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Structural, optical, photocurrent and solar driven photocatalytic properties of vertically aligned samarium doped ZnO nanorod arrays

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ABSTRACT

Vertically aligned, Samarium (Sm) doped zinc oxide (ZnO) nanorod (NR) arrays have been synthesized by simple vapour transport process. The samples were characterized by FESEM, XRD, PL, Raman spectroscopy and XPS. FESEM results showed that incorporation of Sm caused decrease in length of NRs from 25 μm to 9 μm and influence the alignment of NRs. The photocatalytic activities of methylene blue (MB) under natural sunlight irradiation results showed that the enhancement of photocatalytic efficiency from 83.02 to 97.3% for Sm doped (0–6%) ZnO NRs arrays and decreased 95.72% for higher concentration 8% of Sm. The photocurrent measurement shows photosensitivity increased from 1.085, 1.093, 1.268, 3.270 and 1.486 for ZnO NR arrays and Sm doped (2–6%) ZnO NR arrays and decreased for 8% Sm doped ZnO NR arrays. This result revealed that doping of Sm could enhance the visible-light-driven PC properties of ZnO.

1. Introduction

Building block of one dimensional (1D) ZnO nanostructures are considered to be an effective candidates in various applications, including nanogenerators, [1] field effect transistors (FETs), [2] schottky diodes, [3] acoustic resonators, [4] gas sensors, [5] field emitters [6] and solar cells [7]. Preparation of the ordered nanostructures in the form of arrays offer an improved absorbance with promising durability and improved stability on the nanostructural arrays which has applications on the reusable environment remediation for multiple degradation cycles [8,9]. Though ZnO is a good photocatalyst, its wide band gap is not good wide enough for utilize the visible region in the solar radiation [10]. By improvising band structure of ZnO through doping and inducing the defects, where initiated to utilize the solar radiation effectively, by the promotion of visible absorption and impede the recombination of photo generated charge carriers [11–13]. Apart from the transition and noble metal doping strategy, doping of rare earth metal ion could lead to the improvement of functional properties of the semiconductors. Unfilled f orbital function of the rare earth metal ions promotes the carrier distribution by acting as trap states on the host lattice. Introduction of a shallow energy level in the band function delay the carrier recombination and favours the separation of charge carriers [14,15]. Doping of rare earth metal ions in the wide band gap semiconductors (TiO_2 and ZnO) were evidence for the visible responsible applications such as photocatalyst and optoelectronic devices [14,17]. Er, Yb and its co-doping functionality on TiO_2 were exhibits higher visible photocatalytic efficiency due to the highly

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interactive adsorption sites, enhanced surface area, and prevention of electron–hole recombination [18]. Doping on mixed metal oxides structures such as TiO_2–SiO_2 by rare earth metals (La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}) has a similar effect on the properties of TiO_2 although it has been found that Ln(III)/TiO_2–SiO_2 have relatively higher catalytic efficiency in the doping system of TiO_2–SiO_2 nanoparticles [19]. Sol gel process synthesised Er/Nd doped ZnO nanorods allow utilization of visible light, greater separation of e-/h+ pairs and more adsorption of dyes on the catalyst surface as compared to bare ZnO NPs and exhibits the better photocatalytic activity under visible light [20]. In order to improvise the photocatalytic efficiency, Eu doped ZnO matrix reacted as an electron scavenger, which prevented the recombination of the separated carriers on the catalytic surface and there by improved the charge transfer process [21]. Still there is not any clear investigation on the effect of samarium ion on the ZnO host lattice and its influence over carrier transfer ability under visible irradiation for the photocatalytic application [22]. The expectation on the influence of Sm ion with the ZnO based photocatalyst led us to investigate the effect of samarium doping on the photocurrent and photocatalytic activity.

In the present work, we havesynthesised Sm doped on vertically aligned ZnOnanorod arrays and studied the photocatalytic and photocurrent performance with the influence of Sm doping concentration.

2. Materials and method

2.1. Preparation of vertically aligned ZnO NR arrays

The ZnO NR arrays were synthesized using a two-step form of physical process. [23] The deposition of ZnO seed layer (buffer layer) through DC magnetron reactive sputtering with the film thickness around 150 nm on pre cleaned Si substrate has consider to be the first step [24]. The seeded Si substrate were utilized as nucleation platform for the ZnO NR arrays growth and the suspension of well grinded equal weight ratio of ZnO powder (99.99% Sigma Aldrich) and Graphite powder (99.99% Sigma Aldrich) as consider to be the source precursors. Samarium oxide (SmO), with different weight ratios (0, 2, 4, 6, and 8 wt%) relative to ZnO, was mixed to the growth precursor. As the mixture of powder loaded on an alumina boat, the nucleated substrate was placed top down in the centre of the hot tubular furnace. The growth temperature was set as 950 °C and the growth time as 45 min under the Ar gas flow of 80 sccm. After it cools down, samples are collected from the tubular furnace.

2.2. Characterization

The phase and crystalline structure of the as prepared samples were studied using a Bruker Advance Powder X-ray diffractometers (Cu-Kα radiation; λ = 1.5418 Å). The morphology of the prepared samples was studied using a field emission scanning electron microscope (FEI-Quanta-FEG 250) operating at an acceleration voltage of 15 kV. Raman spectra of pure and doped ZnO NR arrays are recorded by Horiba-Jobin, Lab RAM HR. Laser excitation based room temperature photoluminescence (PL) properties of the synthesized nanostructural arrays were investigated under excitation by the 325 nm line of a He Cd laser. X-ray photoelectron spectroscopy (XPS, Thermo K-alpha-monochromated) was used to confirm the oxygen defect states on the surface of rods and their chemical state.

2.3. Photocatalytic experiment

Photocatalytic behaviour of pure and Sm doped ZnO NR arrays were investigated over the catalytic decomposition of methylene blue (MB) dye. Photocatalytic degradation of 15 ppm of MB was carried out under natural sunlight. Catalyst as 10 × 10 mm substrate was immersed to 5 mL of aqueous MB solution. The suspension was placed under dark for 30 min in order to reach the adsorption–desorption balance. Then irradiateunder sunlight (with $\lambda < 400$ nm cutoff filter). The concentration of MB in solution was determined by using a UV–visible spectrophotometer. The efficiency of degradation (η) was calculated by,

$\eta = (C_0 - C_t)/C_0$where, C_0 is the absorption maximum at time t = 0, and C_t is the absorption maximum after complete degradation of MB [25].

2.4. Photocurrent measurement

Photocurrent measurement and UV response was measured by two probe method (**Keysight B2902A SMU**). Photoconductor was made up of Silver contact on top of the film. The UV lamp (365 nm) is the source which is used to study the current–voltage (I–V) characteristics measurements. Readings were taken after a UV light was turned on and off.

3. Results and discussion

The surface morphology of NRs on ZnO seed layer deposited Si substrate was investigated by FESEM. Fig. 1 shows cross sectional and top-view FESEM images of the vertically aligned ZnO NR arrays with different Sm doping concentrations that range from 0 to 8 wt%. The length of the NRs decreased from 22 μm, 16 μm and 12 μm for ZnO NR and Sm dopant (0–4%) respectively The average diameter of ZnO NR increased from 70 to 270 nm, whereas the density decreased from 30 to 17 rods