SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC STUDIES OF CATION (Ag^{+2} and Sn^{+2}) DOPED $\text{Na}_{1.5}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$

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ABSTRACT

A new type of layered titanate, i.e $\text{Na}_{1.5}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$ synthesized by the sol-gel method and the Na^{+} exchanged by Ag^{+} ($\text{Ag}_{1.5}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$) and Sn^{2+} ($\text{Sn}_{0.75}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$). The characterization of new materials $\text{Ag}_{1.5}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$ and $\text{Sn}_{0.75}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$ are done using PXRD, SEM, EDS, TGA, and UV-visible DRS techniques. The photocatalytic degradation studies of 4-chlorophenol and two highly toxic PAHs including anthracene (ANT) and pyrene (Py) are chosen. All the intermediates and photo-degraded products are analyzed by Mass and NMR spectral studies.

Keywords: Sol-gel Method, Photocatalytic Studies, EDX, PXRD, SEM, TGA, UV-visible DRS, NMR.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and derivatives of phenols are an essential cause of environmental pollution due to their stability in the environment and resistance to the natural degradation process.¹⁻³ They are produced through the combustion of fossil fuels, coke ovens, forest and agricultural fires, metal refining processes, and hydrocarbon production, among other processes. PAHs absorb rapidly into suspended particulates and biota, and then accumulate in soil and sediment, resulting in severe soil pollution complications.⁴ Many of them are toxic and carcinogenic, and the US EPA lists sixteen PAHs as priority toxins.⁵ Whereas not as active a carcinogen as benzoanthracene, anthracene is the main mutagen widespread in polluted soils.⁶ Due to the delocalization of the electron, PAHs have a high degree of stability and limited water solubility, which results in their accumulation in food chains.⁷ Mainly, phenols used in the polymer industry are hazardous and generate harsh environmental pollution by discharging highly toxic substances into the aqueous phase. Therefore, the degradation of PAHs and phenols is a currently focused area of research in materials chemistry.⁸⁻¹⁰

In the last two decades, one of the most challenging and costly approaches to degrading PAHs has been photocatalysis in the presence of ultraviolet light.¹¹ At present, various types of ternary oxide-based semiconductors are induced to photocatalysts effectively for the degradation of dangerous organic contaminants but very few reports about the PAH's decomposition under visible light irradiation are up to the mark. In previous studies, photocatalysts used for photo-oxidation or degradation of organic pollutants are binary oxides with a wide variety of dopants such as cations and anions.¹²⁻¹⁵ The benchmark oxide among binary oxides is titanium dioxide (TiO_2), which is widely used as a photocatalyst for the degradation of a wide range of organic contaminants when exposed to ultraviolet light irradiation due to its high bandgap energy.^{16,17} Similarly, some other binary oxides used as photocatalysts under visible light irradiation are BiVO_4 , TiON , and WO_3 . These catalysts show poor performance under visible light due to fast recombination of holes and electrons and also morphology and high bandgap energy.^{1,18,19} As a result, the current emphasis is focused on the application of photocatalysts that operate in the presence of visible light.

The rate of cationic exchange is very fast in ternary oxides with the layered type of structural arrangement due to which they exhibit high catalytic activity.²⁰ Among these layered ternary compounds, the most desirable oxides in photocatalysis are titanates ($\text{A}_2\text{Ti}_n\text{O}_{2n+1}$) due to their versatility in controlling the hole/electron mobility by inserting a wide variety of elements into the A site of the lattice.²⁰ Moreover,

titanates have been shown with ion-exchange features which make them potential materials for several applications.

Several studies have been conducted on the photocatalytic decomposition of these phenols in the presence of semiconductor oxides,^{9,21} as well as the ability of trititanates and hexatitanates to degrade dyes and phenols when exposed to visible light. The photocatalytic activity of these materials can be improved further by the introduction of some cations and/or anions in the lattice framework. Recently, Ravi et al. have developed a new Ag^+ and Cu^{2+} incorporated $\text{Na}_2\text{Ti}_3\text{NO}_{6-x}$ layered oxide photocatalyst, for the mineralization of organic dyes under visible light²² in a continuing search with the aim of degradation of organic pollutants and C-H activation for medicinal and material chemistry.

In this study, we report, the design and preparation of a new type of layered titanate, i.e. $\text{Na}_{1.5}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$. The material is obtained by the sol-gel method and the exchange of Na^+ by Ag^+ and Sn^{2+} into its lattice to improve the visible light photoactivity towards organic pollutant degradation. The characterization of new materials $\text{Ag}_{1.5}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$ and $\text{Sn}_{0.75}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$ is done by EDX, PXRD, SEM, TGA, and UV-visible DRS techniques. The photocatalytic degradation studies of 4-chlorophenol and three highly toxic PAHs, including Naphthalene (Np), anthracene (ANT), and pyrene (Py) were chosen.¹⁷ All the intermediates and photo-degraded products are analyzed by Mass and NMR spectral studies. The reaction pathway suggested was established based on the experimental data.

EXPERIMENTAL

Material Preparation

The $\text{Na}_{1.5}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$ sample was prepared by dissolving stoichiometric amounts of NaNO_3 , $\text{Zn}(\text{NO}_3)_2$ and Ti-peroxo complex in double distilled water via the sol-gel citrate method.¹⁹ Stoichiometric amounts of NaNO_3 , ZnNO_3 and Ti-peroxo are first dissolved in double distilled water separately. The chelating agent, citric acid, was added to the metal ion. The molar ratio of citric acid to the metal ions was 2:1. The pH of the resultant metal citrate solution was adjusted to 6-7 by adding dilute ammonia solution dropwise. The solution was then slowly evaporated on a water bath till a viscous orange-colored liquid was obtained (Sol). At this stage, the gelating reagent, ethylene glycol, was added to the solution. The molar ratio of citric acid to ethylene glycol was 1.0:1.2. This mixture was heated on a hot plate at 100 °C for 2-3 hours with constant stirring. The temperature was increased to 160 - 180 °C at the onset of solidification. The ensuing solid porous mass was ground in an agate mortar using spectral grade acetone. The resultant grey powder was heated in a muffle furnace at 600 °C for 5h to yield crystalline powder.

At room temperature, 1 g of NZTO powder was mixed with 100 mL of 0.1 M $\text{SnCl}_2/\text{AgNO}_3$ solution. To validate the development of products by ion exchange, the colors of the powders were changed, and the stirring was continued for 16 hours. The colors of the powders were changing, and the stirring had been going on for 16 h to confirm the ion exchange development of the compounds. The obtained products were washed with water and dried at 250 °C for 5 h.

Characterization

The thermal stability of NZTO, AZTO, and SZTO was analyzed at a scan rate of 10 °C/min using a Shimadzu differential thermal analyzer (DTG-60H). The morphology of NZTO, AZTO, and SZTO was investigated using a Hitachi S3200N variable pressure scanning electron microscope (VPSEM) equipped with EDS. The X-RD patterns of NZTO, AZTO, and SZTO were captured at a range of 10 - 80° using a Rigaku miniplex powder X-ray diffractometer ($\text{Cu K}\alpha$, $\lambda = 1.5406 \text{ \AA}$). For UV-Vis diffuse reflectance spectra (DRS) measurements in the 200–800 nm range, a JASCO V650 UV-Vis spectrophotometer was used, where BaSO_4 is used as a reference standard.

Photocatalytic Reactions

The photodegradation device involves a 300 W tungsten lamp, a 50 mL quartz reaction cell, and a water cooler (preventing the thermal catalytic effect). In a typical study, 0.005 g of PAH was dissolved in a solvent mixture composed of 25 mL of acetonitrile and 25 mL of water. The PAH solution was then added to a quartz cell containing a predetermined amount of photocatalyst. This mixture was agitated for

two hours with the light on to establish an adsorption/desorption equilibrium of PAHs on the photocatalyst surface.

Consequently, the quartz cell was exposed to visible light irradiated with 300W tungsten. After the reaction was completed, the suspension was removed and centrifuged to eliminate any remaining photocatalyst. Subsequently, dichloromethane was used to extract the products (DCM). The DCM layer dehydrated over anhydrous sodium sulfate was measured and identified using mass spectrometry (MS) (Agilent 6890N, United States) and liquid chromatography-mass spectrometry (LC-MS) (Agilent 6890N/5973I, United States). Additionally, AZTO and SZTO stability experiments were conducted. The optimization of the performance of AZTO with anthracene (ANT) amount was 0.05 and 0.005 g, respectively. In this test, the transformation of anthracene was evaluated by removal of the entire reaction residue, using the discarding method revealed above. Then, the recycled AZTO and SZTO were utilized in the following run of the experiment. At the start of every run, anthracene was added to the reactor to keep the original amount of 0.005 g. The same photoreaction was repeated four times with a 3 h irradiation period between each run. In the assay to determine the active species, the sum of t-butanol, KI, and benzoquinone (BQ) was 2×10^{-4} mol. The hydrogen peroxide concentration in the photocatalytic reaction solution was also determined using the hydrogen peroxide test strip (114731 Hydrogen Peroxide Cell Test).

Flow Chart for Preparation of NZTO

RESULTS AND DISCUSSION

SEM-Studies

The NZTO, AZTO, and SZTO morphologies were analyzed^{23,24} using SEM analysis and the results are displayed in (Fig.-1). SEM photographs of three samples were distinguished by irregularly formed lumps with significant agglomeration, whereas SZTO particles were partially grown as nanotubes, but most of them were agglomerated relative to NZTO (Fig.-1). The crystallite size of nanotubes was in the range 18-25 nm, which is closer to the crystallite size calculated using Scherrer's equation. The crystallite size

distribution is uniform without any agglomeration. This result is consistent with the BET surface area that hierarchical structure leads to an increase in the surface area.

Fig.-1: SEM Images of NZTO, AZTO, and SZTO

EDAX Images of NZTO, AZTO, and SZTO

The atomic ratio of the three samples evaluated from Energy Dispersive Spectra (Fig.-2). The Energy Dispersive Spectra (EDS) were recorded using a scanning electron microscope to confirm the elemental composition of the NZTO, AZTO, and SZTO. EDS profile reveals the ratio of Na, Zn and Ti as 1.5:0.75:2.75. The disappearance of Na peaks and the appearance of Ag and Sn peaks suggesting that the Na^+ are completely exchanged with Ag^+ and Sn^{+2} .

Fig.-2: EDAX Images of NZTO, AZTO, and SZTO

Thermogravimetry Analysis

The thermal stability and the presence of water molecules or hydroxyl groups in the lattice of the material are examined by Thermogravimetric analysis.^{23,24} The thermogram indicates a 2.5% SZTO lattice held by a water molecule (Fig.-3). Water can be present in titanates due to adsorbed water or lattice water. Adsorbed water is typically eliminated between 200 and 400 °C, while lattice water would experience a continual loss up to roughly 600 °C. Ag and Sn doped NZTO were prepared from an aqueous solution, so water molecules may enter the lattice. Thermogravimetric analysis was carried out to estimate the water of hydration in the Ag and Sn doped NZTO (Fig.-3). From the weight loss observed (<500 °C), the molecular formula of Ag and Sn doped NZTO was found to be $\text{Na}_{1.5}\text{Zn}_{0.75}\text{Ti}_{2.75}\text{O}_7$.

XRD Analysis

Figure-4 illustrates the XRD patterns of the prepared samples. All three samples of NZTO, AZTO, and SZTO are highly crystalline, and all diffraction peaks may be ascribed to NZTO. (JCPDF number: 50-0109). AZTO and SZTO phases are observed in a similar pattern with NZTO. However, AZTO particles can be found in the SEM image as nanorods, whereas SZTO particles are partly grown as nanorods but most as agglomeration when compared to NZTO (Fig.-1).

The powder patterns of NZTO, AZTO and SZTO are identical (Fig.-4). Similarly, the powder patterns of NZTO, AZTO and SZTO are also alike. Nevertheless, a close examination of d-spacing shows a systematic shift towards a lower 2θ value indicating the substitution of Ag and Sn into the defect pyrochlore lattice. The slight increase in the unit cell parameter of both the oxides compared to their parent compounds is due to the partial substitution of Ag and Sn into the NZTO lattice and also the incorporation of water into the lattice. The change in the color of Ag and Sn oxides compared to their parent oxides also supports the substitution of Ag and Sn into Na sites in the lattice.

Fig.-3: Thermograms of NZTO, AZTO, and SZTO

Fig.-4: PXRD Pattern of NZTO, AZTO, and SZTO

UV-visible DRS Spectra of NZTO, AZTO, and SZTO

Figure-5 displays the UV-Vis absorption spectra of NZTO, AZTO, and SZTO. NZTO has an absorption band edge at around 360 nm, corresponding to bandgap energy of 3.45 eV. In the case of AZTO and SZTO, the bandgap energy fell to around 0.6 eV, which indicates that the absorption bands have moved towards the redshift, i.e., a higher wavelength region. The improved photocatalytic activity for both Ag and Sn oxides may be attributed to (a) decrease in the bandgap energy of Ag and Sn defect pyrochlores leading to an increase in the number of absorbed photons and (b) defects created in the lattice due to the incorporation of Ag and Sn leading to a decrease in the electron-hole recombination rate. We have also compared the photoactivity of AZTO and SZTO with NZTO. Both Ag and Sn materials have shown higher photoactivity compared to that of NZTO.

Photocatalytic Activity

Figure-6 explains the regular time intervals for the photodegradation of pyrene over NZTO, AZTO, and SZTO. With a longer irradiation time, PAH transformations are accelerated. The Na ions are replaced with Ag and Sn metal ions into NZTO, the activity of doped photocatalysts can be significantly supported. The photooxidation rates of the two PAHs are approximately 70 times larger when exposed to AZTO than when exposed to NZTO. After three hours, ANT oxidized over AZTO. Consistent with the UV-Vis absorption spectra (Fig.-5), the absorption band margins of AZTO and SZTO were observed to

be at longer wavelengths than those of NZTO. Py converted into pyrene-4,5-dione and pyrene-1,6-dione after three hours, evidenced by the $^1\text{H-NMR}$ spectrum as shown in Fig.-7.

Fig.5: UV-visible DRS Spectra of NZTO, AZTO, and SZTO

Fig.-6: Photodegradation Pattern of 2-chlorophenol in the presence of NZTO, AZTO & SZTO

Fig.-7: $^1\text{H-NMR}$ Spectrum of a Mixture of pyrene-1,6-dione and pyrene-4,5-dione.

Both PAHs reacted with hydroxyl radicals to form anthracene-9,10-diol and pyrene-4,5-diol which is confirmed from $^1\text{H-NMR}$ data (Fig.-8).

The variation in the activity of NZTO, AZTO, and SZTO could also be due to the contrast between their absorption of light. The explanation for enhancing photocatalytic behavior will be addressed in more detail later. It was estimated that the conversion of ANT to BiVO_4 was just 8% after eight hours under visible light irradiation.¹

^1H Fig.-8: ^1H -NMR Spectra of Anthracene-9,10 diol ^1H Fig.-9: ^1H -NMR Spectra of pyrene-4,5-diol

The present results indicate that AZTO and SZTO have higher activity for ANT photodegradation than Pt-TaON and BiVO₄ under visible light irradiation^{1,17}. Under visible light irradiation, the photooxidation of ANT over AZTO and SZTO was examined. After one hour of irradiation with AZTO, the ANT deteriorated. Additionally, ANT degrades at a rate of 12.5 % faster than P25 in the same circumstances. The results confirmed that AZTO had a photodegradation activity approximately five times that of P25. Figure-6 depicts the gradual change in ANT concentration during photooxidation of ANT pre-adsorbed on NZTO, AZTO, and SZTO. ANT on the NZTO has no photocatalytic activity when compared to AZTO and SZTO. The two photocatalysts, AZTO and SZTO, have exhibited rapid degradation. Among all the photocatalysts, AZTO is highly active. The following explanations have been made: AZTO can be activated by visible light and oxidizes all PAHs when used as a photocatalyst. Additionally, when oxidized via photocatalysis with AZTO, the ANT absorbs visible light (its maximum absorption wavelength is 410 nm, which is slightly inside the wavelength of a visible lamp), ensuring a prompt

photosensitive reaction to the formation of some major oxidized items. The maximum absorption band of ANT gradually disappeared in the analysis of aqueous solutions, as shown in Fig.-10, and a new band at 230 nm was formed. As a result, as anthracene degraded, the 230 nm absorbance peak increased, indicating the formation of intermediate products.²¹

Fig.10: UV Spectrum of anthracene-9,10-dione

These intermediates have highly soluble acid group functionalities on the ring. However, no additional substantial absorption in aqueous solutions was seen when the AZTO particles were removed, even at complete surface coverage (1×10^{-4} mol/g). It indicates that anthracene on AZTO particles may have achieved complete photodegradation. Most intermediate compounds, which may have an adsorption potential, were strongly formed and eventually mineralized into CO_2 , and there was no intermediate solution in the UV-Vis analysis process (data shown). A photooxidation of pyrene under visible light exhibited an absorption peak at 335 nm.²² Different results were observed for these three PAHs. The above findings show the variation in adsorption capability between the reactants. Pyrene has higher water solubility (4.57 mg L^{-1}) than anthracene (0.132 mg L^{-1}), meaning that pyrene and its intermediate derivatives are more soluble and have a lower affinity for the surface of AZTO and SZTO than anthracene.

CONCLUSION

Polycyclic aromatic hydrocarbon compounds with very low solubility in water were capable of being straightforwardly degraded after the desorption-absorption process on AZTO in an aqueous scattering under visible irradiation. The surface coverage, doped with Ag / Sn, had a pronounced impact on the photooxidation rate of PAHs catalyzed by NZTO, while the dispersion, ratio of Py/AZTO: water, had a minor effect. Some of the essential intermediate products are generated by hydroxylation, ketolysis, and the ring-open reaction. Pyrene can be photo-oxidized and then mineralized to CO_2 when exposed to visible light.

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