INTERNATIONAL JOURNAL OF RESEARCHES IN BIOSCIENCES, AGRICULTURE & TECHNOLOGY
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www.vmsindia.org

Synthesis of nano sized visible light active Ag_2ZrO_3 catalysts via Co-Precipitation process

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Abstract

Visible light active nano silver zirconate has been prepared by Co-precipitation method and the effect of silver modification was studied. Nano Ag_2ZrO_3 has been prepared by mixing high-purity 0.1 M $AgNO_3$ and 0.1 M $ZrOCl_2$ $.6H_2O$ solutions in 2:1 ratios. The structural and optical properties were characterized by X-ray diffraction and UV-VIS diffuse reflectance spectroscopy. The band gap of the sample was determined by the equation $Eg = 1239.8/\lambda$. The band gap of nano Ag_2ZrO_3 was found to be 2.6 eV which is lower than Ag_2ZrO_3 (2.9 eV) synthesized by solid state reaction method. These values show that both the samples are visible light active and have low band gap than TiO_2 and ZrO_2.

Keywords: Nano silver zirconate, Co-precipitation method and band gap.

Introduction

Titanium dioxide is one of the most widely studied semi-conducting photocatalysts for the degradation of organic contaminants from water and air, because of its physical and chemical stability, high catalytic activity, high oxidative power, low cost and ease of production . However, though it is a good catalyst, its wide band gap (3.2 eV) limits TiO_2 use in UV region. Since only about 4% of the solar spectra falls in the UV range, it is appealing to develop efficient visible light-sensitive photocatalysts in view of the better utilization of solar energy. In attempts to prepare visible light-sensitive photocatalysts, some cation ion- or anion ion-doped TiO_2 [1-3] and some multiple-metal oxides [4,5] have been fabricated for organic compounds degradation or water splitting. Among a variety of multiple-metal oxide photocatalysts, special attention was paid to materials containing metal ions with specific nd^{10}, ns^2 outer layer-orbital configurations, such $CaIn_2O_4$ [6], $AgInW_2O_8$ [7], $AgNbO_3$ [8], and $AgGaO_2$ [9]. As a common feature, the completely filled nd^{10} or (nd^{10}) ns^2 outer layer orbitals can hybridize with the O $2p^6$ orbitals in the valence band of a semiconducting material, pushing up the valence band top, and thus leading to a narrowed band gap. The modification of semiconductors with noble metals like platinum (Pt), silver (Ag), gold (Au) has attracted significant attention especially in heterogeneous photocatalysis [10, 11]. It is reported that the insertion of silver ion in the catalyst improve the photocatalytic efficiency of material. Ag doped $NiTiO_3$, $AgSbO_3$, Ag_2ZnGeO_4 are used for degradation of dyes under visible light irradiation [12-14]. Ouyang et al. has studied correlation of crystal structures, electronic structures, and photocatalytic properties in a series of Ag-based oxides: $AgAlO_2$, $AgCrO_2$ and Ag_2CrO_4 [15].A recent study by Yi et al. has shown that orthophosphate (Ag_3PO_4) can harness visible light and exhibit apparent photocatalytic activity in water splitting as well as degradation of organic contaminants, suggesting effective separation of the photogenerated electrons and holes [16]. However, the lack of chemical stability of Ag_3PO_4 and the photocatalytic activity in the UV range has remained largely unexplored. The photodegradation of methyl orange under UV irradiation in presence of Ag_3PO_4/TiO_2 heterostructures was markedly better than the performance of unmodified TiO_2 and Ag_3PO_4 nanoparticles alone [17]. We have also reported visible light active sliver zirconate (Ag_2ZrO_3) prepared by a simple solid state reaction method as efficient visible-light-driven photocatalyst for degradation of methylene blue [18]. However, the number of photocatalyst working in the visible-light region for degradation of organic pollutants is limited, and the efficiency of these catalysts is still low and needs improvement. In this work, we designed a visible light active nano sliver zirconate (nano Ag_2ZrO_3) prepared via Co-precipitation method at low temperature as a efficient visible-light driven photocatalyst.

Experimental Section Sample Preparation

A visible-light-active photocatalyst Ag_2ZrO_3 was prepared by a simple co-precipitation method (CP). High-purity $AgNO_3$ (99.9% Merck) and $ZrOCl_2 .6H_2O$ (99.9% Merck) were use as raw materials. The solution 0.1 M $AgNO_3$ and 0.1 M $ZrOCl_2 .6H_2O$ were mixed in 2:1 ratios. The pH value of the above solution was adjusted to 10.0 by a drop wise addition of concentrated ammonia solution. The resulting white precipitate was washed with distilled water for several times, and then dried, smashed and calcined in muffle furnace at 400 °C for 24 hrs. Thus, the target photocatalyst nano Ag_2ZrO_3 of faint brown colour was obtained which was then used for characterization. **Fig. 1.** shows scheme for synthesis of silver zirconate via co-precipitation method.

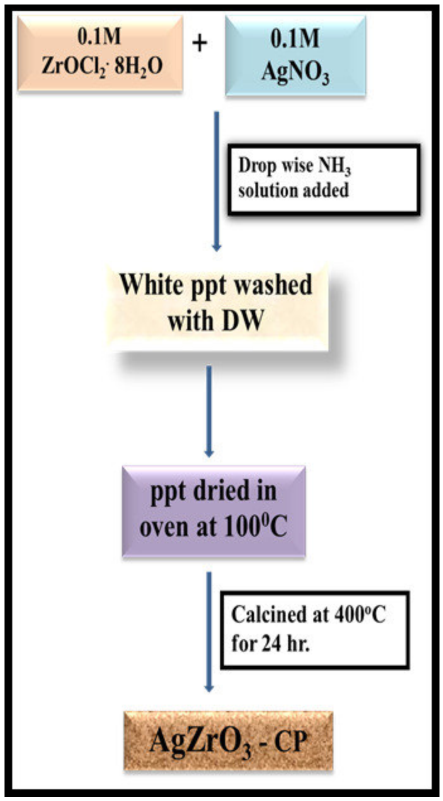

Figure 1: scheme for synthesis of silver zirconate via co-precipitation method.

Characterization of sample

The crystal structure and phase purity were determined with X-ray diffractometer (XPERT-PRO Diffractometer) with monochromatic Cu α K radiation (45 kV, 40 mA). The diffuse reflectance spectra (DRS) of the photocatalyst were measured by UV-visible spectrophotometer (UV-1800, Shimadzu) over spectral range 200 – 800 nm.

Result and Discussion

XRD analysis

X-ray diffraction (XRD) is used to identify the structure of the prepared Powder. **Fig.2** shows XRD pattern of nano Ag_2ZrO_3 calcined at 400 °C for 24 hrs. The sharp peaks in the XRD patterns indicate a well crystalline of the prepared samples. The XRD analysis resulted is similar to Ag_2ZrO_3 synthesized by solid state method, crystalline structures as shown in **Fig. 2** for nano $Ag_2ZrO_3$with no other phases being observed [18].

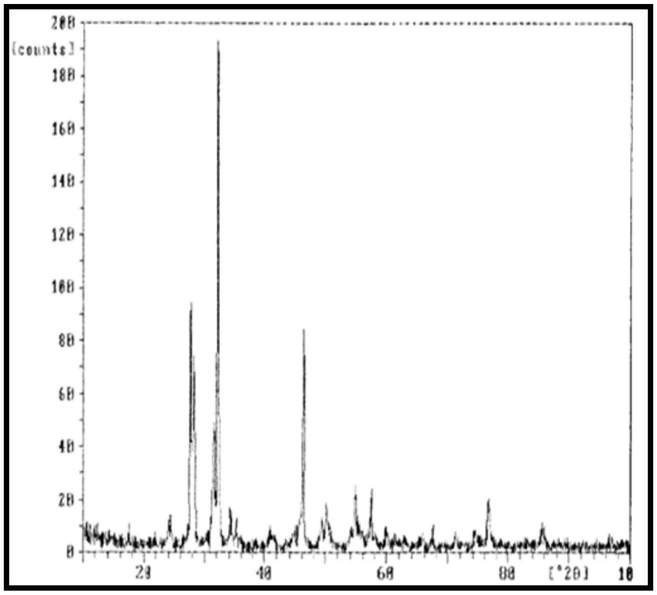

Figure 2: X-ray diffraction patterns of prepared Ag_2ZrO_3 powder at 400 ◦C'

UV- visible Analysis

UV–Visible analysis gives very important information for photocatalytic application as catalyst since it gives information about the band gap of semiconductors. The UV-DRS spectrum of the nano Ag2ZrO3 semiconductor annealed at 4000C is shown in **Fig 3**. The dark brown colored nano Ag2ZrO3 sample exhibits broad and strong absorption in the range from 200 to 600 nm. The band gap of the samples was determined by the equation $Eg = 1239.8/ \lambda$, where Eg the band gap (eV) and λ (nm) the wavelength of the absorption edges in the spectrum The band gap of nano Ag2ZrO3 was found to be 2.6 eV which is lower than Ag2ZrO3 (2.9 eV). These values show that both the samples are visible light active and have low band gap than TiO2 and ZrO2.

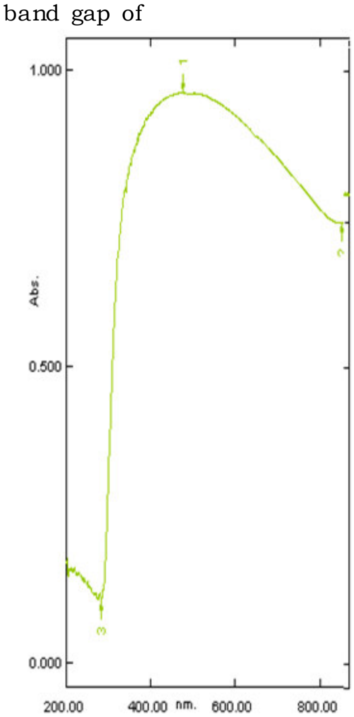

Figure 3: Diffuse Reflectance spectra (DRS) of the prepared nano Ag_2ZrO_3 powder .

Conclusion

We here synthesized nano Ag_2ZrO_3 by Co-precipitation. This method is convenient and easy to handle. As prepared, nano Ag_2ZrO_3 was found to be active under visible light irradiation for degradation of dye methylene blue as well as ots photocatalytic activity was found to be higher than Ag_2ZrO_3 synthesized via solid state method calcined at 900^{0}C. It indicates stability of Ag_2ZrO_3. The present study indicates that, it was feasible to prepare visible light active nano silver zirconate with co-precipitation method.

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