was containing 0.06 mg aspirin, 20 mM Tris-HCl buffer (pH7.4) and 1 ml test sample of different concentrations (20 -100 µg/ml). The mixture was incubated at 37º C for 5 min and then 1 ml 0.8% (w/v) casein was added. The mixture was incubated for an additional 20 min. 2 ml of 70% perchloric acid was added to complete the reaction. Cloudy suspension was centrifuged. The absorbance of the supernatant was maintained at 210 nm. The buffer solution is used as a blank. The experiment was performed in triplicate. The percentage inhibition of proteinase inhibitory activity was calculated.

$$\text{Percentage inhibition} = \frac{\text{(Abs control / Abs sample)}}{\text{Abs control}} \times 100$$

RESULTS AND DISCUSSION

Inhibition of Albumin denaturation

Protein denaturation is a process in which proteins lose their tertiary and secondary structure by application of external stress or compound. The compound such as strong acid, strong base, concentrated Inorganic salt, an organic solvent or heat. Denaturation is a protein is a well-documented cause of inflammation. As part of investigation on the mechanism of the anti- inflammation activity ability of sample to inhibit protein denaturation was studied. Inhibition of albumin denaturation of activity at different concentration as shown in Figure 2 & Table 1. It was effective in inhibiting heat induced albumin denaturation maximum inhibition of 71% was observed at the concentration of 100 µg\ml. Diclofenac is a standard anti inflammation drug shows the maximum inhibition

80% at the concentration of 100 µg\ml compared with control.

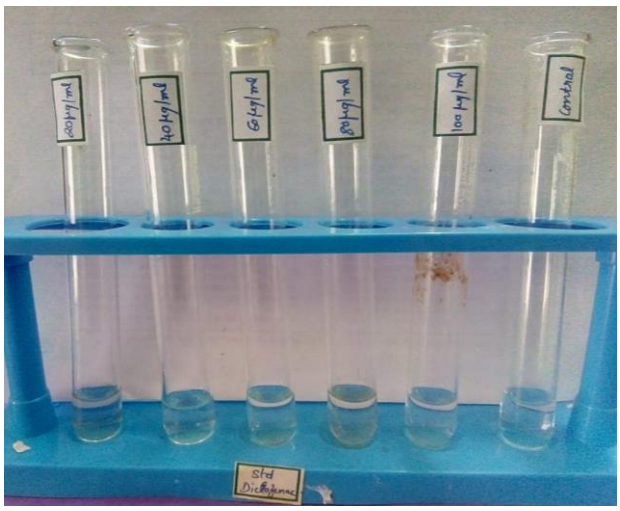

Figure 2: Inhibition of albumin denaturation of standard Diclofenac sodium

Table-1: In vitro activity of the samples using albumin denaturation

S.NO	Concentration	% of Albumin Denaturation	
		Samples	Diclofenac
1	20	36	51
2	40	38	59
3	60	46	71
4	80	49	75
5	100	76	80

Antiproteinase Action

Neutrophils are known to be a rich source of serine proteinase and are localized at lysosomes. It was previously reported that leucocytes proteinase play an important role in the development of tissue damage during inflammatory reactions and significant level of protection was provided proteinase inhibitors. Anti proteinase activity at different concentration as shown in Figure 3 & Table 2.

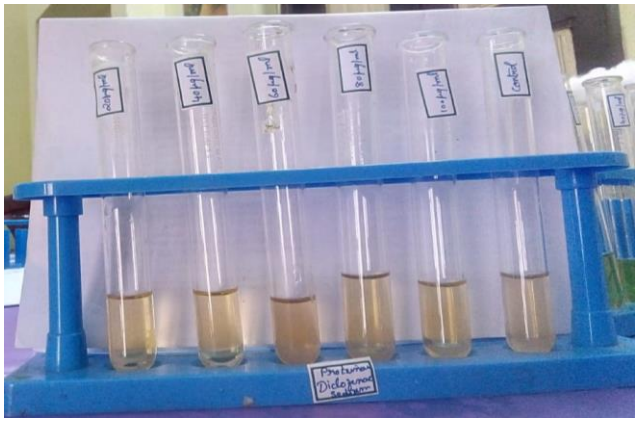

Figure 3: Anti proteinase action in samples

It shows the maximum inhibition of 60% at 100µg\ml. Aspirin shows maximum inhibition 66% at 100µg\ml.

Table 2: *In vitro* activity of the samples using anti protenase action

S.NO	Concentration	% of Anti-protenase Activity	
		Sample	Aspirin
1	20	30	40
2	40	35	49
3	60	38	56
4	80	46	64
5	100	60	66

CONCLUSION

The TiO_2@ZnO–Ag nanocomposite was investigated for anti- inflammation of protein denaturation and proteinase inhibitory activity were calculated. Maximum inhibition of 76% was observed for Albumin denaturation, while 60% for Antiproteinase Action

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