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ZnO nanowires and nanorods based ZnO/WO_3/Pt heterojunction for efficient photocatalytic degradation of estriol (E3) hormone

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ABSTRACT

In this report, ZnO nanowires and nanorods based ZnO/WO_3/Pt heterojunction were successfully prepared on a glass substrates via a facile hydrothermal growth method followed by spraying. The photocatalytic performance was evaluated by the degradation of estriol (E3) hormone under UV light irradiation (~365 nm) in a closed continuous flow reactor. The as-prepared samples achieved an excellent photodegradation rate in the range of 23-37% and 63-86% for the nanorods and nanowires morphology, respectively. This article provides a new insight into the construction of suitable geometrically optimized heterojunction for the remediation of persistent bio toxicants.

Keywords: ZnO, heterojunction, photocatalysis, estrogenic hormone, degradation

1. Introduction

Over the past few decades, the persistent release of bioactive toxicants is putting living beings at risk even at minuscule concentrations (ng/L). Among the commonly discharged steroidal hormones such as estrogen, testosterone, estrone (E1), 178-estradiol (E2), and estriol (E3), adverse physiological effects have been reported. These contaminants of emerging concern fall under a broad category known as endocrine disrupting chemicals (EDCs), which interfere with the physiological functions of hormones, potentially causes numerous illnesses [**1**]. Photocatalysis is currently considered one of the most promising approach for the remediation of environmental pollutants [**2,3**]. To overcome the low efficiency of single components systems, the construction of a heterojunction is deemed to enhance spatial charge separation and modulation of redox potentials [**4,5**]. ZnO is a versatile highly oxidizing photocatalyst possessing a direct energy bandgap of 3.2 eV and its structure can be easily modified to achieve significant improvement in the optical, chemical, and electrical properties. The photocatalytic activity depends both on morphological and structural parameters [**6**]. Different synthesis methods for ZnO yield varied morphological configurations, crystallinity, and surface to volume ratio, such as nanorods, nanoforest, nanospheres [**7,8**]. In comparison to thin films, 1D morphology excels due to pronounced quantum confinement effect and high specific surface area while keeping good adherence to the solid substrate [**9**]. In this work, ZnO in two different morphologies i. e., nanorods and nanowires were synthesized and coupled with WO_3/Pt to form heterojunction samples. The photocatalytic performance was evaluated by the photodegradation of E3 hormone in a closed continuous drip-flow reactor.

2. Experimental section

2.1. Materials and methods

Elongated ZnO structures were prepared by hydrothermal method. First, a seed layer was prepared by using zinc acetate solution coated etched microscope glass followed by annealing at 500 °C. After that, seeded substrate was immersed into equimolar (0.05 M) zinc nitrate hexahydrate and hexamethylenetetramine and (0.016 M) poly-ethyleneimine (PEI) aqueous solution with the seeded substrates up-side down at 93 °C for 16 h to grow (ZnOnr) arrays. By doubling the amount of PEI, nanowires (ZnOnw) were obtained, keeping the same procedure otherwise. The obtained samples were rinsed with deionized water, dried, and annealed at 500 °C in a Muffle furnace to remove PEI and improve ZnO crystallinity prior to heterojunction fabrication. For fabrication of ZnO/WO3/Pt heterojunction, platinized WO_3 nanoparticles (RENECAT, Toshiba, Japan) were sprayed over prepared ZnOnr/nw and left for room drying.

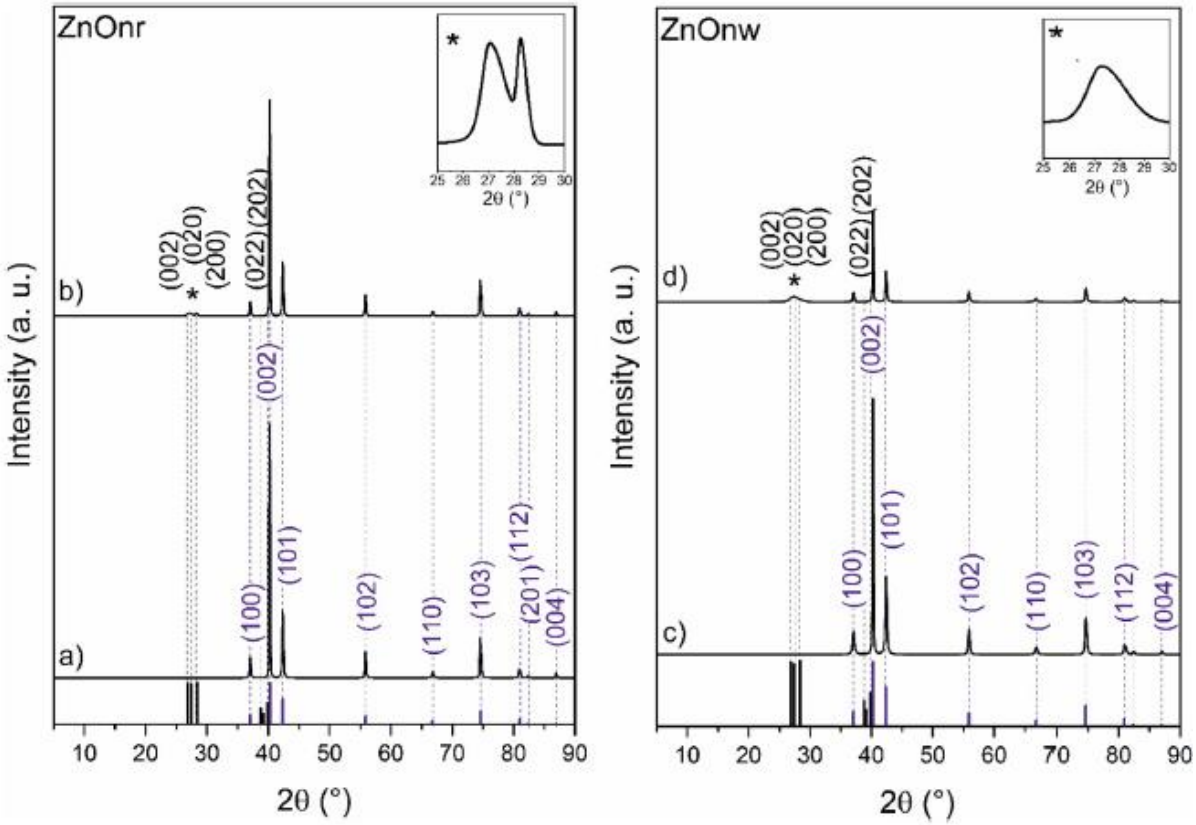

Fig. 1. X-ray diffractogram patterns of ZnOnr (a) and corresponding ZnOnr/WO_3/Pt heterojunction (b) in the left panel, ZnOnw (c) and ZnOnw/WO_3/Pt (d) in the right panel. The peak assignment is blue for ZnO and black for WO_3/Pt.

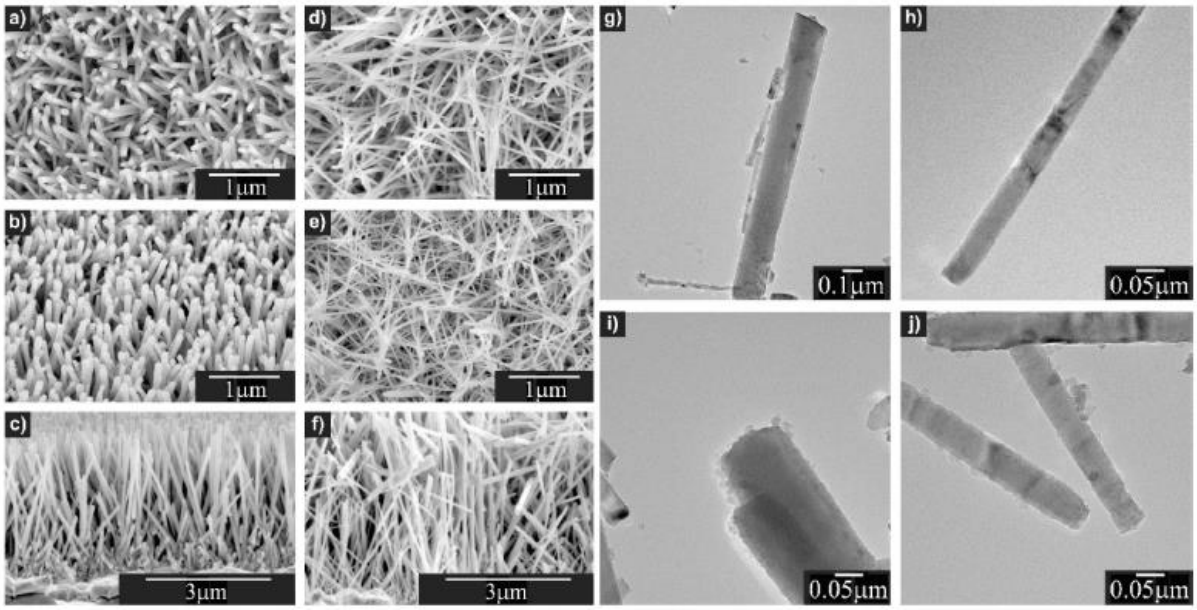

Fig. 2. SEM micrographs of ZnOnr (a), ZnOnr/WO_3/Pt (b) and cross-section of ZnOnr (c), ZnOnw (d), ZnOnw/WO_3/Pt (e), and cross-section of ZnOnw (f). TEM micrographs of ZnOnr (g), ZnOnr/WO_3/Pt (i), ZnOnw (h) and ZnOnw/WO_3/Pt (j).

2.2. Characterization methods

The crystalline phase composition was determined by the X-ray diffractometer using MiniFlex 600 (Rigaku, Japan) with a Co-Kα X-ray source. Morphology was investigated by NovaNanoSEM 450 (FEI, The Netherland) and JEM-2100 TEM (Jeol Ltd., Japan). For the light irradiation source, the UVA light lamp (UVP-XX-15BLB, 15 W, Analytik Jena, Germany) was used at an intensity of 2 mW/cm^2 measured at the surface of the samples.

Table 1 EDX analysis of ZnOnr/nw and corresponding ZnO/WO_3/Pt heterojunction (in atomic %).

Element	ZnOnr	ZnOnr/ WO_3/Pt	ZnOnw	ZnOnw/WO_3/Pt
Si	6.9 ± 0.7	11.5 ± 1.8	8.6 ± 0.7	12.6 ± 1.7
Ca	1.4 ± 0.1	1.9 ± 0.1	1.7 ± 0.1	1.5 ± 0.3
O	45.1 ± 1.1	50.3 ± 2.1	45.5 ± 0.9	47.5 ± 2.4
Zn	46.6 ± 1.9	33.8 ± 2.8	44.1 ± 1.5	36.9 ± 2.8
W	–	1.6 ± 0.8	–	1.2 ± 0.3
Pt	–	0.9 ± 0.4	–	0.4 ± 0.1

Each photodegraded hormone sample was evaluated using HPLC in triplicates and mean values are reported. An uncoated microscopic glass was used as a reference. The method for sampling, detection, and quantification of E3 in water solutions previously reported by Yasir et al. was used [**10**].

3. Results and discussion

Diffractograms of as-grown ZnO nanorods (ZnOnr), nanowires (ZnOnw), and corresponding ZnO/WO_3/Pt heterojunction are shown in the left and right panel in **Fig. 1**, respectively.

The XRD pattern of ZnOnr (**Fig. 1**a) exhibits the wurtzite ZnO hexagonal phase structure (PDF Card No.: 01-073-8765). A dominant diffraction peak for (002) indicates a high degree of orientation with the c-axis perpendicular to the substrate surface. Narrow and intense peaks suggest a high degree of crystallinity. In contrast, the intensity of diffraction peaks for the WO_3 monoclinic phase (PDF Card No.: 01-0720677) identified for ZnOnr/WO_3/Pt (**Fig. 1**b) is very low, and peaks related to the (02 2) and (2 02) planes overlapped (100) and (002) planes indexed for hexagonal ZnO crystalline phase. Diffractograms of ZnOnw and its corresponding ZnOnw/WO_3/Pt heterojunction shown in **Fig. 1**c-d exhibit very similar diffraction patterns like ZnOnr and its heterojunction. The morphology of the samples is shown in a series of micrographs (**Fig. 2**a-f). **Fig. 2**a shows ZnOnr oriented perpendicularly to the plane and arranged in a uniform array on the glass substrate. Their length estimated from cross-section (**Fig. 2**c) is about 3 pm and thickness ~ 100 nm, according to TEM image (**Fig. 2**g). Morphology of ZnOnr/ WO_3/Pt appears very similar to pristine ZnOnr at given magnification.

Nevertheless, a closer inspection (**Fig. 2**b) revealed uniform decoration of ZnOnr by WO_3/Pt nanoparticles, also confirmed by TEM (**Fig. 2**i). Furthermore, an increased amount of PEI significantly influenced the morphology of ZnO. PEI is a well-known capping polymer for enhancing the aspect ratio of the ZnO nanorods [**11**]. In our experiment, doubling the amount of PEI resulted in significant thinning of ZnO crystallites resembling nanowires, ZnOnw (**Fig. 2**d). The orientation of individual nanowires was also changed from perpendicular to a randomly ordered one (**Fig. 2**e). As shown in the cross-section image (**Fig. 2**f), the length of nanowires is slightly higher compared to nanorods, while the thickness is halved to around 50 nm (**Fig. 2**h). Otherwise, the morphology of ZnOnw/WO_3/Pt heterojunction is like those observed for ZnOnr analogue. EDX analysis further confirmed the composition of all samples with no impurities observed and revealed small amount of Pt which is introduced together with WO_3 in RENECAT spray (**Table 1**).

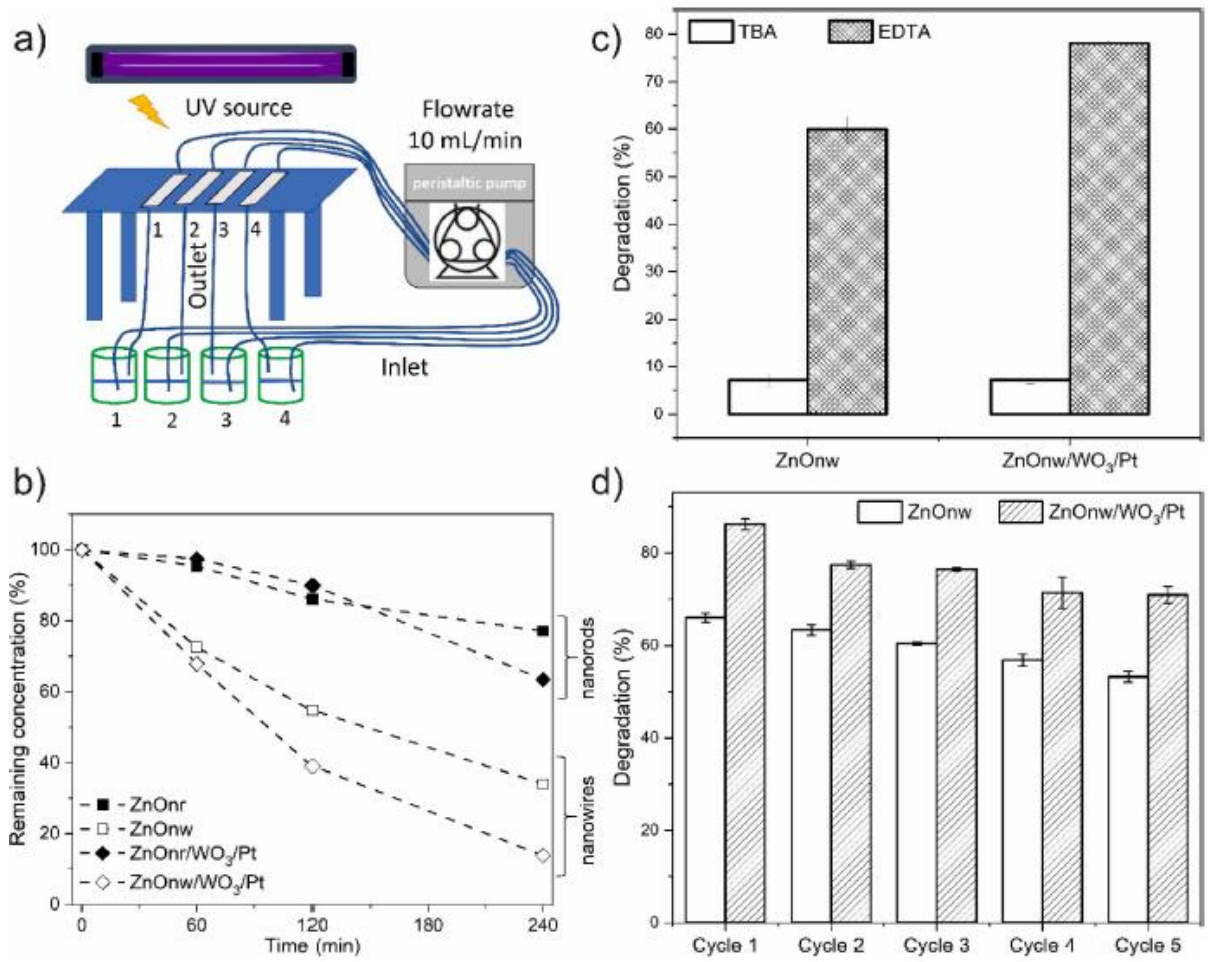

Fig. 3. Schematic of the testing apparatus (a), E3 degradation by ZnOnr, ZnOnw and corresponding $ZnO/WO_3/Pt$ heterojunction under UV irradiation in given time intervals (b), total degradation efficiency in 240 min in the presence of scavengers (c) and reusability testing (d).

The photocatalytic tests were conducted using a repurposed continuous Drip Flow Biofilm Reactor DFR 110-4PET (Biosurface Technologies Corporation, USA) consisting of 4 parallel channels. The polyethylene terephthalate covers of each channel were replaced by borosilicate glass ensuring transparency to UV. Each channel holding one standard microscope glass sample was circulated with 40 mL of E3 solution (0.2 mg/L concentration) by using peristaltic pump at a flow rate of 10 $mL.min^{-1}$. The thickness of the liquid film was 1 mm. Corresponding schematic is given in **Fig. 3**a.

Fig. 3b shows that all samples were able to degrade E3 hormone, however, the difference in their performance is evident. ZnOnw and its heterojunction are more efficient than ZnOnr due to higher aspect ratio and surface area. The highest degradation efficiency of 86.2% was observed for $ZnOnw/WO_3/Pt$ while least for unmodified ZnOnr (22.9%) in 4 h. The superior $ZnOnw/WO_3/Pt$ photoactivity could be due to the formation of a heterojunction and the injection of electrons to the reduction component, resulting in suppression of charge recombination. Thus, the degradation efficiency is enhanced by formation $ZnO/WO_3/Pt$ heterojunction for both ZnOnr and ZnOnw. To investigate the role of active species in the photocatalytic process, disodium ethylenedi-aminetetraacetate (EDTA, as a hole scavenger) and tert-Butyl alcohol (TBA, as a hydroxyl radical scavenger) were used. Results in **Fig. 3**c indicate, that photocatalytic hormone degradation is driven

by hydroxyl radicals rather than holes. Reusability of photocatalysts is another important issue. It was tested by 5 repeated runs of photocatalytic experiments using the same samples of photocatalysts. **Fig. 3**d shows, that both ZnOnw and ZnOnw/WO_3/Pt possess good stability and exhibit 80 and 82% of the initial efficacy after 5 cycles.

4. Conclusions

The ZnO nanorods and nanowires based ZnO/WO_3/Pt heterojunction were successfully synthesized, characterized, and were shown to be suitable materials for the photocatalytic degradation of endocrine disrupting chemicals. This capability was demonstrated on E3 hormone as a representative which is most difficult to be removed from wastewaters by recent methods. The overall range of efficiencies for nanorods were 22.9-36.6% and for nanowires 63.0-86.2%.

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