

NANOTECHNOLOGY IN QUALITY CONTROL: USING NANOMATERIALS TO DEVELOP NEW, HIGHLY SENSITIVE SENSORS FOR DETECTING CONTAMINANTS IN FUELS

Ensuring fuel purity is critical for engine performance, emissions control, and the longevity of industrial systems. Many traditional methods such as chromatography and bulk electrochemical probes require high energy, extensive sample preparation, and sophisticated instrumentation. These conventional techniques face limitations in portability and are not suitable for real-time monitoring. Nanomaterials can enhance sensor performance due to its large surface area, quantum confinement and tunable electronic structures, and their plasmonic enhancement.

Introduction

Nanotechnology is the engineering and manipulation of matter at the atomic or molecular scale, and materials exhibit unique physical, chemical, and optical properties which allow for stronger, lighter, and more conductive materials. Many nanotechnology techniques such as Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), top-down fabrication (nanolithography), and bottom-up assembly (chemical vapor deposition) are used to create advanced electronics and specialized nanomaterials. In the fuel industry, nanotechnology has been used to enhance oil and gas recovery, improve drilling efficiency, optimize refining, and develop advanced fuel cells [1]. Nanomaterial enabled sensors consist of three components: a nanomaterial, a recognition element that provides specificity, and a signal transduction method that provides a means of relaying the presence of the analyte [2]. Sensors can be designed to detect a single analyte or multiple analytes, and some sensors are based on a 'turn-off' or 'on/off' mechanism where a decrease in signal indicates the presence of the analyte. Nanomaterials have enabled advances in sensor design such as miniaturization, portability, and rapid signal response times. Nanoparticles possess an extremely high surface area to volume ratios compared to bulk materials, and facile surface functionalization cause nanomaterials to be highly sensitive to changes and allows nanosensors to achieve low detection limits.

Various Types of Nanomaterials and Detection Mechanisms

Carbon-Based Nanomaterials

Graphene oxide and carbon nanotubes (CNTs) offer high sensitivity for detecting volatile organic compounds and pollutants. Carbon-based nanomaterials have been used to increase the sensitivity of glassy carbon electrodes (GCE) for electrochemical sensing. Graphene has also been used for fluorescence quenching, and are highly effective in fuel sensors due to their large surface area, high electrical conductivity, and flexibility. Their high electron mobility allows rapid transduction of chemical interactions into measurable electrical signals.

Metal and Metal Oxide Nanoparticles

Transition metal oxides are used in chemiresistors for high-performance gas sensing. Nanostructured ZnO, SnO₂, TiO₂, and noble metals like Au, Ag, and Pt, exhibit strong catalytic activity and selective adsorption. Metal-oxide nanowires and nanoparticles possess high sensitivity and tunable surface chemistry, making them suitable for real-time fuel monitoring. Colloidal solutions of gold and silver nanoparticles (AuNP and AgNP, respectively) exhibit unique colors based on the size of the nanomaterial [2]. AuNPs have been used for fabrication of miniaturized optical devices, sensors, and photonic circuits [4]. AuNPs have strong surface plasmon resonance (SPR) absorption with extremely high extinction coefficients in the visible wavelength. The SPR frequency of AuNPs changes dramatically upon varying the refractive index of the local environment or the average distances between AuNPs.

AuNPs appear red when the spheres are in the 5-50 nm range, but appear purple as the size increase towards the 100 nm range. Researchers and scientist use this property in visual colorimetric sensors where the presence of analyte cause small nanoparticles to aggregate and the

solution to appear a certain color [2]. In addition, the systems based on analyte-induced aggregation of AuNPs have been employed for the colorimetric detection of cells, viruses, nucleic acids, proteins, small molecules, and metal ions. AuNPs can be conveniently produced in sizes ranging from 3 to 100 nm in diameter. It can be synthesized through chemical reduction methodologies such as the seeding-growth method, the Turkevich method, green synthesis, the ascorbic acid synthesis, etc. The Turkevich method is a foundational, widely used chemical technique developed in the 1950s through reducing chloroauric acid with sodium citrate in boiling water. The citrate will act as both a reducing agent and capping agent, providing stability against aggregation.

Lun and Xu [6] conducted a study using metal oxide nanocluster functionalized Gallium Nitride (GaN) sensors to realize the sensing of NO₂ molecules. Nanoclusters have developed well in the research and manufacture of gas sensors because of their rich characteristics, such as light stability, excellent biocompatibility, light induced fluorescence and outstanding sensing performance. Under UV irradiation, metal oxide nanocluster photolysis water absorption and water in the GaN create oxygen-producing surface defect active sites and electron-hole pair frameworks. Target analytes undergo chemisorption at these active sites, and adsorption molecules dynamically capture and de-capture change carriers at the active sites for GaN potential modifications of the main chains. These would lead to modulation of sensor currents that are proportional to analyte concentrations. This study enhanced the sensitivity of p semiconductor Pani to CO gas after introducing the AuNPs

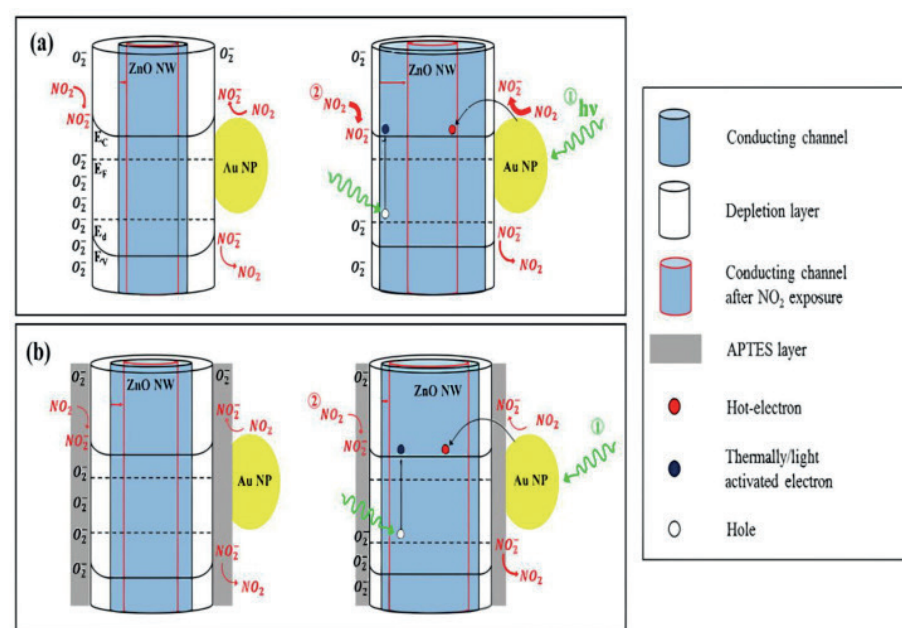


Figure 1. Schematic mechanisms for enhanced NO₂ gas response of Gold Nanoparticles-decorated ZnO nanowires. (a) without (Au-ZnO), (b) with a (3-aminopropyl) triethoxysilane layer (Au-ZnO/APTES), (left) in the dark, (right) under green illumination [6]

In Figure 1, the machine-made strengthened dd gas response of Au-ZnO and Au-ZnO/APTES are illustrated through diagrams, specifically indicating the absorption and suction mechanisms in the dark and under green clearing luminary. In this study, the immediate chemisorption of NO₂ gas onto the ZnO surface by catching the electrons of the ZnO surface itself was discussed in addition to removal of the NO ions from the AuNPs where NO₂ gas catches the electron of the AuNPs. The suction of the NO ions should only emerge on the ZnO surface. As shown in Figure 1s, the AuNPs adherence should enhance the NO₂ gas adsorption under green lighting by engendering plasmon-

mediated hot electrons from AuNPs. At the end, the Au-ZnO achieved the maximum improvement ratio and NO₂ gas response. The APTES layer on the ZnO NW surface exerts an influence in the NO₂ gas absorption of Au-ZnO/APTES. The APTES layer hindered the NO₂ gas adsorption onto the ZnO NW, and testified by the comparatively thin arrows of NO₂, as shown in Figure 1b.

The continuous progress of global industrialization not only improves production and living standards, but also destroys the environment in varying degrees. Due to its high sensitivity, easy preparation and low cost, nanowire materials have developed and play an essential role in the market.

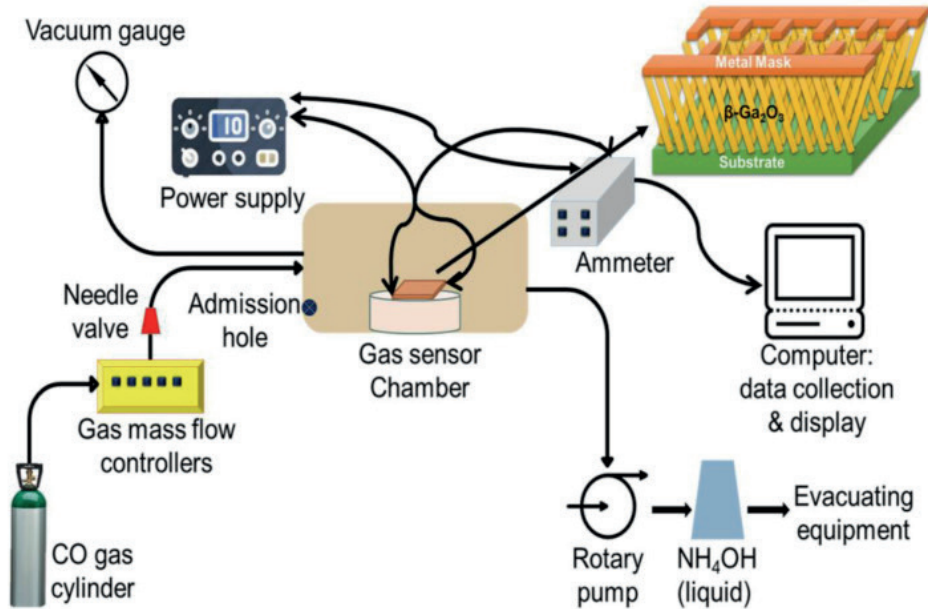


Figure 2. Architecture diagram of CO gas sensor measuring unit [6]

Figure 2 presents the study of analyzing the effect of various gas concentrations on the performance of β -Ga₂O₃ nanowire devices after modification. Different gas sensors result in different measurements of CO gas concentration as each sensing platform relies of distinct transduction mechanism, surface chemistry, and interaction pathway with CO molecules. With the decrease of gas concentration, the response and recovery time gradually decrease and increase. The length of response and recovery time depends on the availability of a large amount of oxygen trapped on the surface of the sample. If the number of oxygen vacancies increase, then the pressure on the surface of the trapped oxygen molecules increases as well. The CO-gas sensor is operated by adsorption, where the resistance decreases when the reducing agent reacts on the surface of the material. After it chemisorbed and absorbed the oxygen in the semiconductor by the reduced gas, the result is a free electron in the form of increased conductivity. In Figure 2, small fragments of the oxygen ion monolayer were adsorbed and formed additional deoxyribonucleic acids near the ion surface.

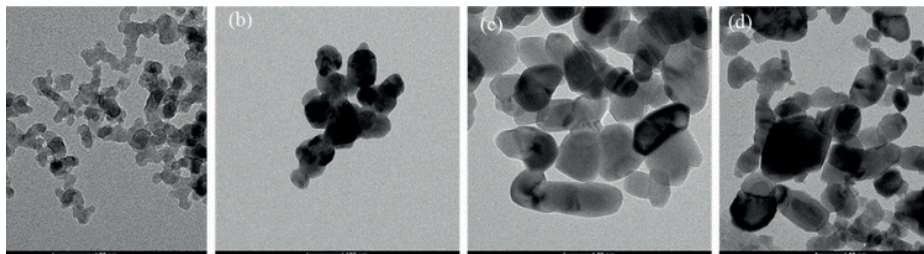


Figure 3. TEM images of metal oxides' nanoparticles: (a) Al, (b) Cu, (c) Ti, (d) Zn

Noble Metal Nanoparticles

Noble metals characterized by their high oxidation and corrosion resistance at high temperatures, namely platinum (Pt), silver (Ag), gold (Au), palladium (Pd), and ruthenium (Ru) NPs have gained significant popularity and have been subjected to extensive research [5]. Noble metals NPs synthesis methodologies comprise of two main approaches: bottom-up and top-down. Top-down approaches involve breaking down bulk materials into smaller nanostructures through physical manipulation techniques such as pyrolysis, lithography and micropatterning. Bottom-up approaches employ chemical transformations, including microwave synthesis, microemulsion techniques, and chemical reduction.

Because of their capacity to be produced in various shapes, their high extinction coefficients, and their facile surface functionalization, noble metal nanoparticles are considered ideal, versatile tools for advanced high-sensitivity applications in biomedicine, chemical sensing, and photonics.

Electrochemical Sensors

Electrochemical sensors use nanostructured electrodes to convert chemical interactions with fuel contaminants into measurable signals. It can enhance electron transfer, improving detection of redox-active contaminants. When a contaminant, such as sulfur species, water, peroxides, or trace metals, interacts with a nanomaterial-modified electrode, the current, potential, or impedance of the system is altered. Nanomaterials such as graphene, carbon nanotubes, and metal oxide nanoparticles, enhance electrochemical sensors by increasing the density of active sites and accelerating electron-transfer kinetics.

Applications in Fuel Quality Control

Adulteration Monitoring

The adulteration of fuel may have detrimental effects on a variety of systems, including automobiles, people's health, and even the environment. Adulteration monitoring is a critical component of fuel-quality assurance that relies on high-resolution sensing platforms to detect the intentional or accidental mixing of fuels with incompatible substances. Adulterants such as kerosene, solvents, water, or degraded hydrocarbons have high surface area to volume ratios that increase interactions with trace impurities, which enables detection of shifts in oxidation potential,

conductivity, refractive index. It can also increase molecular adsorption patterns that would be invisible to conventional probes.

Nanomaterial-based optical and electrochemical sensing systems were able to detect fuel adulteration through measurable shifts in refractive index, fluorescence response, and charge-transfer characteristics, enabling rapid and reliable identification of low-level contaminants in gasoline and diesel. By exploiting nanoscale interactions, adulteration can be detected through distinct signal patterns that correlate with the type and level of contaminant [3]. This will reduce dependence on laboratory analyses and strengthens quality control.

Enhanced Fuel Properties

Enhanced fuel properties can be more accurately monitored when nanomaterials are incorporated into advanced sensing platforms, allowing subtle chemical and physical variations in fuel to be detected with high precision. Nanostructured materials respond strongly to changes in molecular composition, oxidation state, and impurity levels because their catalytic activity, electron-transfer behavior, and adsorption characteristics differ significantly from bulk materials. Recent studies show that metal-oxide nanostructures such as CeO₂, ZnO, and TiO₂ can detect early-stage oxidative degradation by monitoring shifts in redox activity and oxygen-vacancy dynamics, enabling real-time assessment of fuel stability during storage and transport. Carbon-based nanomaterials, including graphene and carbon nanotubes, have shown to identify trace water contamination and dissolved oxygen through rapid charge-transfer interactions, improving the accuracy of fuel-aging diagnostics. Noble-metal nanoparticles such as Au, Pt, and Pd further enhance monitoring capabilities by exploiting plasmonic resonance shifts and catalytic surface reactions to detect sulfur- and nitrogen-containing impurities at extremely low concentrations. These nanomaterial-enabled sensing systems provide high resolution and real-time evaluation of changes in lubricity, aromatic content, volatility, and combustion quality.

Combustion Optimization

Nanomaterial enabled sensors play a critical role in monitoring combustion operations as maintaining optimal fuel composition is essential for efficient energy release and reduced emissions. During combustion, even minor variations in fuel quality, such as the presence of adulterants, water, or oxidative degradation products, can alter ignition delay, flame stability, and pollutant formation. Nanostructured sensing materials provide the sensitivity required to detect these variations in real time, allowing operators to adjust combustion parameters before performance loss occurs. Nanomaterial-based detection systems can identify changes in hydrocarbon structure, volatility, and impurity levels that directly influence combustion efficiency, enabling more precise control of air-to-fuel ratios and thermal output [3]. By capturing these signals, combustion systems can be optimized to minimize soot formation and maintain heat release profiles.

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Biographies

Dr. Raj Shah is the Director at Koehler Instrument Company in New York, where he has worked for the last 25+ years. He is an elected Fellow by his peers at IChemE, AOCS, CMI, STLE, AIC, NLGI, INSTMC, Institute of Physics, The Energy Institute, and The Royal Society of Chemistry.

As an ASTM Eagle award recipient, Dr. Shah recently coedited the bestseller, "Fuels and Lubricants handbook", details of which are available at ASTM's Long Awaited Fuels and Lubricants Handbook 2nd Edition Now Available <https://bit.ly/3u2e6GY>.

He earned his doctorate in Chemical Engineering from The Pennsylvania State University and is a Fellow from The Chartered Management Institute, London.

Dr. Shah is also a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute and a Chartered Engineer with the Engineering Council, UK. Dr. Shah was recently granted the honorific of "Eminent Engineer" with Tau beta Pi, the largest engineering society in the USA.

He is on the Advisory Board of Directors at Farmingdale University (Mechanical Technology), Auburn University (Tribology), SUNY, Farmingdale (Engineering Management), and State University of NY, Stony Brook (Chemical Engineering/Material Science and Engineering).

An Adjunct Professor at the State University of New York, Stony Brook, in the Department of Material Science and Chemical Engineering, Raj also has over 725 publications and has been active in the energy industry for over 3 decades. More information on Raj can be found at <https://tinyurl.com/mbz22vjv>

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