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SURFACE MODIFICATION OF METAL OXIDES FOR FUNCTIONAL MATERIALS

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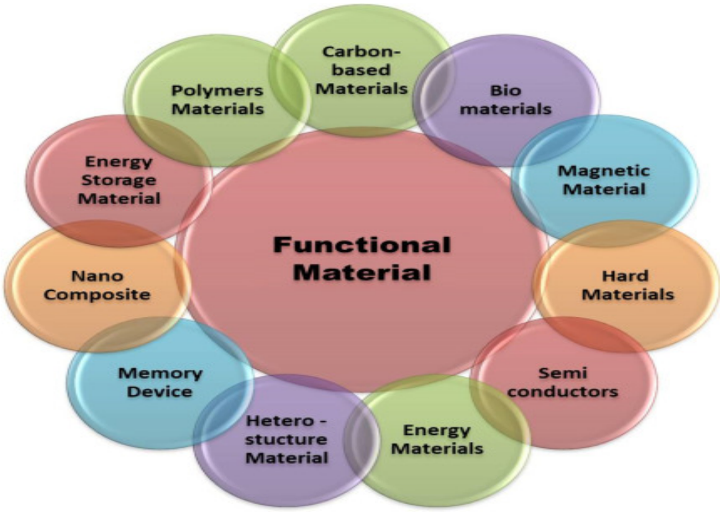
Abstract:
Surface modification using metal oxide materials enhances substrate properties like biocompatibility, corrosion resistance, and antibacterial activity, often applied to nanoparticles or implants such as titanium alloys. Physical methods include plasma spray for dense coatings like hydroxyapatite or Al_2O_3 on titanium, and physical vapor deposition (PVD) for uniform TiN films improving wear resistance. Chemical approaches encompass sol-gel for uniform oxide films like TiO_2, micro-arc oxidation for ceramic layers, and chemical vapor deposition (CVD) for controlled TiO_2 nanowires. Bio-inspired methods use catechol-based dispersants for strong adsorption on oxide nanoparticles, enabling electrophoretic deposition (EPD). Titanium dioxide (TiO_2), iron oxide, alumina (Al_2O_3), zirconia (ZrO_2), and silver oxide (Ag_2O) dominate, often doped with Ag, Sr, or Zn for added bioactivity. Silane coupling agents functionalize metal oxide nanoparticles to reduce agglomeration and improve dispersion in composites. Recent advances include block copolymer-templated metal oxide nanopillars on polymers for tailored surfaces. This article covers the study of functionalizing Fe_3O_4 and ZnO nanoparticles (NPs) for biocompatibility involves coating their surfaces with biocompatible materials to reduce toxicity, prevent agglomeration, and enhance stability in biological environments. Polyaniline (PANI) and aryldiazonium salts (ArN_2^+) are tried as coatings which minimize immune recognition and cytotoxicity up to considerable level. This surface functionalization improves biocompatibility as well efficacy of metal oxide sensors.
Keywords: Metal oxides, Nanoparticles, Surface modification, Biocompatibility

1. Introduction:

The definition of functional materials denotes the ability of a material to perform a specific "function" in response to a specific stimulus. A material is classified as a functional material if the modifications to its properties result in innovative applications in a variety of scientific and technological domains. Functional materials are substances that have been engineered to perform specific functions that extend beyond their fundamental structural support, such as responding to electrical, thermal, magnetic, or optical stimuli. Functional materials are a rapidly expanding category of sophisticated materials and composites that exhibit distinctive properties and/or functions. Magnetic, magnetocaloric, energy storage (battery), energy harvesting (solar cell), piezzoelectric, multiferroic, and other functional materials are among the examples. Functional materials are present in all types of materials, including ceramics, metallics, organics, inorganics, and polymers. They are the driving force behind advancements in environmental, energy, medical, and electronics technologies. These materials possess specific characteristics, such as conductivity, piezoelectricity (which converts mechanical stress to electricity), superconductivity (which results in zero electrical resistance at low temperatures), and shape memory (which restores the material to its original form when heated). The precise control of electrons is facilitated by semiconductors such as silicon, while data storage is facilitated by magnetic ones like iron. Thermoelectric variants convert heat gradients to voltage, catalytic properties, particularly heterocatalysis, and sensing, which detects changes in the chemical or biochemical environment by displaying a change in resistance. Optical variants interact with light for photonics. [1][2][3]



By optimizing interactions with environments through high surface-to-volume ratios, functional materials have implications in power solar cells, batteries, wearable technology, and medical implants. In the field of electronics, they facilitate the creation of flexible displays. In the field of biomedicine, graded composites are used to simulate tissues in order to create more effective implants. They are employed in turbines and purification systems by renewable energy sources.

A) Metal oxides as promising material:

In the field of catalysis and environment, metal oxides such as TiO_2, CeO_2, Fe_2O_3, and WO_3 are employed for photocatalysis, oxidation, pollutant degradation, CO oxidation, and water splitting. Cathode/anode materials employed in batteries and supercapacitors include $LiCoO_2$, $LiFePO_4$, NiO, and MnO_2. In the field of sensors and electronics, SnO_2, ZnO, CuO, and In_2O_3 are frequently employed as gas sensors, transparent conductors, and thin-film transistors. In the field of magnetism and spintronics, Fe_3O_4, CrO_2, $La_{1-x}Sr_xMnO_3$ are utilized as ferromagnetic electrodes, spin-dependent transport, and memory devices. [4][5]

B) Surface modification for tailored applications:

Widespread interest has been generated by the chemical surface modification of metal oxide nanoparticles to regulate their dispersion, aggregation, surface area, functionality. Organic ligands can be employed to introduce functionalities and protect nanoparticles. Preparative options include the grafting of an already functionalized ligand onto the nanoparticle surface, the exchange of a portion or all of the existing ligands on the nanoparticle surface, or the grafting of a ligand onto a nanoparticle followed by modification through organic chemical reactions. Silane modifiers are among the most significant bifunctional modifiers that are frequently employed for the surface treatment of metal oxide nanoparticles. This method is employed to prevent the agglomeration of NPs and enhance the stability of NPs. The efficacy of metal oxide nanoparticles as lubricant additives is restricted by their high surface energy and their propensity to aggregate, agglomerate, and coagulate in lubricating media. In response to these concerns, researchers have implemented tunable surface functionalization of metal and metal oxide nanoparticles. Surface functionalization has been shown to be an effective method for enhancing the efficacy of NPs in composites as reinforcing phases and lubricant additives. [6][7][8]

C) Environmental monitoring for sustainable development:

Gas sensors are smart and functional materials which have created its distinct place in environmental monitoring and toxicity control. In recent years, there is an increasing interest in the discovery of novel materials to facilitate the development of high-performance solid-state gas sensors. Compared to other gas sensor devices, mixed-metal oxide gas sensors are advantageous due to their low cost, straightforward implementation, and high reliability in real-time control systems. Metal oxide-based gas sensors are frequently employed in the monitoring of toxic pollutants, as they can offer the requisite selectivity, sensitivity, and stability that these systems require. Gas sensors have a significant impact on a variety of subjects, including domestic safety, environmental monitoring, automotive applications, sensor networks, spacecraft, residences, and public security. The gas sensor's operation is predicated on the alteration in conductivity that occurs as a result of exposure to gases that are capable of reacting with chemisorbed oxygen. The identification of a variety of oxidizing and reducing gases is a critical requirement for both domestic and industrial applications. Consequently, there is perpetually an ongoing endeavour to identify novel gas sensors. [9][10][11]

D) Transition metal oxides as Gas Sensors:

Most of the transition metal oxides and mixed metal oxides have shown promising place in Gas sensors. In the development of ferrite gas sensors, the numerous parameters, including crystallite size, particle size, phase formation, dopants, surface area, grain size, gas concentration, sensitivity, selectivity, recovery time, response time, and operating temperature, are of significant interest. It is possible to produce ferrite gas sensors using a variety of techniques. Optimizing the concentration of dopants, operating temperatures, sintering temperature, and preparation conditions is the most critical requisite for enhancing the quality of a ferrite gas sensor. In recent years, ferrites have been employed as gas sensors due to their superior selectivity and stability with respect to a specific gas compared to other sensors. Detection is indispensable in a variety of sectors, including industrial domestic security, emission control, vehicle emission control, and environmental monitoring. A significant number of metal oxides, including ZnO, SnO_2, TiO_2, Fe_2O_3, WO_3, and mixed-metal oxides, were discovered to be responsive to specific gases. The spinel-type of mixed metal oxides, which has a general formula of AB_2O_3, is a significant component of gas sensors and has been considered for the detection of both oxidizing and reducing gases. [12][13][14]

E) Biocompatibility of Gas sensors

Metal oxides have become a versatile material for sensor technologies, particularly in biomedical applications, as a result of their tunable electrical, optical, and catalytic properties. Nevertheless, the establishment of biocompatible, selective, and stable interfaces between these materials and biological systems continues to be a significant obstacle. Consequently, the development of high-performance biocompatible sensors has become increasingly dependent on surface modification strategies. The recent developments in the surface modification of metal oxides, with a particular emphasis on the use of chemical, physical, and biofunctionalization techniques to improve the biocompatibility and sensing capabilities of these materials. Surface modification of metal oxides entails the functionalization of the surface with chemical moieties, polymers, biomolecules, or nanostructured coatings to customize properties such as hydrophilicity, protein adsorption, cell adhesion, and electron transfer kinetics. Sensor sensitivity, response time, and in vivo compatibility can be significantly impacted by these modifications. Surface factors, including charge, texture, hydrophilicity, and protein adsorption tendencies, determine the compatibility of a sensor with biological tissues or fluids. When directly exposed to biological environments, bare metal oxide surfaces may induce unwanted responses, including cytotoxicity, inflammation, or nonspecific protein adsorption. Consequently, it is imperative to alter surfaces in order to facilitate favourable bio interactions and mitigate adverse reactions.

Polymeric sensors are becoming more critical in the surveillance of the environment in which we reside, as they offer pertinent data for a variety of applications. Substantial endeavours have been undertaken to develop polymeric sensors that are beneficial for healthcare-related applications, including the sensitive detection of biomolecules and cellular interfacing. Surface modification and/or functionalization using plasma is a technology that is just beginning to emerge as a method to enhance selectivity and sensitivity in the bio detection process within the well-established field of biomedical polymeric sensors. Plasma irradiation treatments for polymer surfaces, which have been traditionally employed for cleaning, etching, activating, or cross-linking, are currently being employed to stimulate the formation of electrocatalytic species that can facilitate the oxidation of bio analytes and/or gas molecules that are detrimental to human health. The primary developments in the application of plasma technologies to the production of polymeric sensors for advanced biomedical applications, including humidity, temperature, pH, neurotransmitter, and glucose sensors. The sensor's response and recovery periods, as well as its sensitivity, are significantly enhanced by plasma treatment and surface irradiation treatment. Furthermore, we evaluated the sensor's selectivity and repeatability and determined that it was more selective for NH_3 than for NO_2 and exhibited exceptional repeatability.

Conducting polymers have demonstrated significant potential for gas detection at ambient temperature. This has resulted in the rapid advancement of these materials for gas sensing, as their conductivity can be modified when they are subjected to oxidant or reductant molecules at room temperature. However, their practical implementations as sensors are hindered by their low sensitivity, selectivity, and thermal instability, which are a result of their relatively high attraction to volatile organic and water molecules and low conductivity. Additionally, semiconducting inorganic (metal oxide) sensors exhibit unique advantages in the sensing of gases, such as high sensitivity, rapid response to low-concentration analytes, versatile exterior or surface chemistry, and a large surface area. Nevertheless, their sensing applications have been restricted by their high-temperature operation, despite their exceptional performance at room temperature. The synergistic effects of combining these two sensitive materials are evident. The hybrid has garnered significant interest in its potential as a sensor due to its enhanced sensitivity, selectivity, long-term stability, and low-temperature operation. The use of semiconducting metal oxides, conducting polymers, and the recent advancement in metal oxide-conducting polymer composites for their gas-sensing applications are summarized in this review. These developments present the advantages and limitations of these sensor materials, and it emphasizes the reasons why the composites provide an exceptional synergistic effect by enhancing sensing performance. Polymer coatings also function as matrices for immobilizing recognition elements while preserving biocompatibility. Efforts are also made to coat aryldiazonium salts on the surface of metal oxides to check the improvements in surface properties and overall efficacy of the gas sensors. [15][16][17]1[8]

2. Experimental Methodology:

Out of the available methods of functionalizing metal oxides to improve biocompatibility, such as physical methods (topography modification), chemical methods, and biofunctionalization. Polymer coating and aryldiazonium salt coating are among the chemical procedures that are implemented in this investigation.

A) Metal oxide synthesis:

Bare metal oxide nanoparticles of ZnO and Fe_3O_4 are prepared by co-precipitating Zn^{2+} and Fe^{2+}/Fe^{3+} compounds in NaOH, and subsequently apply coatings of Polyaniline and Aryldiazonium salts alternatively. To enhance biocompatibility and stability, NPs are dispersed in ethanol. Mix NPs with Polyaniline or Aryldiazonium salts in aqueous solution, stir/sonicate, and purify by centrifugation/magnetic separation.

B) Characterisation:

Metal oxides (ZnO and Fe_3O_4) functionalised with Polyaniline and Aryldiazonium salts are further characterised by BET analyser for surface are, SEM for particle size and zeta potential for characterising coating for surface charge of nanomaterials, which is used to study.

- **i)** **BET analysis** of ArN_2^+ / ZnO and PANI / Fe_3O_4 : Surface area analysis have shown that surface area are 80 and 150 m^2 per gram for ArN_2^+ / ZnO and PANI / Fe_3O_4 respectively.
- **ii)** **SEM images** of these MONP with modified surface have shown particle size below 100nm and have not shown much impact of surface coating on particle size.

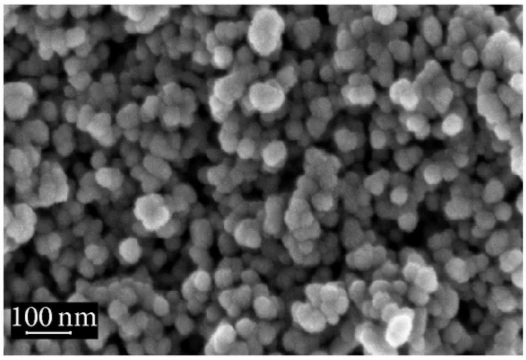


Fig.2 SEM of ArN_2^+ / ZnO

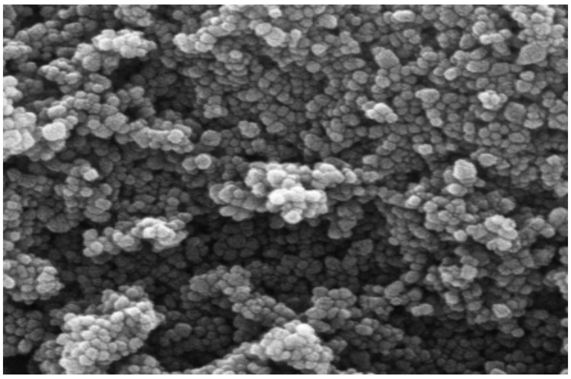


Fig.3 SEM of PANI / Fe_3O_4

iii) **Zeta potential:** For ArN_2^+ / ZnO: Zeta potential value of these surface modified NP is around -15 Mv. This shown that charge reversal of bare ZnO have been done by surface coating. This assures colloidal stability, biomolecule interactions, and sensor performance of coated ZnO NP. Zeta potential for PANI / Fe_3O_4: Zeta potential value of these surface modified NP is around +22 Mv. This shown that biocompatibility and dispersion has been increased.

iv) **Biocompatibility check**:
MTT/ATP assays (>90% viability), flow cytometry for uptake. Coatings enhance cell survival of prepared NPs diminish reactive oxygen species, mitigate apoptosis, and facilitate drug delivery. Evaluate using MTT/ATP for viability, flow cytometry for uptake, and hemolysis with a threshold of less than 5% lysis.

3. **Result and Conclusion:**

Bare NP of ZnO and Fe_3O_4 have shown promising role as biomarker, bioimaging in biomedical applications. Our study for its enhancing biocompatibility using ArN_2^+ / ZnO and PANI / Fe_3O_4 surface coated MONP have shown reduction in cytotoxicity of metal oxides relative to uncoated particles with compromising sensing properties. ArN_2^+ and PANI: provides stealth effect, reduces macrophage uptake; conjugate via carboxyl/amine groups for high biocompatibility. These coating lowers nanoparticle toxicity chiefly by forming a hydrophilic "stealth" layer that conceals particles from immune recognition and biological interactions. This alteration prolongs circulation duration, reduces clearance by the mononuclear phagocyte system (MPS), and diminishes protein adsorption that induces inflammation or cytotoxicity.

References:

1. https://www.sciencedirect.com/topics/materials-science/functional-material
2. Y. Liu, W. Zhu, M.S. Tse, S. Y. Shen, J. Mater. Sci. Lett., 14 (1995) 1185.
3. Watson, J. Magn. Magn. Mater.111 (1992) 29.
4. A review of new methods of surface chemical modification, dispersion and electrophoretic deposition of metal oxide particles M. S. Ata,[a] Y. Liu[a] and I. Zhitomirsky*[a] Issue 43, 2014, RSC Advances.
5. Xue, T., Attarilar, S., Liu, S., Liu, J., Song, X., Li, L., Zhao, B., & Tang, Y. (2020). Surface Modification Techniques of Titanium and its Alloys to Functionally

Optimize Their Biomedical Properties: Thematic Review. Frontiers in bioengineering and biotechnology, 8, 603072. https://doi.org/10.3389/fbioe.2020.603072

6. Zhu, N., Ji, H., Yu, P., Niu, J., Farooq, M. U., Akram, M. W., Udego, I. O., Li, H., & Niu, X. (2018). Surface Modification of Magnetic Iron Oxide Nanoparticles. Nanomaterials (Basel, Switzerland), 8(10), 810. https://doi.org/10.3390/nano8100810
7. Baez Vasquez, J. F., Paiva, A. E., Singh, S., Acosta-Beltrán, S., Fernandez, A. A., & Morris, M. A. (2025). Functionalizing Nonfunctional Surfaces: Creation of Metal Oxide Nanopatterns on High-Performance Polymers via Self-Assembly of PS-b-PEO. ACS applied materials & interfaces, 17(16), 24654–24664. https://doi.org/10.1021/acsami.5c04225
8. Neouze, MA., Schubert, U. Surface Modification and Functionalization of Metal and Metal Oxide Nanoparticles by Organic Ligands. *Monatsh Chem* **139**, 183–195 (2008). https://doi.org/10.1007/s00706-007-0775-2
9. J. S. Wilson, Sensor Technology Handbook, Elsevier, New York, (2005).
10. L. Bruno, C. Pijolat, R. Lalauze, Sens. Actuators, B 18–19 (1994) 195.
11. Recent advances in chemical surface modification of metal oxide nanoparticles with silane coupling agents:A review, Advances in Colloid and Interface Science, Volume 286, 2020, 102298, ISSN 0001-8686, https://doi.org/10.1016/j.cis.2020.102298.
12. Siyuan Wang, Ding Chen, Qiu Hong, Ying Gui, Yucheng Cao, Guanlin Ren, Zhao Liang, Surface functionalization of metal and metal oxide nanoparticles for dispersion and tribological applications – A review, Journal of Molecular Liquids, Volume 389,2023,122821,ISSN 0167-7322, https://doi.org/10.1016/j.molliq.2023.122821
13. H. Suo, F. Wu, Q. Wang, G. Liu, F. Qiu, B. Xu, M. Zhao, Sens. Actuators, B 45 (1997) 245.
14. E. Rossinyol, J. Arbiol, E. Peiro, A. Cornct, J. R. Morante, B. Tain, T. Bo, D. Zhao. Sens. and Actuators; B 109 (2005) 57.
15. Plasma surface modification of polymers for sensor applications: Alemán, Carlos and Fabregat, Georgina and Armelin, Elaine and Buendía, Jorge J. and Llorca, Jordi, Mater. Chem. B, 2018,6, 6515-6533
16. Liu H, Han H, Li HG, Zhang SX, Li XP, Yue YY, Wang MQ, Zhao Y, Fan ZQ. High-Performance NH_3 Sensors Based on Surface Modification by Plasma and Irradiation at Room Temperature. ACS Omega. 2025 Jun 11;10(24):25775-25789. doi: 10.1021/acsomega.5c01879. PMID: 40584361; PMCID: PMC12199011.
17. Modification of Metal Oxide Semiconductor Gas Sensors Using Conducting Polymer Materials by Jonah Wuloh, Eric Selorm Agorku, Nathaniel Owusu Boadi, https://onlinelibrary.wiley.com/doi/10.1155/2023/7427986
18. Polymer-Metal Oxide Composite (PPy–MoO3) for Ammonia and Ethanol Gas Sensor, Yenorkar, Surendra, Zade, Ramesh, Mude, Bhupesh, Mayekar, Vijay, Mude, Kushal, Raulkar, Kishor, Mistry, Ranjeet, Patange, Ashok, Macromolecular Symposia DOI:10.1002/masy.202100049