

DEVELOPMENT OF FUNCTIONAL NANOSTRUCTURES FOR SENSITIVE DETECTION OF ANALYTES IN COMPLEX FLUIDS

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ABSTRACT

The development of functional nanostructured materials, which show unique and versatile characteristics, is highly desirable for important applications, such as catalysis and solar cells. In this review, we first summarize our recent studies on the synthesis of nanohybrid catalysts (such as bimetallic and binary metal oxide nanostructures) and their catalytic behavior in diverse catalytic reactions. We then present our recent developments on plasmonic nanostructures (Au and Ag), and demonstrate and discuss how they may be explored for enhancing photocatalysis and solar cell performance. Subsequently, we describe our work on the synthesis of semiconductor nanocrystals, also known as quantum dots, and their application in solar cells. Besides traditional wet chemical method, we also introduce an alternative, physical method, pulsed laser ablation, toward synthesizing these nanostructures with a unique "bare and clean" surface, highly relevant to catalytic, plasmonic and photovoltaic applications. Finally, perspectives on future advances of nanostructured catalytic and plasmonic materials as well as quantum dots are outlined. Hormones, which are complex biomolecules, play a vital role in various biochemical pathways and the growth of animals. Recently, we have developed a novel family of functionalized nanostructures that exhibit liquid-like behavior in the absence of solvents and preserve their nanostructure in the liquid state. The gallery of nanostructures developed so far includes functionalized silica and magnetic iron oxide nanoparticles.

Keywords: functional nanostructured, semiconductor nanocrystals, nanostructured catalytic, nanohybrid catalysts

INTRODUCTION

Functional nanomaterials involve various nanostructured objects, such as zero-

dimensional (0D), 1D, and 2D nano-objects (nanoparticles, nanowires, nanotubes, nano sheets, etc.), as well as materials with nanostructured surfaces, including metals, semiconductors, and organic materials. These nanomaterials possess a high surface/volume ratio, as well as nano tip- and nano gap-induced physical effects, which lead to functional properties that significantly differ from the nanomaterials' bulk properties and hence afford them with great potential applications in sensing and detection. These functional nanomaterials for sensing and detection are mostly used as transducers in devices such as spectral devices, chemiresistive sensors, and photo detection devices. They are also employed, in the design of nano sensors, as capture agents (e.g., magnetic nanoparticles) and signal amplifiers (plasmonic metals with nano patterned surfaces for surface-enhanced Raman scattering (SERS) chips), as well as identification elements (polymers for molecular imprinting), in addition to other applications. This Special Issue covers the latest advances in the field of these functional nanomaterials for sensing and detection. Functionalized nanomaterials (NM) are of increasing industrial and economic importance in the life sciences and the health sector as well as for applications in nano (bio) technology, optical and sensor technologies, solid state lighting and photo voltaics, as well as opto-

electronic and electronic devices and security applications. Nowadays, NM are used as catalysts, hydrogen storage and energy conversion materials, contrast agents and drug carriers for imaging and therapy in medicine, signal-generating reporters in bio analysis, molecular diagnostics and sensing, as additives for food and cosmetics, in textile industry, and as phosphors for lighting and display technologies. The growing field of nanotechnology impacts many research areas, such as engineer-ing, electronics, energy, environment, biology, and medicine. "Nanotechnology" is the discipline that deals with nanomaterials: the materials whose dimensions are smaller Furthermore, it explores the integration of nanostructures with electrochemical systems in economically significant and future applications, along with the challenges faced by nanotechnology-based industries. The paper also explores the interplay between nanomaterials and biosensors, which play a vital role in electrochemical devices. Overall, this review provides a comprehensive overview of the significance of nanomaterials in the development of cost-effective electrochemical devices for energy storage and conversion. It highlights the need for further research in this rapidly evolving field and serves as a valuable resource for researchers and engineers interested in the latest advancements in nanomaterials for electrochemical devices.

Fluids that display a non-linear behaviors are complex fluids. Various biological structures can be assimilated to complex fluids: DNA, proteins, cells, dispersions of biopolymers and cells, human blood, colloidal fluids, suspensions, gels,

emulsions, micellar and liquid-crystal phases etc. Particle dynamics in complex fluids is nonlinear. Also, the stress of a biological fluid, unlike the Newtonian fluid, depends not only on the actually stress applied, but on the one applied during previous deformation of the fluid.¹²Complex fluids are a very favorable medium for the appearance of instabilities that imply both chaos and self-structuring through generation of ordered complex structures.

LITERATURE REVIEW

Laxmikarthika V. Srinivasan [2024] Nanoparticles (NPs) are particles with unique features that have been used in a variety of fields, including healthcare, farming, and the food industry. Recent research has shown many possible uses for nanoparticles, including gas sensors, waste management, food preservation, high-temperature superconductors, field emission emitters, food processing, food packaging, and agriculture. Nanoparticles application is connected with the nutritive, coating, and sensory properties of food compounds. Nanoparticles have shown specific anticancer, antibacterial, antioxidant activity, and making them an attractive tool for biomedical applications. Because of their extraordinary mechanical, magnetic, electric, thermal, and electric capabilities, some nanoparticles are more important than others. Numerous nanoparticles have been used in the sectors of agriculture, industry, the environment, medicine, sensors, fungicidal, nematicidal therapy, catalysis, and color degradation.

Junzheng Wang et al (2022) by simply adjusting the temperature and the number of materials, rod-like ZnO with different morphology, such as ZnO nano needles,

were synthesized by a flexible thermal evaporation method. The ZnO nano rod array has the lowest turn-on field, the highest current density, and the highest emission efficiency due to its good contact with the substrate and relatively weak field shielding effect. Experiments show that the morphology and orientation of one-dimensional ZnO nanomaterials have a great influence on its conduction field and emission current density, and the nano arrays also contribute to electron emission. The research results have a certain reference value for the application of ZnO nano rod arrays as cathode materials for field emission devices.

S. Akilandeswari et al (2021) nonlinear optical single crystal of Serine Succinate (SSA) was grown from a mixed solvent of water, ethanol and methanol. Since amino acid exhibits nonlinear optical property, it is of interest to dope them in serine. The overwhelming success of molecular engineering in controlling nonlinear optical properties in last decade has prompted better initiative in crystal engineering. In the present study single crystals of serine doped with succinic acid in different ratios have been grown by slow evaporation solution growth method. Grown serine succinate crystals were subjected to various characterization techniques. The cell parameters of the grown crystals were characterized by X-ray diffraction analysis. FT-Raman spectral studies were carried out on the SAA grown material to confirm the synthesized compound and the functional groups of serine succinate single crystal were identified from FTIR analysis.

Rui Su [2020] At present, people are paying more and more attention to the accuracy, convenience, and efficiency of

food quality and safety testing. However, many traditional detection methods have some problems such as inconvenient operation, interference factors, and long detection time. Therefore, functionalized magnetic nanomaterials with higher selectivity and sensitivity are widely used in food detection, such as pesticides, veterinary drugs, heavy metals, additives, and synthetic pigments, pathogenic bacteria, and mycotoxins. In this paper, the practical application of functionalized magnetic nanomaterials and their related detection technologies are reviewed, and their future development direction is discussed. Functional magnetic nanomaterials can solve some problems that exist in magnetic nanomaterials to a great extent, making detection more efficient, economical, accurate, rapid and convenient.

Applications of functional thin films and nanostructure based sensors

Due to increasing demand for sensors in new applications, innovative methods for sensor technologies are pursued where nanotechnology could offer one of the most outstanding influences on the basis of small sensor size, inexpensive, high efficiency, stability, and short sensor response time. The utilization of nanostructured materials with modified or functionalized surfaces is anticipated to enhance a greater sensitivity and selectivity as the case in biosensing applications. Recently, the nanostructured material characteristics become the cornerstone of the construction of innovative nano sensors. Nanoparticles in organic coated thin films generally can convert the physical and chemical quantity either into optical or electrical changes. Some semiconductor

nanoparticles synthesized in solution show optical chemical sensing ability. They are applied for optical sensing. One example is the CdS nanoparticles, which show photochemical properties when adsorbed onto the surface under illumination

Nanowires and nanorods

Nanowires and nanorods are optically active. The optical properties are closely related to electrical and electronic properties. The optical measurements are helping to understand the bandage and the electronic properties of them. Quantum confinements play an inevitable role in the optical properties of nanomaterials. When the nanorods are excited by electromagnetic radiation, they give rise to longitudinal and transverse surface plasmon absorption peaks. The peaks represent the collective oscillation of the quasifree electrons along with the long and short axes. Based on the peaks by different nanorods, their application in various optical fields will be fixed. They give the photo luminescent spectra and their characterization is done using microscopic techniques.

Analyte-mediated formation of nanomaterials

The interaction of the analyte with the precursor materials that constitute the building block of nanoparticles (such as metal ions, carbon materials, etc.), before the formation of nanoparticles, typically involves complexation or redox reactions that yield new reaction products with different properties. Depending on these properties, the yield and the kinetics of the nanoparticle formation reactions may be augmented or inhibited. In either case, the properties of the nanoparticles (such as size, shape, catalytic activity, etc.) when the reactions reach completion differ with

increasing analyte concentration enabling their detection and determination in real samples by monitoring and comparing the optical, electrochemical, or catalytic transitions of the nanomaterial solutions in the presence and absence of the target analyte(s).

Ceramic nanomaterials

Ceramic nanomaterials are small solid particles composed of inorganic and non-metallic materials. It is produced by heat treatment and cooled in specific methods to obtain certain physical and chemical properties. Ceramic nanomaterials are characterized by different shapes and sizes, amorphous, and polycrystalline, with good porosity, high density, and heat resistance. Ceramic nanomaterials are utilized in numerous uses like chemical catalysts, photo catalysts, battery manufacturing, coating materials, photo-analysis of dyes, and imaging fields.

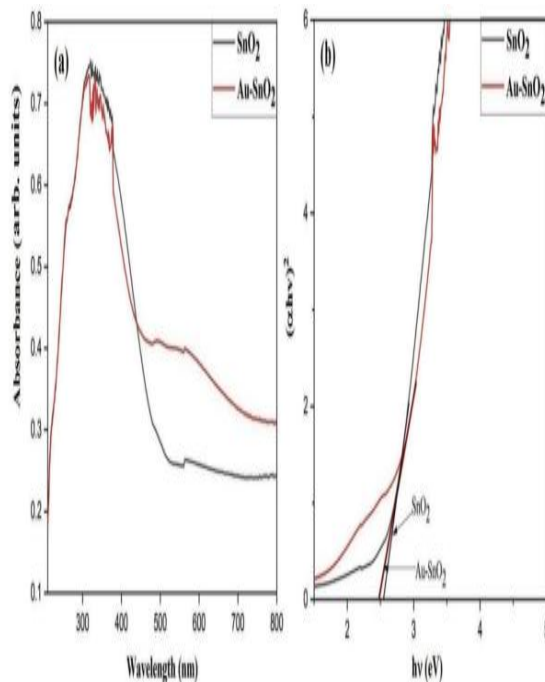
METHODOLOGY

This Trans disciplinary approach to nanoparticle synthesis requires that biologists and biotechnologists understand and learn to use the complex methodology needed to properly characterize these processes. This review targets a bio-oriented audience and summarizes the physico-chemical properties of nanoparticles, and methods used for their characterization. It highlights why nanomaterials are different compared to micro- or bulk materials. We try to provide a comprehensive overview of the different classes of nanoparticles and their novel or enhanced physicochemical properties including mechanical, thermal, magnetic, electronic, optical, and catalytic properties. A comprehensive list of the common methods and techniques used for the

characterization and analysis of these properties is presented together with a large list of examples for biogenic nanoparticles that have been previously synthesized and characterized, including their application in the fields of medicine, electronics, agriculture, and food production. We hope that this makes the many different methods more accessible to the readers, and to help with identifying the proper methodology for any given nanoscience problem.

RESULTS & DISCUSSIONS

A study of the UV-Vis spectrum of the produced nanoparticles was carried out to determine their optical absorption characteristics. The absorbance spectra of SnO₂ and Au-SnO₂ nanoparticles are shown in Graph 1 (a) and (b).

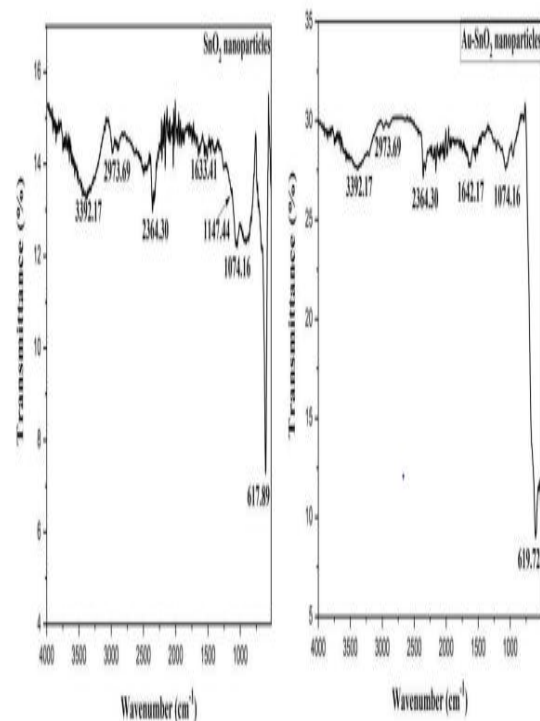


Graph 1: (a) Absorbance spectra and (b) Tauc plot, of pure SnO₂ and Au-SnO₂ nanoparticles.

The modification is produced by either the local disorder or the s, p, and d hybridization. Direct type optical transitions are seen in SnO₂. Optical band

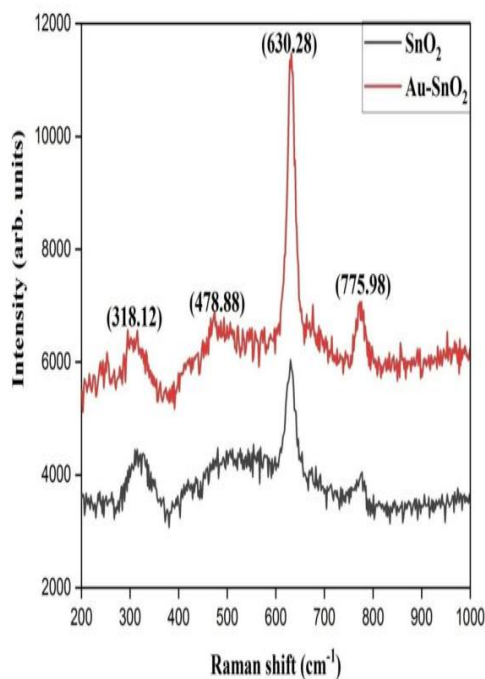
gap (Graph 1 (b)) was computed by plotting $(\alpha h\nu)^2$ against the photon energy $h\nu$ and using Tauc's relation.

FTIR analysis was used to determine the bonding vibration of the produced nanoparticles. A Fourier transform infrared spectrum (Graph 2) was acquired in the wavelength range 400-4000 cm⁻¹. The transmittance peaks between 400 and 900 cm⁻¹, more precisely at 617.89 cm⁻¹, are attributed to the Sn-O-Sn vibrations. The existence of such vibrations established that SnO₂ had been synthesized. However, in synthesized AuSnO₂ nanoparticles, a shift in intensity about 619 cm⁻¹ was detected, which might be attributed to a lack of either Sn or oxygen as a result of their movement to the interstitial position. The formation of Au-O-Sn bonds and the doped samples' small size in comparison to pure SnO₂ may explain the minor change in peak shift observed for AuSnO₂ nanoparticles.



Graph 2: FTIR of pure SnO₂ and Au-SnO₂ nanoparticles.

The A_{2u} (singlet) and E_u (triply degenerated) modes are IR active, whereas the other modes are not. The Raman scattering spectra of pure SnO₂ and Au-SnO₂ nanoparticles are shown in Graph 3. The peak occurring at 478.88 cm⁻¹ belongs to the E_g mode, which is caused by the vibration of oxide ions. The A_{1g} and B_{2g} vibrations are represented by the peaks at 630.28 cm⁻¹ and 775.98 cm⁻¹, respectively, in the spectrum. These modes correspond to the stretching of Sn-O bonds in both symmetric and asymmetric directions, which resulted in the effective confirmation of the tetragonal rutile structure of SnO₂.



Graph 3: Raman spectra of pure SnO₂ and Au-SnO₂ nanoparticles.

CONCLUSION

Functional nanostructures exhibit outstanding analytical features for the analysis of animal hormones. Their unique surface chemistry, optical properties and tunable structures/properties make them good candidates for the analysis of animal hormones in various samples via electrochemical, colorimetric and

fluorescence techniques, respectively. Importantly, the integration of nanostructure materials with unique surface chemistry and optical and electrochemical properties with electrochemical, fluorescence and colorimetric techniques not only improved the analytical features (higher sensitivity and selectivity) but also reduced the sample volume and minimized the sample preparation. However, despite the remarkable progress in functional nanostructures for the analysis of animal hormones, these developed analytical strategies still face some issues, which To realize the use of surface-modified nanostructured materials as probes, efforts need to be devoted to the ligand chemistry of nanostructured materials with good reproducibility, there by offering their extended use in validating devices for the analysis of animal hormones for real-world applications. Finally, we anticipate that functionalized nanostructured materials will show significant improvements in the development of miniaturized analytical devices for the detection of multiple animal hormones in the near future.

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