Characterisation of Semi-Conductor Zinc Oxide (ZnO) thin films as Photocatalysts

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Abstract

The objective of this project was to study the suitability of nanostructured ZnO thin films as efficient photocatalysts and to characterise any issues that may be involved in the scale-up of photocatalytic systems based on these types of immobilised nanostructure ZnO thin films. In particular, this study involved fabricating and then evaluating the effectiveness of a range of nanostructured zinc oxide (ZnO) thin films with different structures and chemistries (i.e. un-doped and doped) as photocatalysts, and thereafter to systematically relate: the initial and reacted surface morphology; photocatalytic activity in terms of reaction rate; reaction intermediates and products; and liquid phase and solid phase reaction mechanisms under both limited and rich oxygen conditions at two different UV irradiation wavelengths (254nm and 340nm). These nanostructured thin films (i.e. undoped ZnO; nitrogen doped ZnO – N:ZnO; cobalt doped ZnO – Co:ZnO) were produced using an innovative combination of magnetron sputtered surfaces and hydrothermal solution deposition that allows the morphology, porosity and thickness to be controlled by varying the composition and processing conditions. SEM, UV-Vis, HPLC, LC-MS, AAS and XRD were used to study the changes in thin film morphology, Methylene Blue (MB) degradation and its reaction intermediates, the presence of Zn metal in the reaction fluid, if any, and crystallinity before and after the photocatalytic reaction respectively.

Undoped ZnO thin films: Results showed a clear relationship between surface morphology (and the related thin film preparation method) and photocatalytic activity for the ZnO thin film supported catalysts: the tallest, most aligned structure had the highest photocatalytic activity, whilst the smallest, least aligned structure had the lowest. Thus, the MB degradation rate was the fastest for the ZnO thin film (S2-MS) with a uniform arrayed structure. Adding oxygen made the films more stable: in oxygen-limited conditions, SEM and atomic absorption spectroscopy indicated zinc leaching had occurred. Furthermore, with additional oxygen the zinc leaching was minimised under the same reaction conditions. It is thought that this additional oxygen is either minimising the release of, or replacing lost ZnO lattice oxygens, indicating that this ZnO photocatalytic oxidation could be occurring via a Mars van Krevelen type redox mechanism.

There was also a significant difference in MB degradation rates, as well as reaction intermediate formation and destruction rates, correlated to the morphologies and crystallinity at both UV wavelengths, with the highest reaction rates at 340nm. Reaction analysis indicates that there is a competition between two different photocatalytic mechanisms: conventional photocatalysed radical oxidation and lattice oxygen-driven oxidation. The dominant reaction mechanism depends on the thin film morphology, crystallinity, availability of oxidant and the wavelength of the incident UV. The surface-photocatalysed radical formation was predominant for more aligned, highly crystalline, morphologies, where there was plentiful oxygen and UV irradiation at 340nm. Lattice oxygen photodegradation was predominant for the less aligned, more amorphous morphologies and UV irradiation at 254nm.

Doped (Co:ZnO) thin films: Results showed that cobalt dopant increases the photo-stability of the corresponding undoped thin films under oxygen-limited conditions − increasing with the increased dopant concentration. This increased stability of Co:ZnO nanostructure thin films comes with a price, however: the photocatalytic activity and concomitant degradation of MB and its azo dyes reaction intermediates is in general lowered, compared to the undoped ZnO thin films. At higher dopant concentrations, under oxygen-rich conditions and with UV irradiation at 254nm and 340nm, the MB degradation most likely occurs via a conventional photocatalytic reaction mechanism and/or via charge transfer of the MB into Azure B (AB) with the absence of Mars van Krevelen type mechanism (because of the increased lattice stability). At lower dopant concentrations under oxygen-limited conditions with UV irradiation at 254nm and 340nm, the Mars van Krevelen type reaction mechanism is probably the main mechanism propagating the oxidation of MB.

Overall, the undoped morphologies were more photocatalytically active compared to the doped morphologies. In general, this work has shown that several different solid and liquid phase photocatalytic reaction mechanisms govern the photocatalytic degradation of azo dyes such as MB on nanostructured ZnO thin films, and that surface morphology, crystallinity, lack or presence of oxygen, and the dopant concentration are the key parameters governing the overall photocatalytic activity and the activation of these different solid and liquid photocatalytic reaction mechanisms.

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Nomenclature

ZnO	Zinc Oxide
N:ZnO	Nitrogen Doped Zinc Oxide
Co:ZnO	Cobalt Doped Zinc Oxide
MB	Methylene Blue
AB	Azure B
AC	Azure C
TH	Thionin
R , $R'^{\bullet}$	Alkyl radicals
TEA	Triethyleneamine
HMT	Hexamethylenetetramine
TFA	Trifluoro Acetic Acid
MO	Metal Oxide
UV	Ultra Violet
HPLC	High Performance Liquid Chromatography
UV-Vis	Ultra Violet Visible Spectrophotometer
AAS	Atomic Absorption Spectroscopy
XRD	X-ray Diffraction
LC-MS	Liquid Chromatography-Mass Spectrometry
EDX	Energy Dispersive X-ray Spectroscopy
µmol/L	Micro Mole per Litre

mg L^{-1}	Milligram per Litre
Wt%	Weight per Cent
rpm	Revolution per Minute
mL	Millilitre
mm	Millimetre
µm	Micrometer
S	Exposed Surface Area
t	Time
N	Number of Moles
K	Adsorption Equilibrium Constant
V	Liquid Volume (m^3)
W	Mass of the Solid Catalyst (kg)
V_s	Volume of the solid catalyst (m^3)
k'_{app}	Apparent Reaction Rate Constant on Mass Basis ($m^3kg^{-1}s^{-1}$)
k''_{app}	Apparent Reaction Rate Constant on Area Basis ($m^3m^{-2}s^{-1}$)
k'''_{app}	Apparent Reaction Rate Constant on Volume Basis ($m^3m^{-3}s^{-1}$)