TAILORING THE DEFECTS IN ZnO AND ZnO-GRAPHENE HYBRIDS FOR VISIBLE LIGHT PHOTOCONDUCTIVITY AND NONLINEAR ABSORPTION

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by

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ABSTRACT

Nano ZnO is projected as future material for optoelectronic application. However, a deep understanding of surface defect is necessary to construct high performance devices. These defects are critical in controlling its optical and electrical properties. The combination of ZnO and graphene provides hybrid materials with excellent optoelectronic properties.

This thesis mainly focuses on the synthesis of ZnO nanocones and its hybrid with graphene, discusses the nature of defects in ZnO and correlates it with optoelectronic properties like visible photoconductivity and nonlinear absorption. Tailoring the morphology and crystal facets of ZnO nanocrystals will facilitate the modification of intrinsic defects, which in turn vary the optoelectronic properties of ZnO. ZnO nanocones are synthesized by solution precipitation and hydrothermal method using polyvinyl pyrrolidone as capping agent. In this method, polyvinyl pyrrolidone enhances the crystallisation of ZnO by its excellent adsorption ability. The growth of ZnO nanocones is mainly controlled by the concentration of hydroxyl ions in the reaction medium (This part of the work is published in Materials Research Bulletin 2014). The cone shaped morphology has polar oxygen terminated facets exposed, which can facilitate oxygen vacancy centres on the surface of ZnO.

The defects in ZnO can modify the optical and electrical properties of ZnO. The photoluminescence of ZnO nanocones and its calcined samples indicate that the as-grown samples have both oxygen and zinc vacancies. After calcination, oxygen vacancies vanish and zinc vacancies enhance. Photoconductivity of the samples reduces significantly upon calcination, due to the reduction in oxygen vacancies. However, the samples exhibit a significant enhancement in the *effective* two-photon absorption upon calcination, indicating that nonlinear optical absorption originates from zinc vacancies. (This part is published in Physical Chemistry Chemical Physics 2014).

Functionalisation of ZnO with graphene can alter the ZnO defect states, by its interfacial interaction. A solution method for the in-situ growth of ZnO on reduced graphene oxide is presented. During this growth, the oxygen vacancy states are healed out by the diffusion of oxygen from graphene oxide to ZnO and the zinc vacancies are retained. The visible photoconductivity of the hybrid is depleted, compared to pure ZnO. These ZnO decorated reduced graphene oxide sheets exhibit good optical limiting property than its individual counterparts, suggesting the Zn vacancy states assisted *effective* two-photon absorption with photoinduced electron transfer between ZnO and graphene sheets. These results suggest its scope as good optical limiting material. (Published in Journal of Materials Chemistry C 2013).

Finally a layer-by-layer self assembly method is proposed for the fabrication of multilayer films with ZnO nanocones and reduced graphene oxide. These films exhibit improved photoconductivity due to efficient charge transfer from ZnO and its shuttling through graphene. Its shows saturable absorption and optical limiting with respect to input intensity.

In conclusion, this thesis presents an understanding of the defects in ZnO nanocones and reduced graphene oxide/ZnO hybrids and its relationship with properties like photoconductivity and nonlinear absorption.