New Low-Cost and Efficient Metal Oxide Based Materials for Sensing and Energy Applications and Their Integration to Design Novel Devices

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Abstract

There is an every growing demand of higher efficient and sensitive chemical/ gas sensing nano-devices in the field of clinical diagnostic, agricultural and environmental monitoring. In this review article we discuss the compatibility of various oxide materials in different nano form that can be utilized in making a highly sensitive sensors for real time monitoring of stress and resource deficit in plants. We also discusses and compare the prerequisites in oxide nanomaterial properties such as high conductivity, higher surface to volume ratio and binder agents free surfaces that is needed in order to realize a high efficient, high capacity with high energy density at low redox voltages electrode materials for Lithium ion batteries for meeting the need of future energy consumption.

1. Introduction

1.1 Metal Oxide based Smart Sensing Devices with High Accuracy, Sensitivity, Reliability and Specificity for Electronic, Power and Agricultural application

Ultra-high sensitivity sensors with ability to detect femto- and micro molar concentration of stimuli particles are of huge significance in the biomedical field such as glucose monitoring, clinical diagnostics, food and environmental monitoring.[1,2] Hence the advancement of extremely accurate and sensitive devices and new approaches that can provide better accuracy at low cost is highly desired in agriculture and food industries.[3,4] So far, several methodologies have been explored such as colorimetric sensors, potentiometric sensors, electrochemical sensors, fluorescent sensors, and Raman spectroscopy-based sensors. Compared with other detection methods;

electrochemistry and fluorescence-based approaches offer low cost and extremely sensitive detectors that allows monitoring of various analytes, large response to recovery times along with small detection limits.

In the field of agriculture by measuring the plant physical status using imaging, fluorescence and spectroscopy technique in the visible to infrared range, plant stress and resource insufficiencies can be examined. Despite that there is a lack of compatibility or early detection methods for some type of stresses or deficits. In addition to that, they also lack the ability to differentiate between specific plant stresses and are not cost effective. Reactive oxygen species (ROS), glucose, sucrose, nitric oxide (NO), abscisic acid (ABA), jasmonic acid, methyl salicylate and ethylene are the molecules present in the plant and can be monitored by nanoscale sensors to examine plants stress and resource deficiency.[5] Real-time sensing of chemical signaling molecules in cops will improve plant health monitoring in the field. Hence development of new sensing tools by applying and utilizing nanotechnology is very much needed for real time monitoring.

Since the discovery in 1962 by Seiyama et al; that electrical conduction of Zinc oxide changes drastically in the existence of chemicals and responsive gas molecules, a great deal of efforts have been put in utilizing semiconducting metal oxides materials as chemical and gas sensors because of their lesser sizes, small cost, and great compatibility with micro-electronic fabrication. The large surface-to-volume ratio, recently, 1D nano nanostructures such as nanowires, nano-rods, nano-tubes, nano-belts and nano-spheres have attracted significantly for fabricating numerous nano-devices for chemical/gas sensors. It is clear that mostly the investigation is done on SnO_2 and ZnO nanotubes. Considerably less amount of work is done in the direction of nano-belts and nano-spheres despite, nano-spheres will have the largest surface-to-volume ratio.

1.2 Rationale for Material of Choice for Sensing and Energy Applications

TiO_2 single crystals have been explored extensively due to their suitability as a sensing element. In 1950's Cronzmeyer and Gilleo examined the bare and hydrogenated rutile TiO_2 single crystals using its optical absorption characteristic. The hydrogenated rutile titanium dioxide's absorption range expanded from visible to IR region and the crystal became blue in color. The wide optical absorbance features of TiO_2 have been explored further and that directed to the growths of black TiO_2,[6,7] an decisive solar light absorber. The formation of black TiO_2 is initiated by the lattice disorder which led to the formation of mid gap energy levels within the energy band gap that guided an improved extended absorption range. The oxygen vacancies in these disordered black TiO_{2-x} enhanced the photo response and thus improves the photo-conversion efficiency. The formation of mid gap energy levels followed by a wide absorption range is the main cause for the enhanced optical and catalytic activity in these nanoparticles. These defective black TiO_{2-x} can be used for fabricating nano-sensing devices due to its high photo catalytic activity. FIG 1 shows a pi chart of various oxide mano-materials used in chemical/gas sensors. The data is plotted based on the number of published work found on science direct search engine. The data suggest that the most studied materials for chemical/gas sensing devices is SnO_2 followed by ZnO. There is also a considerable amount of work done on V_2O_5 materials. Where as among the vast list of nanostructure forms the most explored form is nanotube based sensing devices.

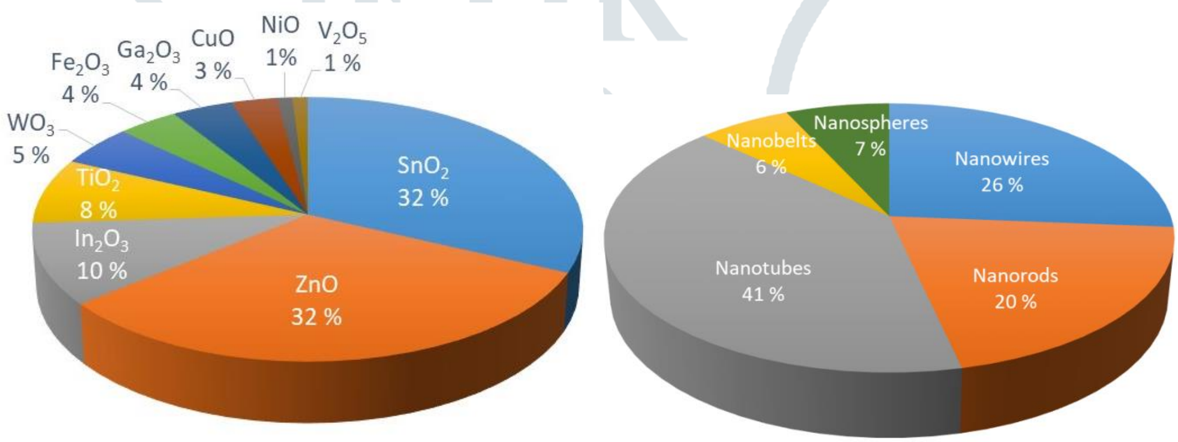

FIG 1. Top ten materials in the 1D nanostructures forms for chemical/gas sensor application. Data is generated based on published work searched on science direct.

Vanadium dioxide (VO_2) on the other hand is another tunable functional material which attracted a lot of attention in past few decades. A lot of applications like smart windows, optical switching devices, memory material with high speed and high density infrared detectors, metamaterials have been proposed and realized utilizing its property of MIT (metal-insulator transition) near the room temperature. The MIT in VO_2 can be triggered using various stimuli such as temperature, mechanical strain light, and electric field. The electrical conduction and optical absorption characteristic modifies across the MIT of VO_2 films. Recently, a plasmonic metamaterials comprising of noble metal nanostructures such as Ag, Au and Pd with vanadium dioxide have been proposed and demonstrated.[2,8,9] The shift in localized surface-plasmon resonance (LSPR) peak and the plasmon-enhanced electric field can be tuned by the intensity of phase transition across the phase transition of VO_2 films due to the change of permittivity in the vicinity of the metal nanoparticle covering VO_2 film surface. The principle of plasma induced single molecule (SM) sensing using nanoparticle is shown FIG 2. The transmission of far-infrared light can be curbed in Ag-VO_2, Au-VO_2 and Pd-VO_2 films by a periodic arrangement of sub-wavelength apertures. Contrary to that the Raman active modes from a hybrid system of Au-VO_2 can be investigated by surface-enhanced Raman spectroscopy (SERS).

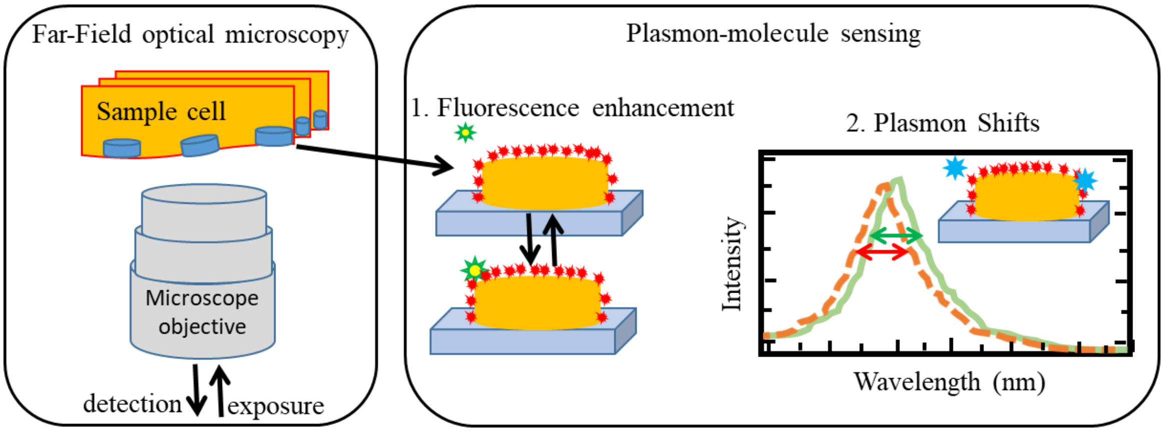

FIG 2. Plasmon-enhanced single-molecule sensing using nanoparticles.[10]

There active tunable properties makes these VO_2 based hybrid systems an interesting sturucture to explore. A relatively less explored area is whether it can be used to fabricate a multifunctional active sensor, for example, can it be utilized to probe fluorescence signals as well as Raman signals simultaneously? A dual mode sensor with Raman and fluorescence mode sensitivity has exceptional potential application in highly sensitive bio-sensing.

1.3 Novel Metal Oxides Materials for Low-Cost, Efficient Energy Devices

In this section of the article we are going to explore the recent development towards the realization of cost effective energy devices. There is an ever growing demand to design better efficiency energy storage materials, not only to furnish the needs of electric vehicles and grid storage, but to also, offer low cost energy storage to electronic and power industry through viable alternatives. Thus, development of new energy storage materials with larger capacity, fast charging and enhanced durability is a prerequisite for realizing such devices. However, nanomaterial devices come with several restrictions such as non-uniform particle size, impurities, and surface free with binding agents. Nano hazards also puts an environmental risks associated with it that restricts its limited use.

Table 1. Comparison of capacity and energy density of various electrode material for LIBs.

Electrode Material	Capacity at redox voltage	Energy Density (Wh/ g)
$LiCoO_2$	274 mAh/g at 4 V	1.1
$LiFePO_4$	165 mAh/g at 3.5 V	0.58
Nb_2O_5	200 mAh/g at 1.2−2.4 V	0.24−0.48
V_2O_5	294 mAh/g at 2.7 V	0.79
VO_2(B)	323 mAh/g at 2.6 V	0.84

In the class of vanadium oxide, especially the layered oxides such as V_2O_5, VO_2(B) has long been viewed as a likely electrode material for Lithium ion batteries (LIBs). First proposed in 1994, by Li et al., owing to the advantages such as cost effective, abundant sources and non-toxicity lot of attention have been given to VO_2(B) phase as a promising electrode material. The estimated theoretical capacity and energy density of VO_2(B) is much higher than those of already commercially available LIB electrodes as tabulated in Table 1. In particular, VO_2(B) due to its unique open framework of edge-sharing VO_6 octahedral stands out pretty good compare to other existing electrode materials. The experimental results suggests the observed low capacity and fast irreversible capacity loss in VO_2(B) electrodes, hindering their future development as one of effective electrode material in LIB. Recently with successful epitaxial growth of VO_2(B) films of Nb-STO substrate[11,12] with high conductivity S. Lee et; al. reported a considerably high capacity 265 mAh/ g along at a high current density 500 mA/ g which is the closest to the theoretical predicted values so far. Hence the high electrical conductivity makes VO_2(B) a promising electrode material for LIBs offering increased energy density to visualize commercially binder free LIBs.

2. Conclusion

Nano devices based sensors offer high spatial/temporal resolution and real time monitoring for aqueous and volatile cops signaling molecules to study and plan future smart plant sensors. By integrating the wireless, optical and electrical signal processing techniques to smart nano-biotechnology-based sensors capable of transforming the chemical signals connected with stress and resource deficiencies of plants can improve the plant growth. On the other hand development of new nano-material systems with better uniformity, less impurity and binding agent free surfaces promises high capacity and high energy density LIBs to meet the future energy need.

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