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Defect engineered visible light active ZnO nanorods for photocatalytic treatment of water

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ABSTRACT

Photocatalytic degradation of organic wastes and microbes in water using solar light is a green technology that requires the design of visible light active photocatalysts. Here we report the fabrication of visible light active zinc oxide nanorods (ZnO NRs), wherein the visible light absorption is enhanced by modulating the surface defects on the NRs. Oxygen vacancies in the NRs as characterized by photoluminescence and X-ray photoelectron spectroscopy are controlled by annealing at different temperatures in the ambient. The role of surface defects on the visible light photocatalytic degradation of an organic dye, industrial waste, bacterial culture and inland brackish water is studied. Results presented here provide a simple strategy to make the wide bandgap ZnO NRs visible light active, enabling their use for the photocatalytic decontamination of water.

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1. Introduction

Pollution of water bodies due to industrialization and population expansion is a serious environmental concern that requires immediate attention. Water pollution can be due to organic, inorganic or microbial contamination that can be removed by adsorption [1,2], electro-chemical processes or membrane separation [3,4], bioremediation [5] and advanced oxidation processes (AOP) [6,7] among others. AOP's are an upcoming technique of choice due to the high degradation efficiency, potency against a wide array of pollutants and negligible introduction of hazardous by-products into water bodies [7].

Photocatalysis (PC) is a green AOP which uses nanostructured oxide materials and light to break down organic and immobilize microbial contaminants in water [8–10]. When excited by light above band gap energy, exciton pairs formed on the photocatalyst surfaces interact with the surroundings to produce highly reactive species that can potentially oxidize or reduce contaminants in their proximity [11,12]. Commonly used photocatalytic materials like titanium dioxide (TiO₂) and zinc oxide (ZnO) [13–16] are inherently wide band-gap semiconductors that predominantly absorb the UV part of sunlight (4% of the spectrum), limiting their efficiency and applications. ZnO is particularly interesting as its wurtzite crystal structure allows it to be synthesized in a variety of nanostructured morphologies having distinct facet energies and surface chemistry [17]. It is an amphoteric oxide which is quasi-insoluble in water, cost effective and has proven antibacterial properties as documented in the formulation of “pushpanjan” for eyes and open wounds in Ancient India (500 BC or before) and by the ancient Greek civilization [18–22].

With a bandgap of 3.37 eV, without modification, ZnO cannot absorb the visible region of sunlight (~45% of the solar spectrum).

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This drawback is typically overcome by modifying the ZnO surfaces with visible light active materials [23–25], doping [26,27] or engineering the defects within the ZnO crystal [28–30]. Prior reports from our group have demonstrated that defect centers in ZnO can be controlled by annealing at different temperatures [15,31] or by simply modulating the growth rate of the nanostructures [29]. The defects which can be vacancies, interstitials or substitution type defects, create intermediate electron and hole traps between the valence band (VB) and conduction band (CB) leading to a reduction of energy required for exciton pair generation, rendering the materials visible light active [32,33]. Although ZnO is intrinsically defective upon synthesis, these defects are typically deep with high formation energies [34] and need to be engineered to effectively contribute to the charge separation process upon light absorption. Oxygen vacancies and zinc interstitials are two predominant intrinsic defects which are reported to be favorable for photocatalysis [34–36]. However the formation of these defects is largely governed by the synthesis environment, where a zinc rich environment typically leads to oxygen vacancies and zinc interstitials and an oxygen rich environment leads to zinc vacancies and oxygen interstitials [37–39]. Association of electrons/holes trapped in these defects with surface adsorbed oxygen and hydroxyl species, leads to the formation of O_2^- , OH^* and other oxygenated radical species [40,41] which are very effective in degrading contaminants in water. In fact if the oxidation power of chlorine is considered as 1, OH^* radicals have a relative oxidation power of 2.6, which is well above that of hydrogen peroxide (H_2O_2) and ozone (O_3) [14], both of which are widely used in the industry. Additionally, the short life-time and localized operating range of the excited species [40] prevents any outfall due to long term effects, which could prove detrimental to the environment and ecology. Thus photocatalysis is a green process of decontaminating water and defect engineering of ZnO leads to a viable alternative towards improving its photocatalytic efficiency in ambient conditions [42].

In this manuscript we focus on the optimization of surface defects in hydrothermally grown ZnO nanorod crystals (ZnO NRs) by annealing them in the ambient at relatively low temperatures (<450 °C). The efficacy of defect engineered ZnO nanorods were evaluated by the degradation of a standard dye (Methylene Blue, ISO Std. 10678:2010) and a model organic contaminant (phenol). Antimicrobial activity was evaluated by following the effects on *Escherichia coli*. Subsequently, photocatalytic inactivation of microbes in real-life situation was studied through the disinfection of inland brackish water under natural sunlight.

2. Experimental details

2.1. Preparation of ZnO NRs coated glass substrate

ZnO NRs were grown on microscopic glass slides following a previously described method [17]. Briefly, a thin layer of ZnO nanocrystallite seeds was deposited on cleaned glass substrates pre-heated to 350 °C, by spraying 25 mL of 10 mM solution of zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$; Merck, Germany) at $\sim 1 \text{ mL min}^{-1}$. The seeded glass substrates were subsequently annealed at 350 °C for 5 h.

Hydrothermal growth of ZnO NRs was carried out by placing the seeded glass substrates in a chemical bath containing equimolar concentrations (10 mM) of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$; APS Ajax Finechem, Australia) and hexamethylenetetramine ($((CH_2)_6N_4$; Sigma-Aldrich, USA), at 90 °C for a total of 10 h, where the precursor solution was changed every 5 h [43]. The as grown ZnO NRs were thoroughly washed with DI water and annealed in an atmospheric furnace at different temperatures (90, 150, 250, 350 and 450 °C) for 1 h.

2.2. Characterization

Morphology of the ZnO NRs was characterized by scanning electron microscopy (SEM; Model: JEOL JSM-7600F, Japan) operated at 20 kV and X-ray diffraction (XRD) pattern of the samples were obtained by using a Rigaku MiniFlex600 X-ray diffractometer (Japan) with $Cu K\alpha$ radiation (wavelength = 1.54 Å). Optical absorption and photoluminescence (PL) spectra of the ZnO NRs were recorded in a UV/Vis spectrometer (Lambda 25 from Perkin Elmer, Italy) and a fluorescence spectrometer (LS55 from Perkin Elmer, Italy) respectively. The surface states of ZnO NRs were studied with X-ray photoemission spectroscopy (XPS; Omicron Nanotechnology, Germany) with a monochromatic $Al K\alpha$ radiation (energy = 1486.6 eV) working at 15 kV. Samples were flooded with electrons prior to the measurements to avoid surface charging and XPS spectra were calibrated to the C 1s feature at 284.6 eV.

2.3. Photocatalytic tests

Photocatalytic degradation of methylene blue (MB) and phenol were carried out under visible light irradiation ($AM 1.5G$, 1 kW m^{-2}) from a solar simulator (SS1.6 kW from Science Tech, Canada), using the ZnO NRs on glass substrates (supported photocatalysts) annealed at different temperatures. A 10 μM aqueous solution of MB was placed along with a ZnO NR substrate ($3 \text{ cm} \times 1 \text{ cm}$) inside poly(methyl methacrylate) (PMMA) cuvettes, with the photocatalyst surface facing the light source. A bare glass substrate of identical size placed in another cuvette containing the MB acted as the control. Following equilibration under dark conditions for 1 h, photocatalytic degradation of MB was carried out under light for 90 min. Similar process was followed for the photocatalytic degradation of phenol, where 10 ppm phenol solution (Sigma-Aldrich) in DI water was used as a test contaminant and photocatalytic degradation was carried out for 180 min.

2.4. Analytical methods

Visible light photocatalytic reduction of MB was monitored by recording the optical absorption spectra of the MB solution at regular intervals. The concentration of MB was estimated from the reduction in absorption intensity of MB at $\lambda_{\text{max}} = 665 \text{ nm}$ and plotted as C_t/C_0 versus time, where C_t represents the concentration of MB at time 't' and C_0 represents the initial concentration of MB.

Concentration of phenol at various stages of photocatalytic degradation process was determined by using high-performance liquid chromatography (HPLC) equipped with a P580 high-precision pump (Dionex, Germany). A C18 column ($5 \mu\text{m}$) maintained at room temperature was used for analysis and the phenol was detected by a Dionex UVD 170S diode array detector set at 245 nm for phenol. The flow rate of phenolic solution was fixed at 1 mL min^{-1} . The mobile phase used for the HPLC analysis was a mixture of methanol and DI water in 45:55 vol ratio with pH 3.0 adjusted by using sulfuric acid. The photocatalytic degradation profile of phenol was then plotted as C_t/C_0 versus illumination time.

A first order exponential equation ($y = ae^{-bx}$) was used to fit the MB and phenol decay curves, where 'a' is a pre-exponential factor and 'b' represents the degradation rate constant in min^{-1} .

2.5. Antimicrobial tests

2.5.1. Inactivation of bacteria

Escherichia coli (*E. coli* ATCC 25922), cultured in Luria Bertani (LB) broth (Difco, USA) (media pH 7.5) at 37 °C for 12 h, were centrifuged at 5000 rpm for 10 min and re-suspended in sterile DI water prior to photocatalysis experiments. Photocatalysis was carried out by

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