



Synthesis of Green nano-composites: Engineering Applications

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ABSTRACT

Novel functionalized nanoparticles (NPs) have attracted much attention in catalysis, sensing, and electronics, as a result of their ultrahigh activity for surface reactions. For reliable employment of M-NPs in various applications, green synthetic methods for the erection of aggregated functional M-NCs with diameters less than a few nanometers are needed. The M-NCs will be prepared by green methods such as hydrothermal and phytochemical. The nanocomposites will characterize with different spectroscopic and microscopic techniques such as FTIR, BET, TG-DTA, UV-Visible, TEM, EDAX, Scanning electron microscopy (SEM) and X-ray diffraction analysis. The size and growth rate of the trimetallic nanocomposites can be changed by capping agent, and those composites' shapes are found based on selected area electron diffraction (SAED) and transmission electron microscope (TEM) data. Effectual produced MNCs have a high aptitude for stability and sensitivity to gas sensors and other applications.

Herein, other author's present functional assemblies of ultra-small capped and reduced M-NCs produced within high stability and sensitivity. Meticulously, M-NCs can be readily generated with precision dimensional control down to 1 nm. These NPs with porous polymers display superior hydrogen (H₂) sensing properties at room temperature in air. By following green methodologies, we are expecting to produce highly efficient sustainable and eco-friendly sensors for hydrogen, chemical, optical and electrical sensors. Compared with traditional methods, noble nanoparticle-based colorimetry possesses high sensitivity, and it does not need expensive equipment, and are simple. Due to their unique optical properties, narrow size distributions, and good biological affinity, gold nanoparticles and other noble nanoparticles (Ag, Pt, Pd) have been widely applied in sensing analysis, catalytic, environmental monitoring, and disease therapy. These properties are often used in the detection of hazardous chemicals, such as pesticide residues, heavy metals, banned additives, and biotoxins, in food. As author mentioned above, because the gold nanoparticles-colorimetric sensing strategy is simple, quick, and sensitive, this method has extensive applications in real-time on-site monitoring and rapid testing of food quality and safety. Herein, we propose the preparation methods, functional modification, photochemical properties, and applications of metallic nanocomposites with noble metals and other sensible nanoparticle sensors in rapid testing. In addition, we would like elaborate on the colorimetric sensing mechanisms. Finally, we will investigate the advantages and disadvantages of colorimetric sensors based on noble nanoparticles, and directions for future development.

KEY WORDS: Nano composites, Green methods, Eco-friendly, Capping agent



INTRODUCTION

GAS SENSING

Gas sensors are commonly understood to provide a measurement of the concentration of an analyte of interest, such as CO, CO₂, NO_x, or SO₂, without delving into the numerous underlying approaches, such as optical absorption, electrical conductivity, electrochemical, and catalytic bead.

Gas sensors measure simple physical properties of the ambient environment such as temperature, pressure, flow, thermal conductivity and specific heat, or more complex properties such as calorific value, super compressibility and octane number of gaseous fuels. The latter may require destructive testing, such as by capital-intensive (engine) or combustion, or involve measuring a large number of parameters that serve as correlation inputs to complex properties of interest.

We are going to discuss about Hydrogen gas sensors and its methods as hydrogen is used abundantly in various industrial and space related applications, therefore definitely showed how to strictly manage clean energy demands of the world. As hydrogen gas has high energy density, becomes explosive when concentration exceeds 4%. Therefore, the production, storage and transportation of hydrogen gas become very risky. Hence, it is essential to monitor the concentration level of hydrogen gas to avoid any hazardous situation. To monitor the traces of hydrogen concentration, analytical instruments such as IR spectroscopy, chemiluminescence spectrometer, UV adsorption spectroscope and gas chromatography columns have been used abundantly. There are some limitations like large size and weight, high cost, time consuming process, etc.

To restrict from above limitations, sensor development technology based on metal-oxide semiconductors have emerged as a light weight, cost effective, fast, sensitive, and simple detection method. The materials mostly used in metal oxide semiconductor are Zinc oxide (ZnO), Titanium dioxide (TiO₂), Tin oxide (SnO₂), Tungsten oxide (WO₃), Vanadium pentoxide (V₂O₅), and Iron oxide (Fe₂O₃) etc. and also carbon based materials such as grapheme oxide (GO) and CNT for sensitive detection.

Sensor performance by using different elements have enhanced in recent times which includes sensitivity and selectivity towards different types of gases, low response and recovery times of the sensing element, low operating temperature at which sensing may be carried out, and low power utilization etc. The methods used for performance enhancement includes light assisted sensing, doping of metal nanoparticles with MOS, and making composite with carbon based materials.



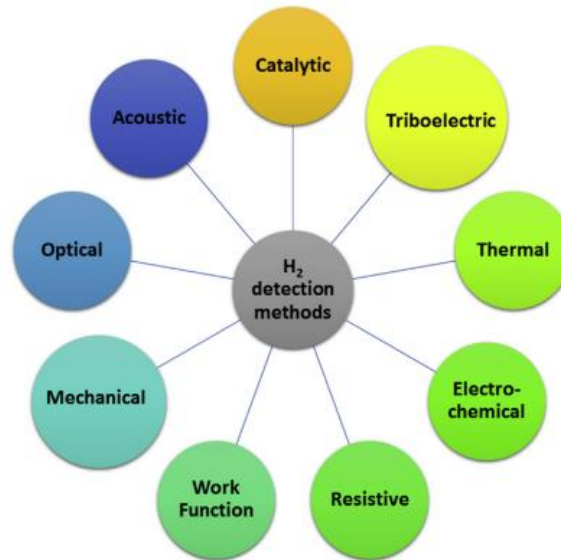
The polymer based chemiresistive sensors are also found suitable for H₂ gas sensing applications like TiO₂ decorated PANI thin films, indium doped ZnO, etc.,. Some of the biological entities such as bacteria *Rhodobactercapsulatus* can also be used as H₂ sensing medium through fluorescent response, this is done by detecting H₂ production by algae. As the hydrogen gas is also used in radioactive environment and requires very developed monitoring system to avoid any catastrophic disaster, gamma ray irradiation on H₂ gas sensing property of Pd-SnO₂ thin films is studied by Duy et al and similarly, Reddepp et al. added reduced graphene oxide (rGO) with GaNnanorods and used the nanocomposite material for the detection of H₂ gas under UV light illumination

The hydrogen sensors are being redesigned continuously with various performance improvements over past several years. The present technological scenario has now geared to sensing of extremely trace (ppb) level leakage detection of hydrogen gas. Hydrogen gas molecules leak through very small cracks and holes with high flow rate due to its smaller size. The concentration of the H₂ gas can reach to the explosive limit in no time. Hence, the H₂ gas monitoring is essential in various industrial applications to avoid any loss of money and human life. The requirements for a reliable hydrogen gas sensor can be summarised as follows:

- i. The sensor should indicate low to moderate level of gas concentrations (0.01-10%).
- ii. The sensor should detect the gases with precision and accuracy.
- iii. The interference of humidity and other gases should be minimum.
- iv. It should work properly even at unfavourable operating conditions such as: high pressure, temperature, gas flow rate etc.
- v. The signal given by sensors should have a low overall noise.
- vi. The response and recovery times should be less (<5s)
- vii. Fabrication and maintenance cost should be less.
- viii. The sensor should be small and compact

H₂ SENSING TECHNOLOGIES/METHODS

Generally, gas sensors are used to measure the leakages of a particular gas in the vicinity of its storage tank, transport pipes, and working area. However, the hydrogen gas sensors are required to trace very small leakages (~ppb level leakages) because of the explosive behaviour of hydrogen gas itself. The H₂ gas sensing technology utilizes various methods where a specific property of a sensing element changes in presence of H₂ gas.



Schematic diagram representing the methods of detection for hydrogen sensing

MATERIALS FOR HYDROGEN GAS DETECTION

A variety of materials and material systems have been used for hydrogen gas sensing. The selection criteria for material for gas sensing application are primarily the material specific physical, chemical, electrical, and optical properties. To simplify the understanding of these materials, we have classified them into following four different categories:

- i. Metals
- ii. Metal oxide semiconducting materials (MOS)
- iii. Carbon based materials
- iv. Polymers

Parts per billion (ppb) level hydrogen gas detection

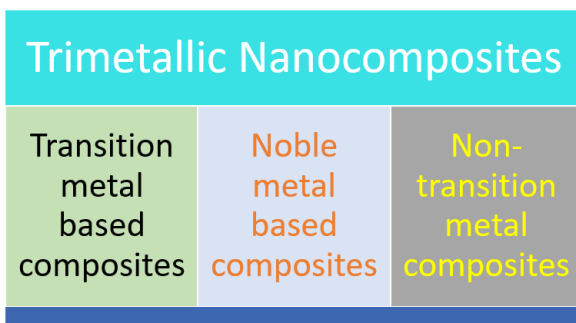
The detection of H₂ gas leakage at ppb level is very important due to following reasons:

- i. The small molecular size of H₂ allows it to leak through the small holes and cracks.
- ii. Due to fast leakage, it will not take much time to reach the explosive concentration level.
- iii. Early detection of the H₂ gas leakage at ppb level is important, so that safety measures can be taken on time.



To avoid any damage to human and machinery the explosive gases should be detected as early as possible and at lowest possible concentrations

2. OBJECTIVE:



- A) Synthesis of Trimetallicnanocomposites (TMNCs) from green methodologies.
- B) Characterization of synthesized TMNCs with different spectroscopic and microscopic .
- C) Highly selective, detective and LOD nano composites for better sensing applications such as hydrogen gas, electrochemical sensing.

3. BACKGROUND:

Additionally, they may allow the shrinking of nanometer-sized sensors and gadgets (nanosensors and nanobiosensors) in order to achieve higher sensitivity, greater specificity, and faster identification rates than possible with existing technologies. Nanomaterials' morphology and size are typically related to their chemical, electrical, and optical properties. Intriguing analytical uses for a wide range of nanostructures have been documented in the literature. These include metal oxide nanowires, organic and inorganic nanotubes, nanoparticles, and nanowires. Due to their biocompatibility and technologically significant combination of properties, such as high surface area, good electrical properties, and chemical stability, these materials have offered promising building blocks for the realization of nanoscale electrochemical biosensors. Due to the ease with which the material and the transduction system may be miniaturised, the incorporation of nanomaterials in electrochemical devices opens the door to the development of portable, simple-to-use, and inexpensive sensors. This field has been thoroughly studied and a tonne of articles have been published in the previous ten years. Wei-Han Hsiao et.al, designed two silver nanostructured sensors for H_2O_2 based on urchin-like Ag NWs and Ag NPs.



Nanotechnology is a crucial field for electrochemical, optical, and mass sensitive sensors. Nanomaterials are employed as efficient catalytic tools for electron transfer, immobilisation platforms, as well as electroactive and optical labels to boost the sensing performance in terms of high sensitivity, specificity, and stability. Nanomaterials or nanoparticles such as carbon nanotubes, metal nanoparticles (Au, Pt, and Pd, etc.), nanowires, quantum dots, and hybrid nanocomposites play a crucial role in the development of various sensing systems for the detection of foodborne pathogens.

This paragraph highlights the previous work done on different sensing materials like optical, chemical and bio sensors. There are several publications on this area, but eco-friendly methodologies are few as per our knowledge concern. The author would like to project on methodologies in the synthesis part to develop high sensitive sensors as well as economic sensors for industrial and domestic problems. The aim of the work is to prepare trimetallic composites for the betterment of society. Trimetallic hybrid nanoflower-decorated MoS₂nanosheet-modified sensor for in situ monitoring of H₂O₂ secreted from live MCF-7 cancer cells, Baoting Dou et.al. The Au-Pd-Pt nanoflower-dispersed MoS₂nanosheets are synthesized by a simple wet-chemistry method, and the resulting nanosheet composites exhibit significantly enhanced catalytic activity toward electrochemical reduction of H₂O₂, due to the synergistic effect of the highly dispersed trimetallic hybrid nanoflowers and the MoS₂nanosheets, thereby resulting in ultra-sensitive detection of H₂O₂ with a sub-nanomolar level detection limit in vitro. The literature reveals the preparation of trimetallic NPs as Sn-Zn-Cu Roshanghias, A et.al, (2016), Pt₆₀Ni₃Cu₃₇, Lan, J. et.al (2019), Au-Pt-Pd Dong et.al, (2018), and Au-Pt-Ag Yadav, N. et.al (2018). Pd-Cu-Au trimetallic nanoparticles with good stability were produced using a straightforward one-pot process, and due to their special optical properties, they showed promise as temperature sensors for sensitively detecting variations in fluorescence intensity, Nie, F et.al (2018). In another work, the ascorbic acid, dopamine, acetaminophen, and tryptophan concentrations were simultaneously determined using a nanocomposite sensor (based on Au-Ag-Pd NPs) that was evenly capped by electro-pre-treated GO, Abdelwahab, A.A et.al, (2020). Green synthesis refers to the fabrication of nanoparticles employing plant extracts as potential capping and reducing agents. The properties of the synthesised nanoparticles can be influenced by plant extracts from the leaves, fruit, roots, and seeds in order to improve their functionality for sensing and biological applications. Aisida SO et.al, 2020.

4. SIGNIFICANCE:

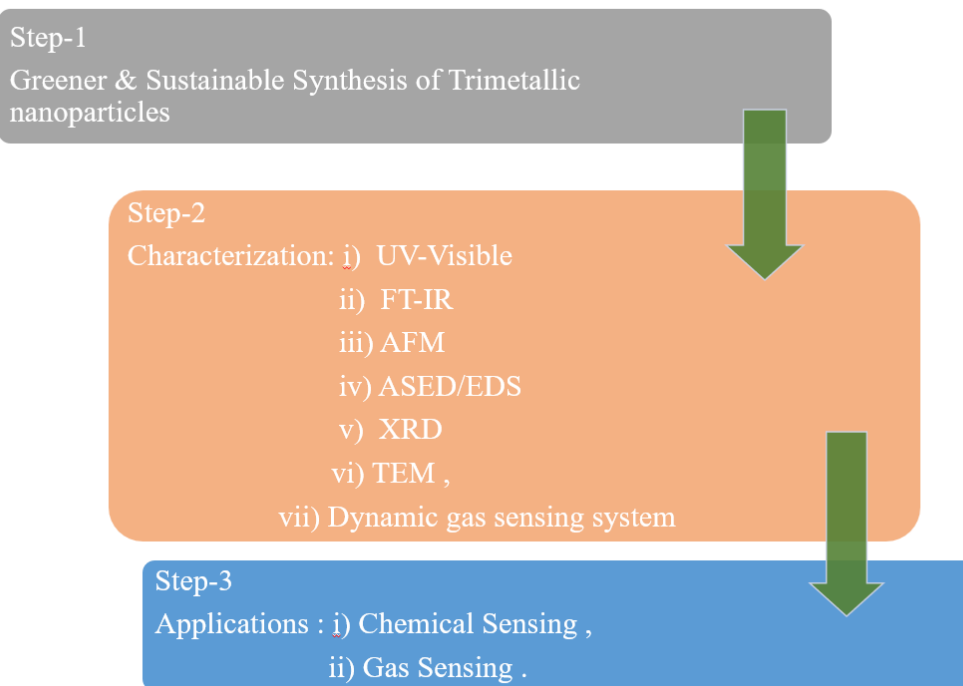
- Green synthesized trimetallic nanocomposites are easy to fabricate and they possess high sensitivity to electrical and optical sensitivity.
- The created trimetallic nanocomposites with high electronic conductivity, high surface area, and great detection sensitivity.
- Synthetic techniques to enhance improved sensitivity and detection capacity.



- The suggested sensor shows outstanding capabilities when compared to other analytical methods, including low limit of detection, wide linear range, excellent sensitivity and selectivity, good repeatability, high stability, and excellent recovery rates.
- Compared to monometallic NPs, transition bi- and trimetallic NPs display higher catalytic selectivity/activity/sensitivity and excellent efficiency in numerous applications.
- Gas sensors and biosensors are essential in human health hazards and Industrial disasters, because gas leakages are threat for human life and economy of our country. To avoid health complications and anthropological problems, we need to detect early diseases and gas leakages at the industry and household areas.

5. PLAN:

The preparation of leaf extract capped trimetallic core-shell-structured NPs comprising one metal is core, second is inner layer, and outer shell of nanoporous third metal. Nano-sized Trimetallic crystalline particles are synthesized by hydrothermal and sol-gel methods at suitable temperature in which leaf extract used as capping and reducing agent. The morphology of synthesized nanoparticles is examined by Scanning electron microscopy and X-ray diffraction analysis. Size and growth rate of the trimetallic nanoparticles can be changed by capping agent, and those particles shape is find based on selected area electron diffraction (SAED) and transmission electron microscope data. These capping/stabilizing agents play a key role in altering the sensing activities and environmental perspective. During the synthesis process to control the influence of precursors like pH, precursors, mixing ratio, reaction time, concentration, reaction temperature, reducing and stabilizing/capping agents. In the characterization part, Hydrogen sensing system is present with UGC faculty Dr. K. Suresh (Inorganic chemistry department). He is working in the same field; we have done few projects with him. Dynamic gas sensing system is available in our university. As we are doing projects from IIT Guwahati under INUP programme in the department of Nano technology. We have done few projects and MOU. The author and supervisor had very good collaboration with gas sensing experts (Dr. K. Suresh) and IITG Nanotechnology, we can do work very confidently without doubt.



6. APPROACH/METHODOLOGY:

There are different synthetic strategies for the preparation, characterization and applications. Among them we would like to choose phytochemical method for the synthesis of Nnanocomposites. Eco-friendly methods will be followed in this proposal.

Multimetallic NPs can be produced using a variety of synthetic methods, including electrochemical, chemical, and hydrothermal synthesis, coprecipitation, microemulsion, laser ablation, sol-gel, lithography, gas-phase condensation, microwave irradiation, mechanical alloying, and solvothermal technologies. Some of these synthetic methods may have some drawbacks, namely the use of potentially hazardous reducing/capping agents (e.g., hydrazine and poly-N-vinylpyrrolidone) and toxic solvents. Additionally, the conventional physicochemical procedures entail time consuming, expensive/special equipment requiring high energy, pressure, and temperature, culminating in the formation of toxic by-products/wastes and hazardous materials.

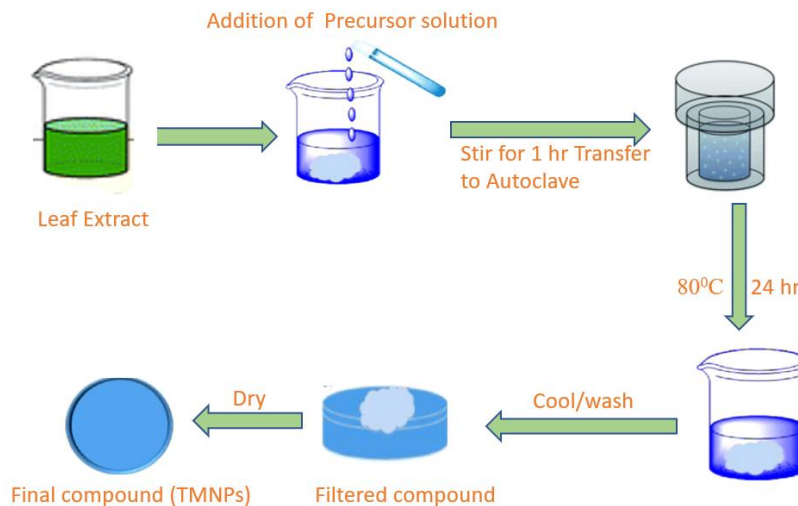
Therefore, the design of greener and sustainable synthetic routes is preferred since they are safe, environmentally salubrious, and often cost-effective. Here author prepared to the following two methods for the synthesis of transition trimetallicnanocomposites.



GREEN SYNTHESIS:

a) Hydrothermal Method

Hydrothermal method is a unique technique for trimetallicnanocomposites from high temperature aqueous solution at high vapour pressure. The employed surfactant-free hydrothermal method for the sensing element synthesis is found to be efficient in yielding hierarchical nanoarchitectures.

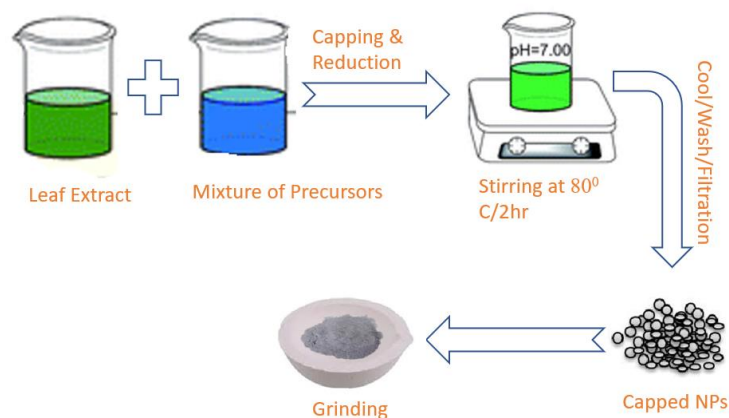


Schematic diagram of Hydrothermal method

The research community concentrated on creating heterostructures using the hydrothermal approach in a substantial percentage of the publications that were examined.

b) Phytochemical Synthesis

Green synthesis refers to the fabrication of nanoparticles employing plant extracts as potential capping and reducing agents.



Schematic diagram of Phytochemical Synthesis

CONCLUSION

This is an environmentally friendly method presenting a different way of thinking in chemistry intended to eliminate toxic waste, reduce energy consumption, and use ecological solvents (water, ethanol, ethyl acetate, etc.). However, these methods are preferred due to their eco-friendly, clean, safe, cost-effective, easy, and effective sources for high productivity and purity.

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