Thesis Title:

Nanostructures of Gallium Oxide and its Hybrid for Photocatalytic and Field-Emission Applications

Abstract

Index No: 120/18/Phys./26

Nanostructured gallium oxide (Ga_2O_3) has drawn much attention during the last few decades due to its extraordinary optical and electrical properties. They also include various facilities of tunable structural properties. Ga_2O_3 is a UV-transparent material exhibiting a wide band gap (~4.9 eV) and a higher room temperature mobility (~150-184 $cm^2/V.s$) which results a good charge separation between the photo-generated electron-hole pairs assisting it to become a potential photocatalytic agent for the degradation of different organic and inorganic hazardous pollutants. Also, Ga_2O_3 has its uses in display industry for making different types of field emission display units, flexible displays, and many other electronic devices due to its suitable work function, electron affinity, crystal structures and variety of morphologies. Although a huge volume of literature exists on the work done on gallium oxide nanostructure, still there are a number of problems regarding the controlled growth of novel nanostructures, understanding its electrical, optical and structural properties and many other aspects. This thesis entitled — "**Nanostructures of gallium oxide and its hybrid for photocatalytic and field-emission applications**" aimed to investigate the synthesis processes, properties and applications of different gallium oxide nanostructures. Another major goal of this thesis is to synthesize new types of gallium oxide based hybrid nanostructures and exploiting their properties for further enhancement of multipurpose performances.

Aiming to this, firstly, porous brick-like low dimensional Ga_2O_3 nanostructures were synthesized through a low-cost chemical route followed by calcination at different temperatures. The pore-density was varied by varying synthesis temperatures and the materials were exhibited a transformation from α-hexagonal to β-monoclinic phase. With traditional structural and morphological characterizations, detailed contaminant removal properties were investigated for the as-prepared samples. The green cleaning efficiency was recognized to be influenced by crystal structure, surface morphology and surface charge type of the catalyst. All of the synthesized material showed promising performance in degradation of traditional organic hazardous dyes like rhodamine B (RhB), methyl orange (MO) and apparently invisible harmful water soluble chemical like phenol. An interesting feature, i.e., obtaining dye specific adsorbent out of the same materials and the mechanism for the ion-selective dye degradation process have been presented in this work. High degradation rate constants of 0.072, 0.051 and 0.18 min^{-1} were obtained for RhB, MO and mixed dyes respectively with almost complete removal of the dyes. The role of •OH, $•O_2^-$ and h^+ radicals was correlated with catalytic performances depending upon modification of band positions of the dyes. The mesoporous Ga_2O_3 structures are hence inferred as potential candidates for future water safety issues.

Encouraged by the fruitful application of mesoporous nanocrystalline Ga_2O_3 in green water disinfection technology, introduction of junctions in the Ga_2O_3 system was attempted aiming an enhancement of its photocatalytic efficiency. For this, Ag_2O-Ga_2O_3 based type II p-n nanoheterojunctions were designed using ex-situ chemical reduction technique with different densities of Ag_2O attachment on Ga_2O_3 surface. A systematic optimization was carried out to establish best performing junction; targeting the photodegradation of noxious organic dye methyl orange (MO). Thorough theoretical and experimental studies were performed to determine relative band positions and ensure charge transfer between the counterparts. Favorable alignment of the electronic bands of Ag_2O and Ga_2O_3 was identified as a key factor for prompt separation of photogenerated e^-/h^+ pair leading to faster decomposition of water contaminant dyes. The optimized nanoheterojunction sample also performed remarkably fast in degrading carcinogenic hazardous phenol and other dyes like RhB, aniline blue (AB), eosin B (EB) and mixtures of dyes with different ionic identities. Additional advantages of these junction-based catalysts were also reflected in retainment of catalytic efficiency over multiple water disinfection cycles and its appreciable performance in active media of different pH values. With high degradation rate constants of 0.4158, 0.3306,

0.2436 and 0.207 min^{-1} for RhB, AB, MO, EB respectively, and multidimensional performance as green cleaning agent, this newly explored Ag_2O_3-Ga_2O_3 nanoheterojunctions are identified as a strong candidate for future water cleaning technology.

After the successful junction triggered catalytic activity, photocatalytic applications of Ga_2O_3 in visible region was further attempted. To achieve this goal, low dimensional Ga_2O_3 was synthesized via a facile chemical route aiming at easy morphological tuning. Different gallia-precursors as starting materials for hydrothermal synthesis eventually led to spherical nanoparticles and fractured nanobricks as the end product. In addition to the regular characterization of phase, morphology, chemical bond, and surface-related investigations; both the samples were subjected to visible-light-induced photocatalytic degradation of toxic organic pollutants. Despite its wide band gap, the samples showed an efficient dye degradation ability under visible excitation which was explained as originating due to sensitization of the dyes. In the thorough investigation of RhB dye-degradation, the nitrate-salt originated nanobricks appeared to be more efficient than the nanospheres fabricated using chloride-salt with degradation rate constants of 0.0394 min^{-1} and 0.0057 min^{-1} respectively. The performances of the samples differed due to their electronic band position. Also, morphological features like higher specific surface area, porosity, and aspect ratio enabled faster degradation of RhB for nanobricks. However, lower surface area, as reflected from BET studies and inherent agglomeration, caused comparatively weaker degradation performance of the nanospheres. This remediation technology can provide a lead for the optimization of similar future catalyst systems to be fabricated using the hydrothermal-synthesis route for the purpose of wastewater treatment.

Successful application of Ga_2O_3 in different aspects of waste water treatment encouraged us to find out whether the material can be used in a true multipurpose way. For this, gallium oxide had to response in some novel electrical application. Among different novel electrical applications, cold electron emission was identified as an important emerging sector.

Aiming for efficient cold cathode applications in low dimension, pure and rGO wrapped gallium oxide micro/nanobricks were synthesized via cost-effective solid-state and hydrothermal routes. The synthesized samples were characterized using X-ray diffractometry, field emission scanning electron microscopy, high-resolution transmission electron microscopy, and Raman spectroscopy for phase, morphology, composition, and structure-related investigations. In addition, all samples were thoroughly investigated, and as a result, experimental modifications were adapted accordingly for improving the field emission properties. Remarkable enhancement of field-emission performances with a high emission current-density of 1.08 mA/cm^2 and enhancement factor of 7400 has been observed as an effect of rGO wrapping. The results have been correlated with the increase in the availability of emission sites and proper charge carrier transport between the components in the hybrid structure. Furthermore, the probability of charge carrier transport across Ga_2O_3 /rGO junction was validated using theoretical analysis via DFT calculations. Moreover, the improvement of field emission properties due to rGO wrapping was also predicted from ANSYS simulations. Hence, 3.5 times increment of current density and 2.5 times lowering of turn-on field, the Ga_2O_3/rGO hybrid system emerged as one of the most functional future cold cathodes. This work opens up new applications for Ga_2O_3-based composites beyond the sensing and catalysis sectors.

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