Extended Abstract

(For Ph.D. Open Seminar)

Novel Oxide Materials Prepared by Bulk and Polymer Assisted Sol-Gel Method for Environmental Pollutant Remediation through Adsorptive and Visible Light Induced Photocatalytic Route

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In today's world, with energy and environmental concerns at the forefront of global issues, recent advancements in materials science & engineering have placed significant emphasis on the discovery of innovative, eco-friendly methods for energy generation, storage, and conservation. An intriguing domain within this field is visible light photocatalysis, which harnesses solar radiation to catalyse energy-demanding reactions, especially those involving the degradation of environmentally harmful substances. In my thesis work, I have explored the ways to improve adsorption and visible light induced photocatalytic activities in the novel metal oxides and their composites, targeting removal of hazardous chemicals from wastewater as a potential application. This thesis work involves synthesis and characterization of novel polymer-ceramic nanocomposite materials by sol-gel and electrospinning routes with potential application in adsorptive and visible light induced photocatalytic dye removal.

Oxide semiconductors are promising materials for applications targeting environmental remediation. In semiconducting material, electrons can be freed up from valence to conduction band under electromagnetic radiation, which in turn can trigger other chemical reaction. This makes them promising candidate materials for photocatalysis applications. Owing to the tunability in the band gap (e.g. by doping) and availability of multiple processing methods leading to different morphology, these materials has been successfully employed as photocatalytic as well as adsorptive materials.

Among such oxide semiconductors, ZnO and TiO_2 have been extensively studied for their outstanding physical, optical, and optoelectronic properties. These photocatalysts offer affordability, non-toxicity, eco-friendliness, and exhibit good chemical and thermal stability. Despite their recognition as photocatalysts, ZnO and TiO_2 exhibit significant inadequacies when considered in isolation, primarily due to the fast electron-hole pair recombination resulting from their wide band gap. Wide band gaps lying in UV region also prevent their use in visible light induced photocatalytic applications. This adversely affects the efficiency of the material in photocatalytic reactions. In this thesis we have prepared inhomogeneous and homogeneous materials from ZnO and TiO_2 and explored several approaches to modify and enhance the performance of these materials as photocatalysts and adsorbent materials. In the first approach we have prepared multi-layered thin films of ZnO and TiO_2 which result into partial formation of a zinc titanate crystalline phase at the interface after high temperature treatment.

In another approach, ZnO and TiO_2 sols are electrospun with a polymer. Earlier, it was reported by our lab that when used with PVA as the carrier polymer, this method yields rhombohedral zinc titanate (Rh-ZTO) nanoparticles with bandgap lying in the visible region. These nanoparticles were shown to enhance phenol degradation in presence of visible light. However, the method yields other impurity phases. These impurity phases not only cause reduction in photocatalytic efficiency, but also make the interpretation of data difficult. Therefore, to overcome this limitation, it is imperative to prepare samples with high purity. We have devised a way to prepare *one hundred percent pure* Rh-ZTO phase by using low molecular weight PVP as a carrier polymer. It has been found that increasing the polymer concentration so as to restrict the operation in electro*spraying* mode (so that spinning is prevented) systematically improves

purity. But as the polymer concentration is increased too high such that electro*spinning* mode sets in, the impurity fractions start to go up again. We propose a model that considers the physics of charge and multipole separation under inhomogeneous electric field as the possible reason behind this observation. In addition, the one hundred percent pure Rh-ZTO samples prepared by this method also show photocatalytic reduction of 4-nitrophenol (4-NP) under visible light illumination. Unlike previous photocatalytic reduction of 4-NP that required presence of additional reducing agent such as $NaBH_4$, the Rh-ZTO particles prepared by our method don't require any additional reducing agents. We propose that enhanced oxygen vacancies in the Rh-ZTO lead to photo-reduction of 4-NP.

In a third approach, we have prepared nanocomposites of ZTO with vanadium oxide to prepare an effective adsorbent material. A compound of vanadium is chosen because it is the closest transition metal to titanium exhibiting similar valence and octahedral coordination as titanium. We find that VZTO has much better adsorption towards the congo-red dye as compared to either vanadium oxide or the ZTO. The adsorption is attributed to the chemical affinity of vanadium towards nitrogen which, appears to be enhanced in presence of titanium.

As an alternative metal oxide, we have explored the bismuth ferrite (BFO), which is a multiferroic material with high Neel Temperature, for the adsorptive removal of dyes, as well as their use as an additive to oil well cement that enhances cement's compressive strength significantly.

Finally, we present a novel way to prepare silica (SiO_2, a non-metal oxide) particles using PDMS foam. We find that a mixture of these lab-prepared silica particles mixed with water and THF shows remarkably significant increase in steady shear viscosity as the water fraction in the mixture is increased at room temperature.

A brief introduction of the thesis chapters is given below.

Chapter 1: This section comprises an extensive introduction and literature review focused on metal oxide nanomaterials, specifically their potential application in the removal of organic pollutants from wastewater. In this chapter, we explore the versatile applications of semiconductor metal oxide nanomaterial, including their effectiveness in adsorption and visible light-induced photocatalytic degradation.

Chapter 2: It includes a list of chemicals used, various equipment employed, synthetic methods, and spectroscopic and microscopic characterizations techniques. These characterization techniques have been used in the data collection for the current research work. Furthermore, we have also discussed the experimental setup for adsorption and photocatalysis measurement activity.

Chapter 3: This chapter concerns primarily the development of morphology and crystalline phases in multilayer ZnO and TiO2 films on two glass and quartz substrates. In this chapter, we report that fabrication of multilayer films with alternate layers of zinc and titanium sols on glass and quartz, when prepared following two different protocols, shows significantly altered morphology after calcination. On glass, after calcination at 500°C, it showed a network of vertical walls with sharp as well as wrinkled boundaries. On quartz, upon calcination at 900°C,

it showed a flat polycrystalline films as well as vertically stacked crystallites. We conclude that the viscosity of the sols of the two oxides play an important role in influencing the observed morphology. Additionally, samples on quartz substrate showed formation of rhombohedral zinc-titanate due to higher temperature, and photocatalytic activity towards Methylene Blue (MB) dye degradation under visible light illumination.

Chapter 4: This chapter concerns improving the purity of the rhombohedral phase of zinc titanate prepared by sol-electropinning method. In this chapter, we demonstrate that when the PVP mixed ZTO sol is electrosprayed instead of electrospun, the phase purity improves, and as the concentration of PVP, the carrier polymer in the spinning precursor solution, is increased in the *electrospraying* mode, the powders obtained after calcination of the as-spun films become richer in the rhombohedral zinc titanate. 100% percent purity is achieved with PVP fraction of 31.25 wt%. Furthermore, we explore the application of the samples with 100% pure rhombohedral ZTO as a photocatalyst for treating 4-nitrophenol (4-NP), a very important environmental pollutant.

Chapter 5: In this chapter, we present preparation of a nanocomposite consisting of vanadium trioxide with different concentrations and zinc titanate (VZTO) prepared through an aqueous sol-gel route, which serves as a highly effective adsorbent for the removal of Congo red (CR) dye from aqueous solutions. The prepared composite samples showed adsorption up to 90% (of 500 ppm) of CR within 10 minutes. The adsorption data have been recorded and fit to various well-established theoretical models and interpreted. Weber-Morris's equation infers the film diffusion as a rate-controlling step in adsorption.

Chapter 6: This chapter presents a non-aqueous sol-gel synthesis of bismuth ferrite (BFO) particles in THF, DMF, and DMSO solvents, their subsequent utilization in adsorption of methylene blue, and a comparison of their adsorption efficiencies. XRD analysis revealed a mixture of primary rhombohedral and secondary orthorhombic phases in all solvents, with varying fractions. Adsorption efficiency followed the order: DMF < THF < DMSO, with DMSO based samples being the most efficient (96.54%). DMSO's higher refractive index and donicity improved solvation and sulfur incorporation during the sol-gel reaction, favoring enhanced adsorption. Analysis of adsorption kinetics indicated film-diffusion and intra-particle diffusion, with faster diffusion at higher dye concentrations. DMSO based samples also showed an excellent adsorption performance under high pH conditions.

Chapter 7: In this chapter, previously prepared DMSO based BFO NPs have been used as an additive in oil well cement to enhance the cement properties. With the addition of 1 % BWOC BFO NPs in the cement slurry, the HPHT fluid loss reduces to ~64% of the base slurry while the compressive strength improves by ~136% due to the formation of tricalcium silicate with higher crystallinity in presence of BFO NPs. Furthermore, it can be conjectured that the exposed facets of BFO containing oxygen act as nucleating sites that promote the ordering of the silicate tetrahedra thereby increasing the strength and crystallinity and reducing the water loss. Thus, the experimental results confirm that the BFO NPs have the ability to improve the properties of oil well cement slurry and can be used as an additive in cement for HPHT conditions.

Chapter 8: In this chapter, we report a simple technique to produce SiO_2 with two widely different morphologies, starting from the commercially available PDMS (Sylgard 184, Dow Chemicals). We first prepare PDMS sponge, and subsequently the sponge pieces are heat treated under two distinct conditions, resulting in SiO_2 materials with entirely different morphologies. In the first case we obtained a very soft powder whereas in the second case we obtain brittle SiO_2 particles. The BET surface area of brittle SiO_2 particles is much higher than the soft SiO_2 nanoparticles. These particles give stable suspensions when mixed with THF and water. The suspensions with brittle particles show higher viscosity for the same composition. Remarkably, the viscosity of these suspensions increase as the water fraction in the mixture in increased. However, the mixture can uniformly accommodate water up to about 30 wt%, after which phase separation occurs. The addition of 30 wt% DI water significantly increased viscosity, nearly 10 times for soft and 20 times for brittle SiO_2 particles compared to the water-free mixture.

Chapter 9: In this chapter, we bring our thesis work to a conclusion and outline some potential scope and suggestions for future work. Additionally, we provide a brief overview of ongoing research that remains incomplete.

Publication List

1. Processing induced morphology change in ZnO-TiO_2 multilayer thin films and its effect on their photocatalytic activity under visible light irradiation, *Journal of Materials Science and Engineering B,* 2022, 288 (116164): 9. **https://doi.org/10.1016/j.mseb.2022.116164**. **[IF: 4.01]**

2. Enhanced adsorption of methylene blue by mixed-phase bismuth ferrite prepared by non-aqueous sol-gel route, *Journal of Environmental Chemical Engineering, Volume 11, Issue 1, February* 2023, 109229*,* **https://doi.org/10.1016/j.jece.2022.109229**. **[IF: 7.969]**

3. Enhancing Oil Well Cement Properties with Synthesized Bismuth Ferrite Nanoparticles: A Performance Study, *Cement Concrete and Composite,* 2023. **(Under Review)**

4. PVP assisted sol-electrospraying, unlike sol electrospinning, yields highly pure rhombohedral zinc titanate particles that reduce 4-nitrophenol under visible light, *Journal of Alloys, and Compounds*, 2023. **(Accepted)**

5. SiO_2 particles prepared from PDMS foam/sponge with potential use as a viscosity enhancer. **(Under Submission)**

6. Enhanced adsorption of Congo Red dye using a Novel VZTO nanocomposite by aqueous sol-gel route: A highly efficient adsorbent **(Manuscript Under Preparation)**

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