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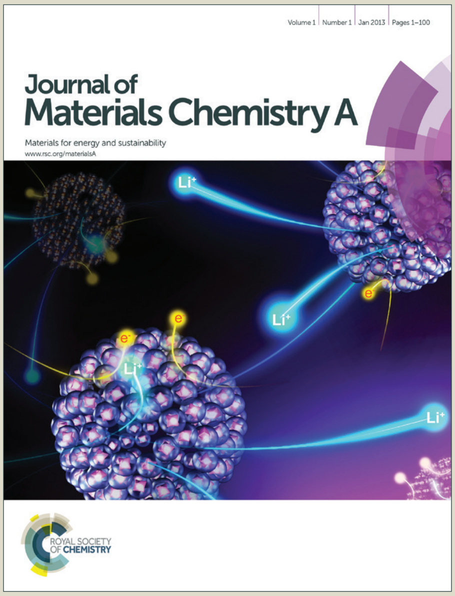

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ARTICLE

Photocatalytic hydrogen evolution using nanocrystalline gallium oxynitride spinel

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Photocatalytic hydrogen evolution from water was observed over nanocrystalline gallium oxynitride spinel under simulated solar light irradiation (320 nm < λ < 800 nm). Up to 8 μmol/h of H_2 was evolved without co-catalyst loading. The photocatalyst was synthesized by the ammonolysis of gallium nitrate hydrate ($Ga(NO_3)_3.xH_2O$). Optical measurements indicate an indirect gap (E_g) in the visible region (E_g = 2.50 eV) which is ascribed to photoexcitations from the N 2p valence states. A direct gap has an onset at ultraviolet energies (E_g = 3.69 eV), which is ascribed to photoexcitations from lower energy O 2p valence states.

Introduction

Visible light driven photocatalytic water splitting is proposed as a sustainable method for producing chemical fuel without accompanying CO_2 emissions.[1] The hydrogen fuel produced in this manner can be readily stored, allowing solar energy to be accessed even at times when sunlight is not directly available. Most photocatalysts are wide band gap metal oxides (E_g > 3 eV) that absorb only in the UV region and thereby are transparent to the vast majority of solar photons and thus have a limited utility for solar water splitting.[2] On the other hand, oxynitride compounds containing cations with d^0 and/or d^{10} electronic configurations commonly have band gaps below 3 eV that can much more efficiently harvest solar energy.[1, 2] The introduction of nitrogen is particularly important for reducing semiconductor band gaps and enabling visible light absorption. For example, ZnO (3.2 eV)[3], GaN (3.4 eV)[3], and $ZnGa_2O_4$ (4.3 eV)[4] are wide band gap semiconductors, while compounds in the GaN-ZnO solid solution typically have band gaps of 2.5 – 3.0 eV[3, 5] and can efficiently split water under visible light.[3, 5] It is therefore of great importance to discover novel oxynitride photocatalysts which may be even more effective in using visible light for solar fuel production.

In this manuscript, we report for the first time the photocatalytic evolution of hydrogen by gallium oxynitride spinel (GOS). Since first being predicted by Lowther et al.,[6] there have been numerous reports of the synthesis of GOS. The phase was first synthesized as an impurity in GaN thin films.[7, 8] It has also been synthesized at high pressures,[9-13] by ammonolysis of gallium nitrate[10] and solvothermally.[14] Products obtained solvothermally have large reported band gaps, varying from 4.1 eV to 4.9 eV,[15] while the GOS synthesized at high pressure is dark brown in colour, indicating absorption in the visible range.[9] These results suggest that the band gap might be tuned by varying synthetic conditions. While there are no reports that GOS is a photocatalyst, the reported band gaps and its appearance suggest that the material might be a good candidate for water splitting and may be useful as a platform for further study of the relationships between stoichiometry, order/disorder and local structure on photocatalytic activity.

Experimental

Nanocrystalline GOS was prepared in a tube furnace by ammonolyzing ~0.5 g of finely ground gallium nitrate hydrate ($Ga(NO_3)_3$•×H_2O Sigma-Aldrich 99.9%) in a fused silica boat. Ammonolysis was carried out under an NH_3 flow (Praxair inc., 99.99%) of 100 mL/min. The sample was heated to 550 °C at a rate of 40 °C/min and held at that temperature for 3 hrs. The furnace was then switched off and the sample allowed to cool over ~1 hr to 200 °C under flowing ammonia. At 200 °C the atmosphere was switched to extra-dry nitrogen (General Welding Supply Corp, 99.99%, 100 mL/min) and the product was quenched to room temperature. The recovered product was reground and the ammonolysis was repeated using the conditions described above to obtain the final product.

X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV diffractometer with CuKα radiation. Chemical analyses for oxygen and nitrogen were carried out using inert gas fusion by Luvak Inc., Boylston, MA, USA. Samples were heated to 120 °C for 20 min prior to analysis to remove any adsorbed species.

Photocatalytic reactions were carried out in a customized Pyrex reactor, with a closed gas evacuation and circulation system. 100 mg of sample were dispersed in 100 mL of aqueous solution containing 20 vol% methanol. The suspension was purged and degassed with argon while being stirred in the dark for 30 min, before adjusting the pressure to 40 Torr of argon (to serve as a carrier gas). Afterwards, the suspension was irradiated by a 300 W Xe lamp (Newport, Model 66984), equipped with a 10 cm water filter to eliminate IR radiation ($\lambda > 800$ nm) and a cut-off filter to eliminate light with $\lambda < 320$ nm. The amount of evolved hydrogen was detected by an inline GC-TCD system (Agilent, 7890A).

UV-Vis diffuse reflectance data were collected in a PerkinElmer Lambda 950 spectrometer over a range of 200-860 nm with a scan rate of 182 nm/min using $BaSO_4$ (Alfa Aesar, 99.998%) as a 100% reflectance standard. Powder samples were loaded into a cylindrical powder holder with a circular quartz window 16.60 mm in diameter and 1.50 mm thick mounted vertically adjacent to a 60 mm diameter Spectralon-coated integrating sphere.

For stability tests, two suspensions of 400 mg of GOS dispersed in 400 mL of aqueous solution containing 20 vol% methanol were prepared. One suspension was exposed to light for 6 hrs under the same conditions as used for the photocatalytic reaction testing. The other suspension was kept in the dark for 6 hrs. Both samples were recovered and dried at 50°C for 2 hrs.

Results and Discussion

Synthesis: An ammonolysis temperature of 550 °C was chosen for the synthesis of GOS from $Ga(NO_3)_3{\bullet}\times H_2O$ based upon several observations gleaned from the literature, since a reaction temperature was not specified in the original report.[10] Thermal treatments of the solvothermally produced spinel show that the structure is retained even after heating to 500 °C[15] while it is known that ammonolyzing $Ga(NO_3)_3{\bullet}\times H_2O$ above 600 °C[16] will produce wurtzite GaN. The XRD pattern (Figure 1) acquired for gallium oxynitride spinel produced at 550 °C (GOS-550) indicates the presence of only the nanocrystalline spinel phase.

The chemical analysis obtained for the GOS-550 sample shows N and O mass percentages of 1.85% and 24.1%, respectively, yielding a stoichiometry close to $Ga_{2.78}O_{3.65}N_{0.35}$ if a filled anion model is assumed. There are a number of stoichiometries for GOS reported in the literature, and these vary depending on the method of synthesis. For GOS obtained at 5 GPa and 1250 °C the reported stoichiometry is nitrogen rich, $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$ ($\square$ = vacancy).[12] A wide variation in stoichiometry (N molar composition 0.6% to 13.9%) was observed in solvothermally prepared GOS products after subjecting to thermal treatment under air, argon and ammonia.[15] However, these values may be limited in accuracy due to the presence of absorbates.[15]

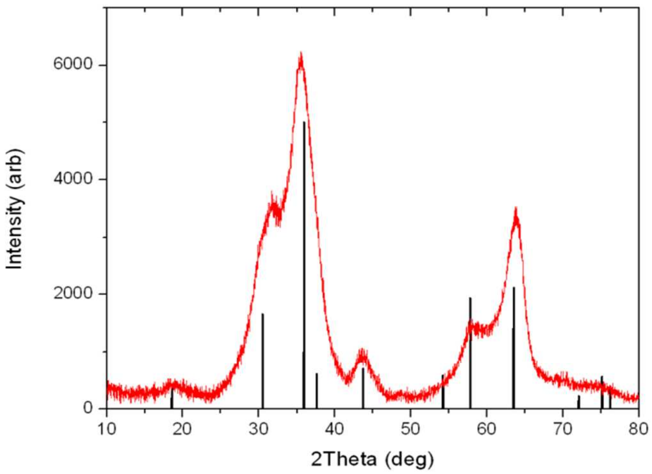

Figure 1. XRD pattern (background subtracted) of gallium oxynitride spinel products synthesized from $Ga(NO_3)_3{\cdot}\times H_2O$ at 550ºC with calculated reflections shown for Ga_3O_3N with a cell parameter of 8.25 Å.

Optical Properties: The UV-Vis diffuse reflectance data for GOS-550 indicate the absorption of visible light (Figure 2), with $0.1 < \alpha_{KM} < 1$ for energies (E) between 2.5 eV and 3 eV. The relative absorption is obtained by the Kubelka-Munk transform of the diffuse reflectance data, R, through the formula (1).

$$\alpha_{KM}(E) = (1-R)^2/(2R) \qquad (1)$$

The exponential rise in the data below 2.5 eV can be fit to an Urbach tail that precedes the optical gap, and has the functional form of (2),

$$\alpha_{Urbach} = A_U \exp\,[(E - E_g)/E_U] \qquad (2)$$

where E_U is a characteristic Urbach energy reflecting the degree of broadening, E_g is a characteristic gap energy that is often slightly (direct) or substantially (indirect) larger than the optical gap energy, depending on its nature, and A_U is a scaling prefactor. The fit indicates a modest degree of Urbach broadening ($E_U = 0.16$ eV), and the characteristic gap energy is substantially higher in energy than the regime over which Urbach scaling is followed, suggesting that the present system has an indirect gap (Figure 3).

Optical transitions typically follow the scaling relationship (3),

$$\alpha_{KM} = A\,(E - E_g)^n / E \qquad (3)$$

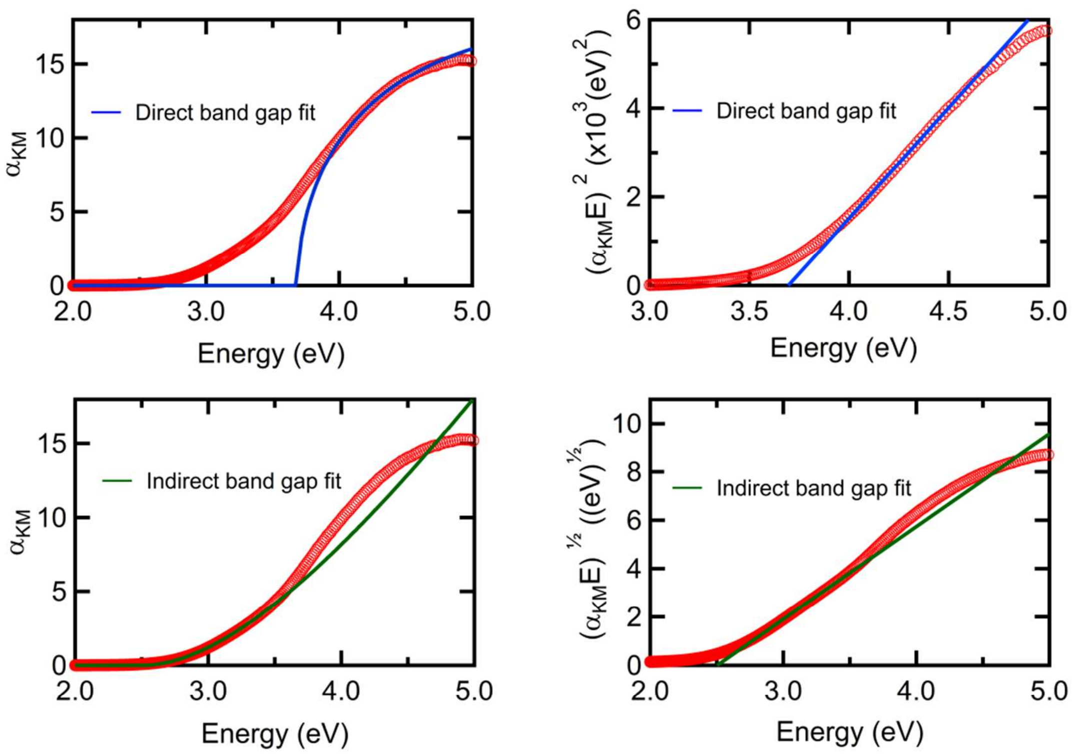

Figure 2. Regimes over which gallium oxynitride spinel exhibits an indirect (top, green lines) and direct (bottom, blue lines) optical gap, as shown for the relative absorption data obtained by the Kubleka-Munk transform of diffuse reflectance (left) and for the same data rescaled to appear linear when the functional form for this absorption is obeyed (right).

with a power n = 2 for indirect excitations and n = 0.5 for direct excitations, where E_g is the gap energy, and A is a prefactor related to the intensity of the transition.[17] The energies over which this relationship is followed will appear linear when the data are appropriately rescaled, and indicate that the lowest energy optical gap is indirect in nature for the present system. There is also appears to be an allowed direct gap optical transition whose onset is about 1 eV higher in energy (Figure 2). Quantitative fits (Figure 2, solid lines) to the appropriate regions indicate that the indirect gap is 2.50 eV while the direct gap is 3.69 eV. Based on analogues with other oxynitride compounds such as the wurtzite $(GaN)_{1-x}(ZnO)_x$ solid solution, we hypothesize that the lower energy indirect transitions originate in localized limited minority N 2p anion states while the more intense direct states are associated with strongly hybridized O 2p anion states that are about 1 eV lower in energy due to the higher electronegativity of O relative to N. These band gaps are substantially lower than those previously reported for solvothermally-prepared GOS (4.1– 4.9 eV direct gap).[15] It is not known if the difference in the determined optical gaps is due to differences in the quantification methodology or in the different sample stoichiometries that may result from different synthesis routes. Optical properties of high-pressure GOS have not been reported. Because of their increased N content, high-pressure GOS samples are expected stronger visible light absorption relative to ammonolyzed products. In contrast to the GOS product reported here nitrogen rich wurtzite type gallium oxynitrides were found to have direct band gaps.[18] Similarly, a direct band gap of 2.7 eV has been reported for a bimetallic zinc gallium oxynitride spinel.[19]

Indirect band gap materials can be efficient water splitters despite their lower light absorption rates compared to materials with direct band gaps. For example, a significant difference in photocatalytic activity was observed between two polymorphs of $NaTaO_3$, one with a direct band gap (~4.0 eV) and the other having

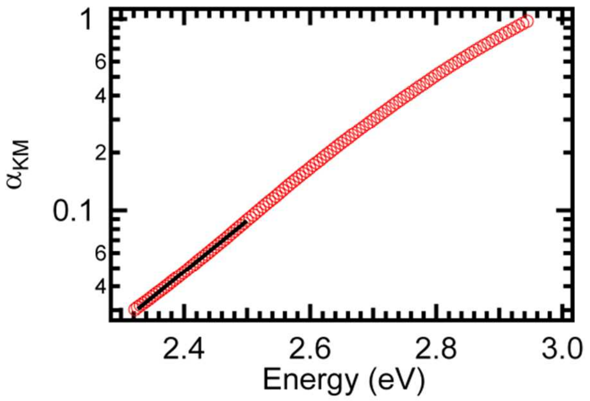

Figure 3. Relative absorption (α_{KM}) on a log scale for gallium oxynitride spinel synthesized by ammonolyzing $Ga(NO_3)_3 \cdot xH_2O$. Fit to the low-energy Urbach tail is overlaid (black line).

an indirect gap (~4.1 eV).[20] The polymorph with the indirect band gap showed about 150 times higher H_2 evolution rate than the other polymorph under same conditions.[20] The same phenomena is observed with anatase (direct band gap ~3.2 eV) and rutile (indirect band gap ~3.0 eV) TiO_2.[21] It has been suggested that the longer charge carrier life arising from the lower recombination rate of hole-electron pairs in indirect band gap materials is one of the contributing factors for higher activity,[20, 21] and thus higher internal quantum efficiencies may be expected for indirect gap semiconductors.

Photocatalytic H_2 production and stability in water: The photocatalytic activity for GOS-550 was tested under simulated solar light irradiation (320 nm < λ < 800 nm) with methanol as a sacrificial reagent. GOS-550 has a maximum H_2 evolution rate of 8 µmol/hr, although there was a slight induction delay in photocatalytic activity (Figure 4). The observed photocatalytic activity confirms that the conduction band edge of $Ga_{2.78}O_{3.65}N_{0.35}$ is low enough for H^+ reduction. It is also important to note that this activity was measured without loading the surface with co-catalysts often used to increase the H_2 production rate. For example, TiO_2, a well-known semiconductor exhibiting high photocatalytic activity under UV irradiation, does not produce hydrogen without the loading of co-catalysts.[2] A comparison between maximum activities for H_2 evolution for the catalyst produced in this project and other Ga-based oxides described in literature (under UV irradiation with methanol as a sacrificial reagent) is shown in Table 1. GOS-550 compares favourably with these photocatalysts considering that no surface modification was performed.

Table 1. Comparison of gallium oxynitride spinel H_2 evolution activity under UV radiation (methanol sacrificial reagent) with that of Ga based oxides

Oxide	Band Gap (eV)	Co-catalyst	H_2 evolution rate (µmol/h)	References
$Ga_{2.78}O_{3.65}N_{0.35}$	2.50	None	8	This work
$ZnGa_2O_4$	4.3	None	1.5	Ref. 4
$ZnGa_2O_4$	4.3	RuO_2	10	Ref. 4
β–Ga_2O_3	4.6	Pt	50	Ref. 22
$Ga_{1.14}In_{0.86}O_3$	3.7	Pt	30	Ref. 22

Despite the promising initial photocatalytic activity, the longer term activity of GOS decreases sharply after 4 hours. Further experiments were carried out to investigate the reason for this change. Optical analysis of the GOS sample irradiated in a 20% methanol solution for 6 hours shows a complete loss of band gap absorption in the visible region (Figure 5). Photo-degradation occurring due to photo-generated holes is a common issue with many non-oxide semiconductors, including other previously studied oxynitrides.[23-25] However, GOS is unusual in that nearly complete degradation occurs even without irradiation (Figure 5), suggesting indicates that GOS also slowly reacts with aqueous solutions. The loss of nitrogen due to both photo-oxidation and water corrosion rapidly diminishes the ability of GOS powders to absorb light in the visible region, stopping the photocatalytic reaction. The XRD patterns for degraded samples show that gallium oxide hydroxide, GaO(OH) forms in the irradiated sample, but not in the dark sample (Figure 6). The degradation mechanism is ascribed to the initial water-induced loss of N from the GOS, followed by the photo-induced degradation producing GaO(OH).

In order to improve the stability and the photocatalytic activity of GOS, several strategies can be pursued. In a recent study Hu et al demonstrated that Si, GaAs, and GaP photo anodes can be stabilized in water by depositing thin TiO_2 films over the catalyst, eliminating direct contact with the aqueous solution.[26] Also, introduction of a co-catalyst is known to improve the photostability of oxynitrides.[23-25] In the case of TaON adding IrO_2 as a co-catalyst substantially decreased the rate of N loss due to photo-oxidation.[23]

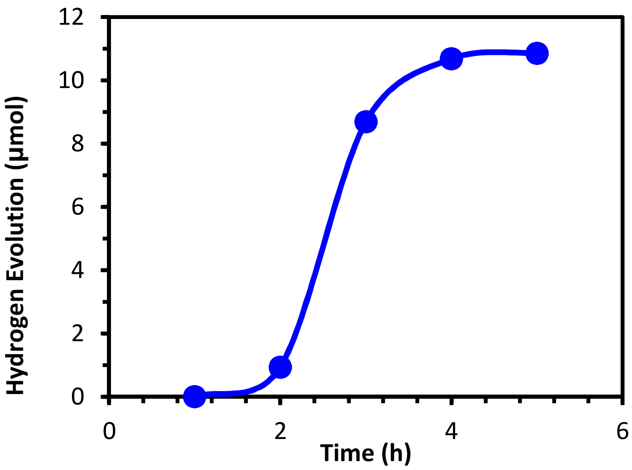

Figure 4. Evolution of hydrogen from spinel gallium oxynitride suspension over a 20% methanol in water solution irradiated with a 300 W UV lamp (320 nm).

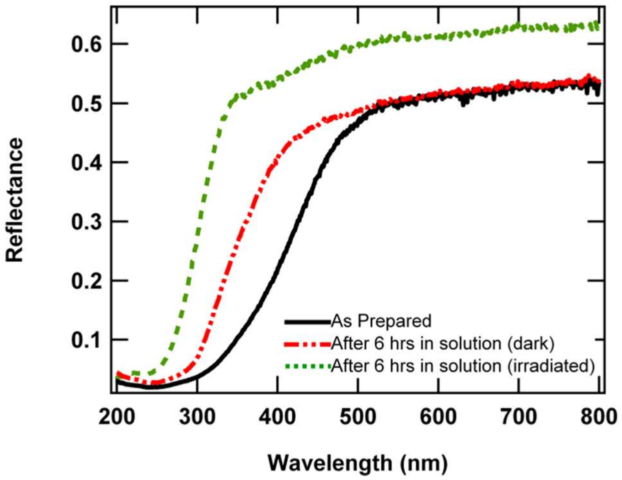

Figure 5. The UV-Visible diffuse reflectance spectra of GOS as prepared (black), after 6hrs in 20% methanol solution in dark (red) and after 6 hrs in solution under irradiation (green)

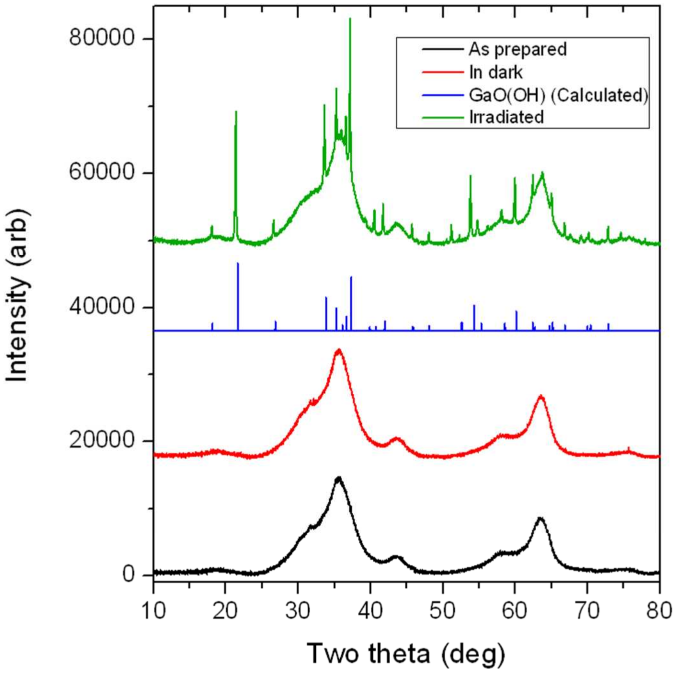

Figure 6. The XRD patterns of GOS, as prepared (black), after 6 hrs in 20% methanol solution in dark (red) and after 6 hrs in 20% methanol solution under irradiation (green). The calculated pattern for GaO(OH) is shown in blue.

Increasing the crystallinity is a possible approach to increase the activity of GOS. High crystallinity is often correlated to high photocatalytic activity as crystal defects can act as recombination sites for photo-generated holes and electrons, thereby preventing the carriers from reaching the surface of the particle. As a result, crystal defects are often linked to reduction in the overall quantum efficiency of photocatalysts.[2] For example, the photocatalytic water splitting activity of GaN-ZnO solid solution showed about threefold increase after calcination at 873 K and the associated decrease of recombination between photogenerated carriers due to reduced defect concentration was suggested as the cause.[27] In $NaTaO_3$ the crystallinity was improved by adjusting the concentrations of NaOH in the reaction mixture which corresponded to about seven fold increase in photocatalytic H_2 production activity.[28] Even in highly crystalline materials surface defects can reduce photocatalytic activity as observed in nanoparticulate ZrO_2-TaON solid solution where activity was improved by the reduction of surface defect density.[29] Along with improving its crystallinity and decreasing surface defect concentrations, surface modifications with a co-catalyst (Table 1) may also improve photocatalytic activity for GOS. There are few systems with both strong visible light absorption and conduction band levels appropriate positioned to enable the production of H_2 gas, so it is of great interest to determine if the activity of the GOS can be further improved by these methods for optimization.

Conclusions

A visible light absorbing gallium oxynitride spinel is demonstrated to be capable of photocatalytically evolving hydrogen. A maximum H_2-evolution rate of about 8 μmol/hr was observed without the use of co-catalysts on the nanocrystalline gallium oxynitride spinel synthesized by an ammonolysis route. This sample has light absorption in the visible region corresponding to an indirect band gap of ~2.50 eV and the absorption at photon energies higher than 3.5 eV is consistent with a direct band gap of ~3.7 eV. Stability tests indicate that GOS is susceptible to corrosion from water and photo-oxidation, which produces GaO(OH). Further improvement of this system must begin with the development of good coating procedures, such as the ALD titanate films that have proved effective in improving the performance of other non-oxide semiconductors.

Acknowledgements

The National Science Foundation (United States) supported the synthesis, characterization, catalytic testing and manuscript preparation (Grant DMR-1231586). This work was in part carried out at Brookhaven National Laboratory (including the collection of optical data at the Center for Functional Nanomaterials), which is supported by the Department of Energy under grant DE-AC02-98CH10886. The optical characterization of semiconductors (HH, PGK) was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (Grant DE-FG02-11ER16266).

Notes and references

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