Development of Visible Light Based Photocatalysts with Improved Band Gaps

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Introduction

Volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids and include a variety of chemicals (benzene, trichloroethylene), some of which may have short- and long-term adverse health effects [1]. Photocatalytic oxidation has the potential to decompose these VOCs but there is still considerable work to be done in the development of visible light based photocatalysts with activities comparable to TiO_2. Thus, research has recently progressed in the development of various oxynitrides of Zn, Ga, Ti, Li, Ge and the combination of these metals, in the hope of preparing photocatalysts with band gaps less than 3 eV [2,3]. The substitution for the orbitals of O by orbitals of N raises the highest occupied molecular orbital, and thereby lowers the band gap for catalysts with d-orbitals in the conduction band [4]. Zinc gallium oxynitrides (ZGONs) are being investigated for the degradation of acetaldehyde. Earlier, ZGONs have been the focus of research by Domen's group in Japan who have split water under visible light upon co-loading these with RuO_2 to produce 1000 µmol/hr of H_2 [5,6]. The band gaps of these samples are also known to be related to the final zinc content in the sample [7].

Materials and Methods

The catalysts were prepared under a continuous ammonia flow of 250 ml/min for a period of 15 hours with the initial molar ratio of Zn to Ga varied from 0.5 to 2 at temperatures ranging from 550°C to 850°C. The ZGONs were then analyzed using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), uv-vis spectroscopy, photoluminescence (PL) spectroscopy, inductively coupled plasma (ICP), Brunauer, Emmett and Teller (BET) surface area and other techniques. Sol-gel method of synthesis involved the crystallization of zinc gallium oxide from nitrate hydrates of zinc and gallium using NH_4OH.

Results and Discussion

The XRD data shows that the samples prepared at higher temperatures are solid solutions of ZnO and GaN with surface areas less than 10 m^2/g (BET measurements), whereas the samples prepared at lower temperatures are a combination of the two phases (confirmed also by SEM images). The bulk (ICP) and surface (XPS) zinc content are found to decrease with increasing nitridation temperatures. The surface is predominantly GaN with little ZnO. Figure 1 shows the UV – visible diffuse reflectance spectra of the samples prepared at various temperatures along with reference spectra for gallium nitride (3.4 eV) and zinc oxide (3.2 eV). As can be seen from figure 1 that the spectra for samples prepared at 650°C, 750°C & 850°C tend to red shift and the band gaps are consequently between 2.6 to 2.8 eV [8]. The reduction in band gap is attributable to the presence of zinc acceptor levels in between the valence and the conduction bands. These samples are also photocatalytically active in visible light by their 60% degradation of rhodamine B dye compared to just 20% with no catalyst in 6 hours of irradiation. Further photocatalytic tests (degradation of acetaldehyde) are being carried out to test the activities of these materials and will then be compared with TiO_2.

Improvement of these ZGONs hinges on optimizing the zinc content [7], a sol-gel technique is then employed to crystallize zinc gallium oxide which is subsequently nitrided to produce a sample with a combination of the oxide and oxyniride phases having a much lower band gap (2.4 eV) attributed to lower volatilization of zinc.

Significance

ZGONs can be employed for a variety of catalytic applications, decomposition of VOCs being one; they can also be employed in air conditioning units and possibly production of H_2 from water. These photocatalysts being active in visible light also negates the need to use expensive UV light sources.

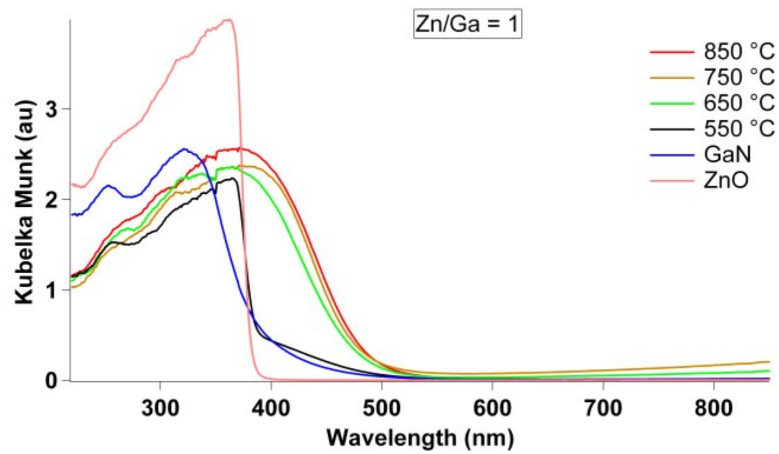

Figure 1. UV-Vis spectra of ZGONs with Zn/Ga =1

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