



Role of Semiconductor Oxides in Forensic Sciences: A Review

Vidit Pandey¹, Priyanka Nehla^{2,3,*}

¹Department of Physics, Aligarh Muslim University, Aligarh-202002, India.

²Department of Materials and Engineering, Ångström Laboratory, Uppsala University, 75103 Uppsala, SE, Sweden.

³Centre for Neutron Scattering, Ångström Laboratory, Uppsala University, 75103 Uppsala, SE, Sweden.

[nehlapriyanka93@gmail.com] (Corresponding Author)*

Abstract

Semiconductor oxides are playing an important role in the advancing modern forensic science, offering sensitive, selective, and rapid analyses. At nanoscale, they have a high surface area, unique chemical and physical properties, versatility, tunable optical, electrical, and magnetic characteristics. Applying different characterization techniques with semiconductor oxides on the nano-forensic evidences can provide the accurate and efficient results. Key semiconductor oxides such as ZnO, TiO₂, CuO, or Iron oxides can be used in drugs/toxic powder detection, gun powder/explosive residue analyses, fingerprint detection, and other forensic applications as photocatalysis, artificial olfactory system, powder suspension, auxiliary agent, colorimetric, gas, and electrochemical sensing.

Keywords: *Semiconductor Oxides, Forensic Science, Forensic Applications, Explosive, Drugs*

1. Introduction

Over the decade, semiconductor oxides have been applied in novel applications including resistive switching memory devices [1], cancer treatments, energy storage, and tracing of evidences at crime's sites [2]. Their unique physical and chemical properties at the nano-scale provide better response compared to bulk materials. Apart from this, they can be easily and rapidly fabricated by low-cost, eco-friendly, and control synthesis methods [3], and are non-toxic, non-hazardous, non-explosive, stable, and recyclable. Generally, on the basis of nano-scale (1-100 nm) dimensions, semiconductor oxides can be classified into four types; (I) Zero dimension (0D), (II) One dimension (1D), (II) Two dimension (2D), and Three dimensions (3D). On the other sides, they can also be distributed on the basis of organic, inorganic, metal, carbon, intrinsic, extrinsic, etc. [2]. Due to unique properties and versatility, semiconductor oxides can be used in forensic science's applications such as explosive detection [4], chemical warfare agents [5], illegal drug detection [6], etc.

Forensic science and its branches have been instrumental in solving many critical criminal cases to ensure fair justice in modern times [7]. Forensic techniques play a vital role to identify the true victims

and exoneration of innocent for fair justice. Forensic science is a interdisciplinary approach, which brings together various scientific field such as physics, biology, chemistry, computer science, mathematics, engineering, etc [8]. Still, forensic techniques require more precision, accuracy, and rapidity in finding results in criminal cases. Semiconductor oxides are contributed significantly to forensic analysis by offering precise and prompt results with minimum complexity. These materials enable selective and sensitive detection methods, which are crucial for identifying and analyzing forensic evidence. Many forensic applications like DNA analysis, toxic and explosive elements' detection, fingerprinting, drug detection, currency examination, etc. have benefited by utilizing semiconductor oxides.

In this short review, we explore the properties of semiconductor oxides, their characterization techniques, and applications in forensic science. Some specific semiconductor oxides such as TiO_2 , ZnO , SnO_2 , Fe_2O_3 , metal ferrites, etc. and their advantage in forensic science have been discussed in detail.

2. Properties of Semiconductor Oxides

Semiconductor oxides have properties of both semiconductors and oxides classes. They contain metal cations and oxygen anions [9]. At nano-scale, they exhibit in different nanostructures such as nanoparticles, thin films, nanotube, quantum dots, nanocubes [10], etc. Numerous synthesis techniques like sol-gel, spin coating, co-precipitation, spray-coating, hydrothermal, solid-state route, pulse laser deposition, microwave irradiation, etc. are used to fabricate semiconductor oxides. Their properties can be tuned by various factors like synthesis methods, annealing temperature, doping of other elements, applied pressure, amount of chemical's precursor, reaction time, wave irradiation, external magnetic and electric field [11]. Some properties of oxides are discussed below.

2.1 Structural and Chemical Properties: Semiconductor oxides have high surface area over volume, which enhance their reactivity, making them suitable for detecting and sensing various substances. The structural and chemical of semiconductor oxides are stable as well as tunable, which allow us to customize them for specific forensic needs [12]. Roger et al. [13] described that redox-active nature based semiconductor oxides (also known as reducible oxides) are suitable candidate for the sensors and detectors. Besides, some semiconductor oxides (Mn_2O_7 , Co_3O_4 , Fe_3O_4 , etc.) have mixed cation valences and adjustable oxygen deficiency features, which enhance their application in forensic science [14].

2.2 Optical Properties: The band gap influence the optical properties of semiconductor oxides [15]. They may exhibit transparency or absorption of light depending on the energy of the photons with respect to the band gap. Generally, optical properties of semiconductor oxides can be tuned by various factors. V. Pandey et al. [3] was successfully tuned the optical properties of Co_3O_4 and Mn_3O_4 by annealing temperature and coating layers, respectively and suggested that semiconductor oxides can be used in optical sensors, opto-electronic devices, light-trackers, etc. by controlling the optical properties. Other optical parameters such as refractive index, skin depth, optical conductivity, excitation factor, etc. are also the deciding factors to choose semiconductor oxides for specific forensic application. Some semiconductor oxides (ZnO , ZrO_2 , TiO_2 [16], etc.) have wide optical band gap (2.8 ~ 5.5 eV) and lies under the ultraviolet region. While, some (Mn_3O_4 , CoFe_2O_4 [17], ZnFe_2O_4 [18]) have narrow band gap (1 ~ 2.7 eV) and belong to visible range.

2.3 Electrical Properties: Semiconductor oxides have electrical conductivity between insulating and conducting materials. External temperature, doping, effective surface area, applied electric and magnetic field, crystalline structure, defect density, band gap, carrier concentration, etc. affect the electrical properties of semiconductor oxides [19]. Generally, semiconductor oxides show two type of conduction, (I) injection limited and (II) transport

limited (Fig. 1) [20]. Semiconductor oxides show different kinds of conduction pattern like hopping, Poole-Frenkel, Schottky barrier, space charge limited conduction, direct or indirect tunneling, ionic, etc. in non-ohmic mode. Understanding and controlling these electrical properties are essential for optimizing the performance of semiconductor oxides in forensic applications.

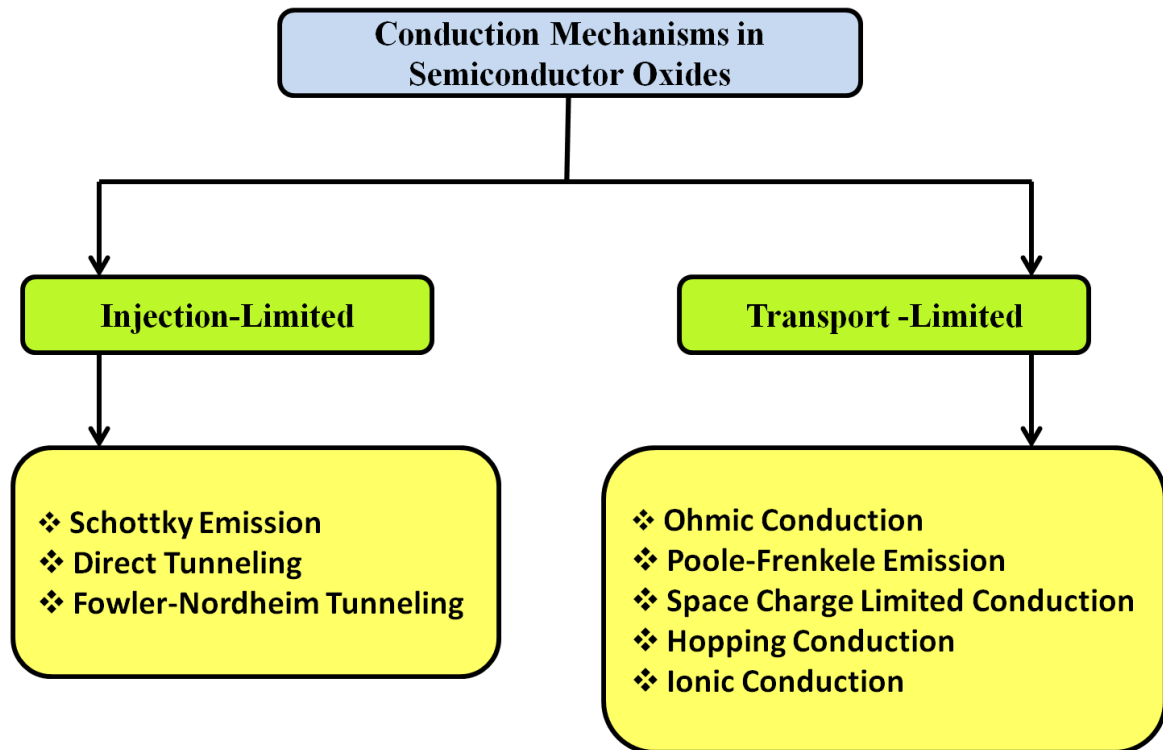


Figure 1. Types of conduction mechanism of semiconductor oxides.

2.4 Magnetic Properties: Semiconductor oxides have moderate magnetic properties. They are neither a pure magnet nor magnetism like metal. Their magnetic properties are typically dependent on several factors, including the specific composition of the oxide, its crystal structure, and any defects/vacancies or doping/impurity present [21]. In transition metal oxides, the unpaired d sub-cell electrons decide the magnetic nature of materials. The dilute magnetic semiconductors are suitable for magnetic sensors.

3. Detection and Analysis Techniques

In order to identify the exact properties of semiconductor oxides for forensic application, detection and analysis steps are very crucial. On the basis of quantitative and qualitative analyses, characterization techniques can be categorized into four types i.e., (I) Spectroscopic, (II) Microscopic, (III) Chromatographic, and (IV) Electrochemical. Many instruments/machines are used in these characterization methods (Table 1).

Table 1. Characterization techniques and their instruments/machines.

Sr. No.		Characterization Technique	Instruments/Machines	References
1		Spectroscopic	Mass Spectroscopy Energy Dispersive X-ray X-ray Diffraction X-ray Fluorescence Nuclear Magnetic Resonance Raman Spectroscopy Ultra-Violet Visible Infrared Spectroscopy Fourier Transform Infrared X-ray Photoelectron Spectroscopy	[1, 3, 22-24]
2		Microscopic	Atomic Force Microscopy Scanning Electron Microscopy Transmission Electron Microscopy	[2, 22]
3		Chromatographic	Liquid Chromatography Gas Chromatography Hydrodynamic Chromatography Magnetic Chromatography Thin-layer Chromatography High-performance Chromatography Capillary Electro Chromatography	[2, 25]
4		Electrochemical	Cyclic Voltammeter Impedance Spectroscopy	[26, 27]

4. Forensic Applications of Semiconductor Oxides

Semiconductor oxides are significantly used in numerous applications of forensic science. They offer rapid, selectivity, and sensitive detection capabilities to solve the criminal cases on the crime sites and in forensic laboratory. Semiconductor oxides such as TiO_2 , ZnO , In_2O_3 , SnO_2 , etc. can be used in numerous forensic applications such as fingerprint detection, trace evidence analysis, drug detection, explosive residue analysis, toxic and hazardous substance identification, gas sensors, etc. (Fig. 2). Some applications of forensic fields are discussed below.

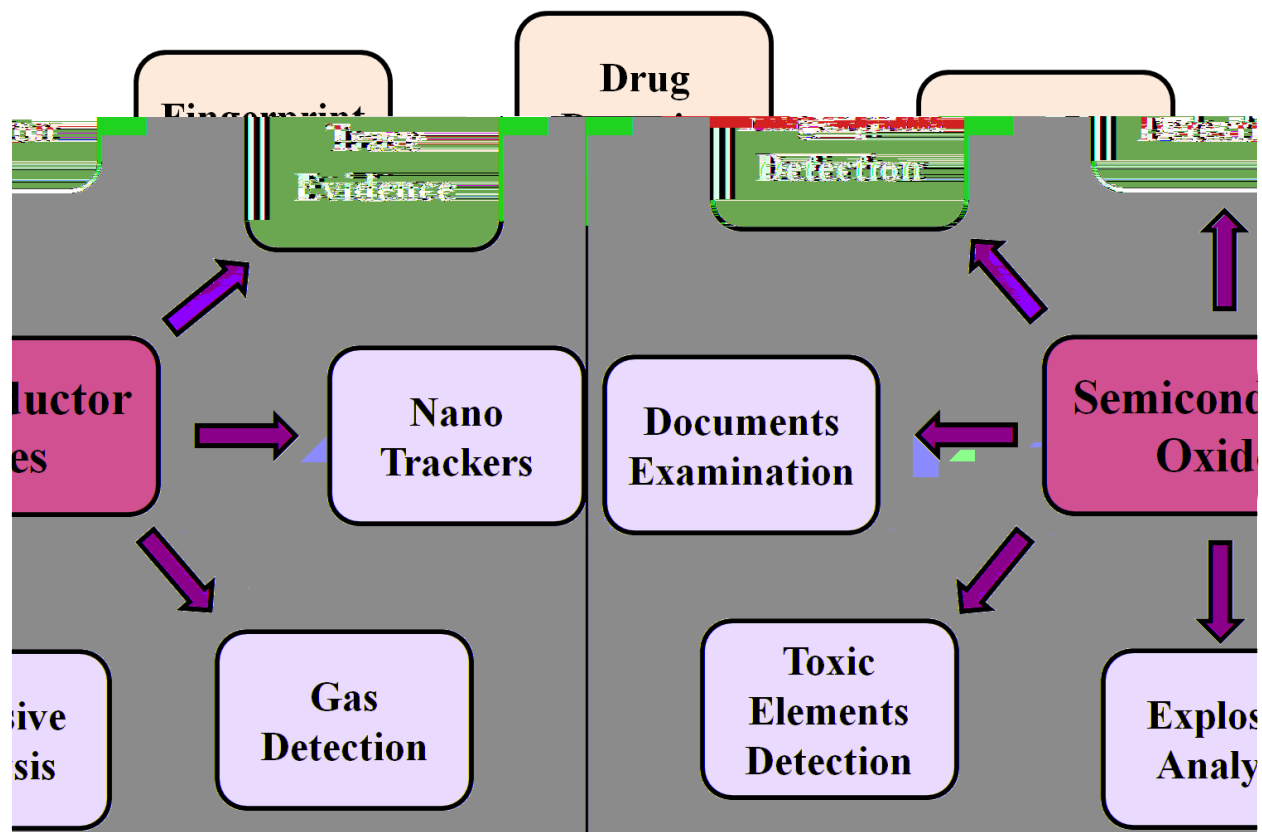


Figure 2. Applications of semiconductor oxides in Forensic.

4.1 Trace Evidence Analysis: Even a small traces such as glass, hair, duct and electric tapes, paints, metal and plastic pieces, biological samples explosive residue, etc. can give valuable information about crime's pattern, criminals, and victims [28]. Different kinds of evidences at crime sites are shown in Fig. 3. Semiconductor oxides can be employed in trace evidence analysis in forensic science in several ways like surface enhancement for microscopic analysis, elemental mapping, photocatalytic degradation of containments, gas sensing for residue detection, trace explosive detection, etc.

Evidences can be visible more in microscope by applying semiconductor oxides-based thin films (TiO_2) on the surface of evidence (hair, clothes, threads, fiber, etc.). Photocatalytic properties equipped oxides such as TiO_2 [16], NiO , ZnO [29], or CoFe_2O_4 are used to degrade the organic contaminates presents on the evidence's surface. Gunshot residue and other explosive evidences can easily trace with the help of semiconductor oxides-based quantum dots due to good luminescence [30]. The volatile organic compounds, i.e., VOCs (petrol,

diesel, kerosene, alcohol, nepam, etc.) are used in some vehicular accidents and criminal activities. Semiconductor oxides show sensitivity to these compound [31].



Figure 3. Different kinds of samples at crime's site for forensic investigations.

4.2 Fingerprint Detection: Fingerprints are one of the important evidences in forensic science and it can be obtained from weapons, glass, knife, documents, or any object at crime place. Fingerprint verification depends on fingerprint minutiae such as scar, island, delta, bridge, core, ridge ending, sweat pores, etc. [32]. Since last decade, many semiconductor oxides are employed by the researcher to investigate the fingerprints residues due to their spectral properties, small size, physicochemical characteristics, and significant surface area. Apart from this, semiconductor oxides are able to identify the both aged and recent fingerprints. Powder-dusting route is one of the effective techniques to detect the fingerprints [33]. In this approach, conventional powders face some difficulties to trace the fingerprints due to intricate patterns, limited sensitivity, lack of fluorescence, background interference, and low contrast [34]. Bhagat et al. [35] used green synthesized CuO to detect the fingerprints on glass, steel, butter paper, and white paper by powder dusting technique. Peng et al. [36] synthesized novel Co_2TiO_4 to detect the latent and blood fingerprints by small particle reagent route, and suggested that this oxide is suitable for rapid identification of fingerprints at crime scenes. ZnO and TiO_2 semiconductors are widely used to highlight the fingerprints due to strong photocatalytic properties, surface-enhanced Raman scattering capability, and ability to emit fluorescence under UV light [30]. Fe_3O_4 can interact with various chemical

groups such as amino acids, lipids, and other organic compounds in fingerprints. This interaction can be measured electrochemically to visualize the fingerprint.

4.3 Drug and Pesticide Detection: Hazardous pesticides and toxic drugs are used for poisoning, spreading pandemic, murders, suicides, sexual assault, date rapes, destroying livestock of a big area, demolishing the biological and medicines products, etc. [37]. Pesticides and drugs detection become a challenging task in forensic laboratories. Pesticides can be categorized into two groups, i.e., (I) natural (plant-based agro-chemicals and mineral oils) and (II) synthetics (organic and inorganic). The chronic exposure to pesticides may leads in drug resistance, imbalances in hormones, reduced immunity power, etc. So, detection of hazardous pesticides is important for public health, food safety, and environmental monitoring. SnO₂ and ZnO-based gas sensors are effective to sense the gases like nitrous oxides, methane, or carbon mono oxides, which release during the decomposition of pesticides [38]. The adsorption of these gases on the ZnO or SnO₂ surface changes its electrical resistance, providing a measurable signal. Metal ferrites (MnFe₂O₄, CuFe₂O₄, NiFe₂O₄, and ZnFe₂O₄) are used as an auxiliary agent with mass spectroscopy to detect the pesticide's residue in urine and blood serum [39]. Semiconductor oxides are helpful in forensic toxicology for the identification of numerous toxic drugs from various evidences like cadaver bones, fingerprints, urine, saliva, blood, hair, etc. Sometimes, drug detections become difficult for narcotics department since the drug can't be obtained in its original forms in the forensic evidences. Generally, illegal drugs (Morphine, Ketamine, Khat, Cocaine, MDMA, Opiates, etc.) are collected in the forensic evidences at drug facilitated crime sites [40]. Hasan and co-workers [41] fabricated Zn₂SnO₄-based electrochemical sensors to detect the Morphine and Codeine. As an electrode, Zn₂SnO₄ offers high conductivity, large surface area, and fast electron transfer rate during the interaction with drugs. Cadmium Sulfide has ability to identify the methamphetamine through chemiluminescence and florescence process [42]. CuO can interact with hazardous drugs, causing changes in their optical parameters. These changes can be detected using spectrophotometric methods (UV- Visible, Raman, or Photoluminance spectra) to identify and quantify the presence of drugs.

4.4 Explosive Residue Analysis: Explosives and VOCs are commonly used in terrorism, murder, robbery, pre-planned accidents, riots, demolish of buildings, war, etc. with the help of different kind of weapons. Till date, many explosive detection techniques have been developed in forms of electrochemical, optical, biosensors, and trained animals [43], which are depicted in detail in Fig. 4. Further, there is need to develop the sensors/techniques to identify the exact explosive material rapidly and accurately at crime sites or in forensic laboratories. On the basis chemical formula, explosive materials cab be categorized into four types, i.e., (I) Peroxides (triacetone triperoxide, hexamethylene triperoxide diamine), (II) Nitramines (RDX), (III) Nitrate esters (ETN), and (IV) Nitroaromatics (Picric Acid, TNT) [44]. Semiconductor oxides are suitable candidates to detect the both low and high explosive due to their unique chemical and physical properties. In the starting of 1960 to 1990, semiconductor oxides were used to design the mechanical and electrical nose to detect the gases of explosive materials [43]. Various scientific techniques such as gas sensing, surface enhanced Raman scattering, photocatalytic, colorimetric, electro-optical, etc. are used by forensic professionals to identify the explosive materials (Fig. 4). Liu et al. [44] used aluminum oxides (AlO_x)-based colorimetric sensors for the sensing of nitroaromatic-based explosive materials (TNT). Lauren et al. [45] fabricated WO₃/CTO hetrojunction (p/n junction)-based electronic nose type system to detect the explosive. Guo and co-workers [46] developed the SiN/TiO₂/rGO optoelectronic Schottky sensor-based artificial olfactory systems to identify the TNT, RDX, AN, PA, Urea, PNT, DNT, etc. This fabricated sensor is qualitative, sensitive, and semiquantitative detection towards gas phase explosives. Apart

from this, SnO_2 , ZnO , CuO , Fe_2O_3 , Cu_2O , etc. have been explored widely by researchers in the detection of explosive materials through various techniques.

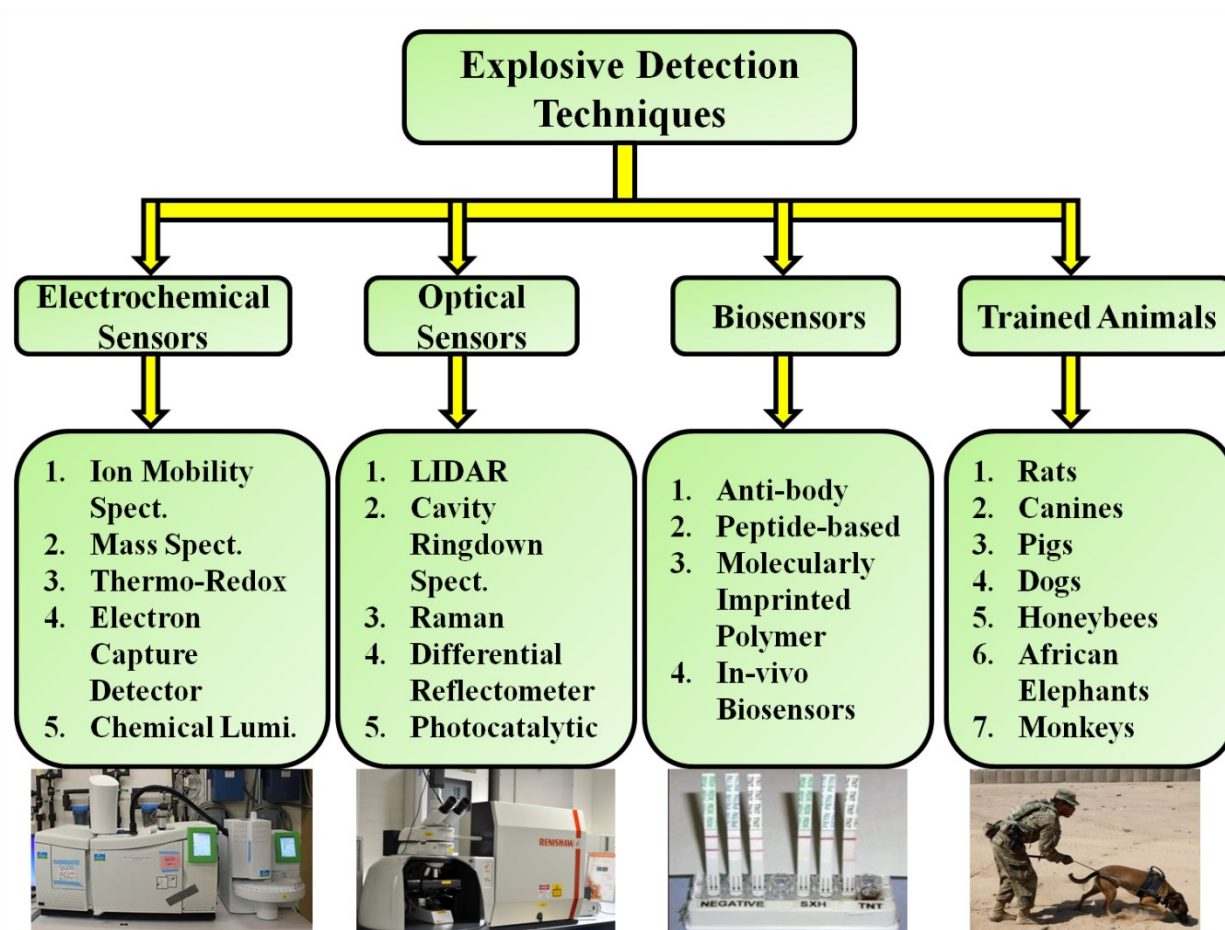


Figure 4. Different kinds of explosive detection techniques.

4.5 Document Examination and Ink Analysis: At crime site, the documents (paper, files, cash, bank cheque, IDs, etc.) and their printed inks are one of the important forensic evidences. Semiconductor oxides have potential to trace the evidences among highly sensitivity and chemical stability. These oxides can help to authenticate the documents, provide age estimation of papers, detect the alteration, and differentiate among inks of the paper [30]. Non-destructive, high precision, and versatility are the main advantages of using semiconductor oxides in documents analyses [47]. Fe_2O_3 , ZnO , SnO_2 , TiO_2 , etc. are commonly used in document examination via surfaced enhanced Raman technology, photoluminance, gas sensing, etc. techniques.

5. Key Semiconductor Oxides in Forensic Applications

Till date, semiconductor oxides have been become the promising candidates for the forensic applications due to offering sensitive, selective, rapid, and accurate results in detecting and tracing the forensic evidences. These materials can be engineered into different forms like nanoparticles, nanorods, nanowires, thin films, or nanocubes, broadening their applicability in forensic science [48]. They can be

more efficient by doping of other elements, modifying synthesis routes, coupling with other materials to form a heterojunction, and applying beam irradiation [49]. Some key semiconductor oxides with their forensic applications and properties/working are tabulated in Table 2. These materials play significant roles in advancing forensic science.

Table 2. Some semiconductor oxides with their applications in forensic science and properties/working.

Sr. No.	Semiconductor Oxides	Forensic Applications	Properties/Working	References
1	ZnO	Fingerprint detection	Strong photocatalytic and emit fluorescence under UV light	[30, 38]
		Pesticide/Drug Detection	Altering the electrical properties during toxic gas interaction	
2	TiO ₂	Fingerprint detection	Emit fluorescence under UV light	[30, 46]
		Explosive detection	Artificial olfactory system	
3	Fe ₃ O ₄ /Fe ₂ O ₃	Fingerprint detection	Powder suspension	[50]
4	CuO	Fingerprint detection	Powder dusting technique	[35]
5	Co ₂ TiO ₄	Fingerprint detection	Small particle reagent route	[36]
6	SnO ₂	Pesticide detection	Altering the electrical properties during toxic gas interaction	[38]
7	Zn ₂ SnO ₄	Drug detection	Electrochemical sensing	[41]
8	AlO _x	Explosive detection	Colorimetric sensing	[44]
9	WO ₃	Explosive detection	Artificial olfactory system	[45]
10	Metal Ferrites (ZnFe ₂ O ₄ , MnFe ₂ O ₄ , CuFe ₂ O ₄ , NiFe ₂ O ₄)	Pesticide/ Drug/ Toxic chemicals identification	Auxiliary agent with mass spectroscopy	[39]
11	Cu ₂ O	Explosive detection	QCM gas sensing	[43]

6. Conclusion

Semiconductor oxides play a critical role in forensic analyses, providing innovative solutions for evidence detection. They open the door for the nano-forensics, which offers efficient and rapid means for detecting evidence, such as explosive and illicit drugs. These oxides contribute to develop the advance

sensors, detectors, hetero-junctions, portable nano-chips, luminance powder, and more. The key semiconductor oxides such as ZnO, TiO₂, Iron oxides, SnO₂, metal ferrites, etc. have been used in various forensic applications including fingerprints identification, drugs/pesticide detection, and explosive residue analyses. Various analytical machines like XRD, XPS, Raman, UV-Vis., FTIR, LCMS, TEM, etc. are used with semiconductor oxides to analyze the nano-evidences. Still, continued research and engineering is needed to fully exploit the potential of semiconductor oxides in forensic applications. Despite some limitations, the future of semiconductor oxides in forensic applications looks promising.

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Author Contributions

All authors listed on this manuscript have made substantial contributions to its creation and are accountable for all aspects of the work. Each author has participated in the following aspects of the research and manuscript preparation:

- **Conceptualization:** VP, PN
- **Methodology:** VP
- **Writing - Original Draft:** VP
- **Writing - Review & Editing:** VP, PN
- **Supervision:** PN

About the Authors

Vidit Pandey:

Dr. Vidit Pandey has completed his Ph.D. in condensed matter physics from Aligarh Muslim University in 2024. His research area belongs to material science and their applications including resistive switching memory (RRAM) devices and waste-water management.



Priyanka Nehla:

Dr. Priyanka Nehla completed her Ph.D. in physics from Indian Institute of Technology Delhi, India. She has worked at Department of Materials and Engineering, Ångström Laboratory, Uppsala University, Sweden. Her research area includes nanomaterials, Heusler alloys, memory devices, battery materials etc.

