ZNO/CU$_2$O HETEROJUNCTIONS TREATED GLASS SURFACE FOR PHOTOCATALYTIC AND SELF-CLEANING APPLICATIONS

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Abstract

Here we report the synthesis route for glass surface functionalization by ZnO nanorods and nanowires-based Cu_2O heterojunction. In the first step, ZnO elongated structures were grown on a seeded substrate following the classic hydrothermal method, and their thickness can be controlled by polyethyleneimine (PEI) concentration. In the second step, ZnO/Cu_2O heterojunctions were fabricated by immersion of ZnO-grown substrate upside-down into the copper sulfate solution with glucose as a reducing agent. After characterization of prepared ZnO/Cu_2O heterojunction by SEM, TEM, and XRD, its application capability for waste-water treatment was successfully demonstrated on Estriol (E_3) hormone degradation under UV light by using a continuous Drip Flow Biofilm Reactor. Furthermore, functionalized glasses were shown to be effective for designing self-cleaning surfaces. The photocatalytic-induced self-cleaning ability was demonstrated by resazurin-based smart ink and *tert*-butyl alcohol-based methylene blue ink.

Keywords: ZnO, self-cleaning, photocatalytic, Estriol

1. INTRODUCTION

In recent years, the persistent release of toxicants has been of grave concern to humans and the environment. Many bioactive toxicants are dangerous for human life, even in small concentrations. Adverse physiological effects have been reported among the commonly discharged steroidal hormones such as Testosterone, Estrogen, 17ß-Estradiol (E_2), and Estriol (E_3). These contaminants are in the category called endocrine-disrupting chemicals (EDCs). Interfering these toxicants with the physiological functions of hormones potentially causes numerous illnesses [1]. Recent technologies currently in use at the wastewater treatment plant (WWTP) are ineffective in eliminating EDCs and usually cause secondary pollution.

On the other hand, photocatalysis is considered the most cost-energy-effective approach for the remediation of environmental pollutants [2]. The essential strategy is to prepare a surface containing the multifunctional semiconductor-based photocatalyst. Surface functionalization is a widely adopted technique for surface modification that allows researchers to customize surfaces to further applications. The functionalized glass was promising in applications that may benefit from photocatalytic-induced self-cleaning, day-night switchable hydrophilicity/hydrophobicity, and antibacterial [3]. According to these observations, many different synthesis routes for ZnO yield varied morphological configurations, crystallinity, and surface-to-volume ratio, such as nanorods, nanoforests, and nanospheres, were described [4 - 6]. One of the most promising synthesis routes for glass surface functionalization by ZnO nanorods and nanowires is presented. ZnO wire structures were grown on a seeded substrate following the classic hydrothermal method, and their thickness can be controlled by polyethyleneimine (PEI) concentration [7]. Next, ZnO/Cu_2O heterojunctions were fabricated by immersion of ZnO-grown substrate upside-down into the copper sulfate solution with glucose as a reducing agent [8].

This work presented two different morphologies of ZnO, i.e., nanorods and nanowires, which are synthesized and coupled with Cu_2O as a heterojunction. Furthermore, the photodegradation of the E_3 hormone in a closed cross-flow reactor showed its successful degradation. In addition, the photocatalytic activity of prepared samples under UV irradiation was evaluated by a photocatalytic test kit called "Explorer" (Ink Intelligent, Belfast, United Kingdom). This kit is suitable for assessing moderate active surfaces such as photocatalytic glass and similar products. The experiment was held according to the ISO 21066:2018 (Fine ceramics (advanced ceramics, advanced technical ceramics) — Qualitative and semiquantitative assessment of the photocatalytic activities of surfaces by the reduction of resazurin in a deposited ink film). [9] Finally, a new approach to blue-dye (Methylene blue, MB) degradation on the sample surface was demonstrated.

2. MATERIALS PREPARATION AND MEASUREMENTS METHODS

All chemicals were used as bought without any further purification. First, a solution for the seed layer was prepared using ZnO dissolved in a mixture of peroxide and ammonia (ZnO_2 seed solution). Microscope slides (Cat. No. 7105 - one side frosted) were covered by this solution via cotton wool. ZnO_2 evaporates rapidly from the surface. Slides covered in this way were annealed at 500 °C for 30 minutes in a Muffle furnace. Next, a standard hydrothermal method synthesized ZnO one-dimension elongated structures - nanorods (ZnOnr) and nanowires (ZnOnw). For the ZnO nanostructure growth (growth solution) were used zinc nitrate hexahydrate (0.05M; Sigma Aldrich), hexamethylenetetramine (0.05M; Penta), and polyethyleneimine (0.016M; Sigma Aldrich) – for ZnOnw preparation. Seeded slides were placed upside-down for growth at 94.1 °C for 12 h. Seeded substrates were immersed in the solution after the initial precipitation of the growth solution to avoid the first massive accumulation of unwanted ZnO structures (for two hours). By adding the amount of PEI, nanowires were obtained. The samples were rinsed with de-ionized water, dried, and annealed at 500 °C for 30 minutes in a Muffle furnace to remove PEI and improve ZnO crystallinity. For the fabrication of ZnO/Cu_2O heterojunctions, a method reported in the literature using glucose as a reducing agent was employed [8].

Morphology of prepared samples was performed via NovaNanoSEM 450 microscope (The Netherland, FEI company). Microscopic images were taken using an ETD (topographic contrast) detector at an accelerating 5 kV voltage. Distance up to sample (WD – Working Distance) 5 mm.

The crystalline phase composition and diffraction lines position of all as-prepared samples was determined by the X-ray diffractometer MiniFlex 600 (Japan, Rigaku) with a Co-Kα X-ray source working at 40 kV and 15 mA. The detailed morphology and composition of samples were observed by JEM-2100 TEM (Jeol Ltd., Japan) at an operational voltage of 250 kV.

All UV-light-dependent experiments used UVA light (UVP-XX-15BLB, 15W, PN 95-0042-11, Analytik Jena). The light intensity at the top of the microscopic slides with samples was optimized by radiometer RM-22 (Opsytec Dr. Gröbel GmbH) to be 2 mW/cm2.

Each photodegraded E_3 sample of $ZnOnw/Cu_2O$, and $ZnOnr/Cu_2O$ heterojunctions on the functionalized glass surface were evaluated using HPLC in triplicates, and mean values were reported.

The photocatalytic activity with a hole-dependent mechanism was evaluated by the photocatalytic test kit Explorer (Ink Intelligent, Belfast, United Kingdom). The photocatalytic activity based on the electron pathway was measured by MB discoloration.

3. RESULTS AND DISCUSSION

The morphology, surface structure composition, and detail of ZnO/Cu_2O heterojunction, microscopy slide, and Cu_2O microparticles are shown in **Figure 2**. It shows that ZnO wires and rods are arranged in a uniform array and oriented orthogonally to the plane of the glass slides. The length was estimated to be 3 microns and the thickness to be 100 nm, according to the TEM detailed image. The morphology of $ZnOnr/Cu_2O$ heterojunction shows many Cu_2O particles with dimensions ranging from 500 nm to 1 micron entangled in ZnOnr. Observed Cu_2O microparticles are not growing at the top of nanorods but instead seem to be pierced through the nanorods. The addition of PEI resulted in significant lengthening and tapering of rods resembling nanowires, ZnOnw.

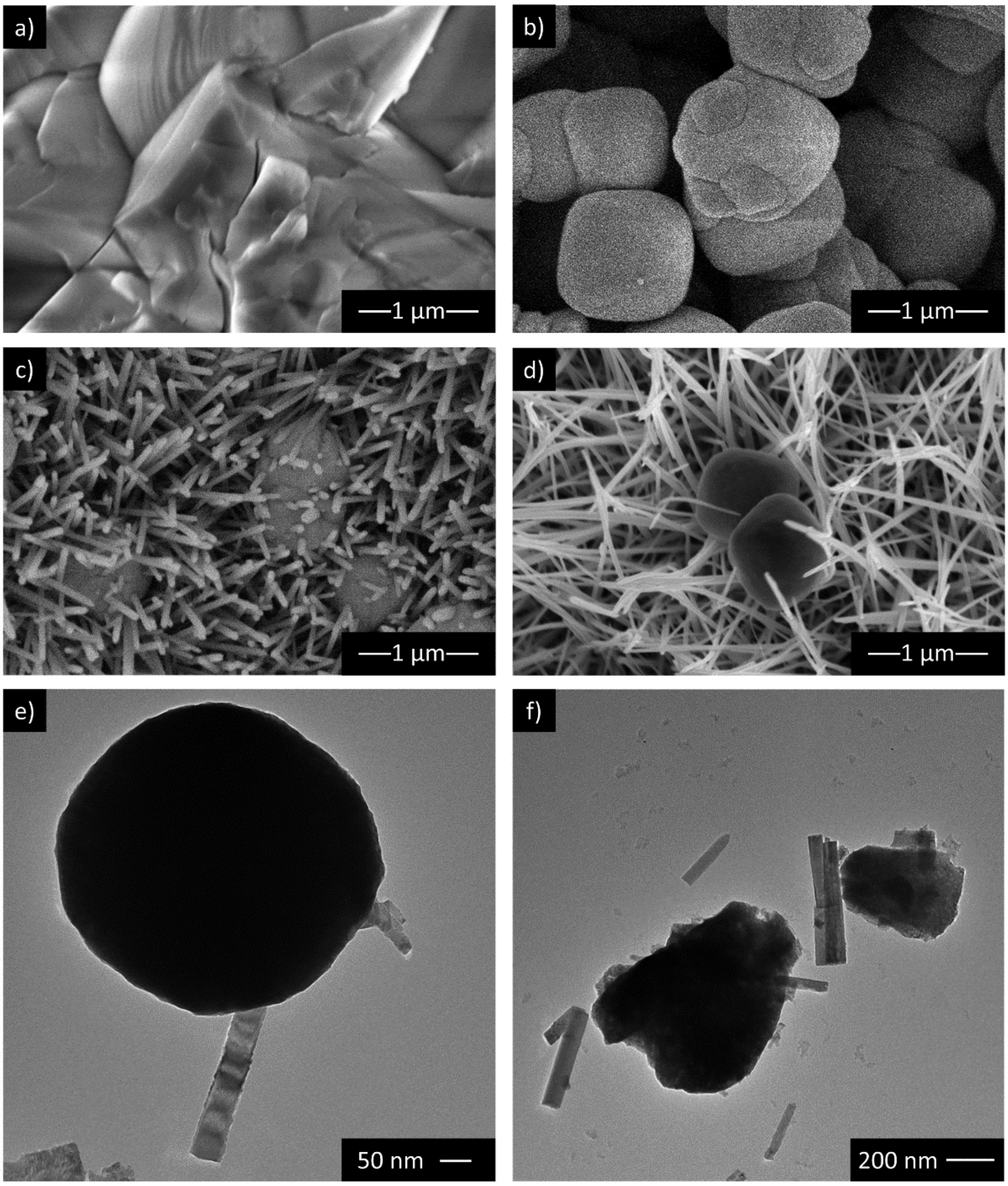

Figure 2 SEM images of a Microscopy slide (a), Cu_2O particles (b), ZnOnr/Cu_2O (c), ZnOnw/Cu_2O (d), and detailed TEM images of separated rods with Cu_2O particles (e, f).

Figure 3 shows the E_3 hormone degradation rate and total efficiency. The UV-photogenerated E_3 degradation test was conducted using a continuous Drip Flow Biofilm Reactor DFR 110-4PET (Biosurface Technologies Corporation). It consists of 4 parallel channels made from polyethylene terephthalate (PET). Nevertheless, the system was slightly modified by replacing the PET cover with borosilicate glass. The scheme of this apparatus as used can be seen in **Figure 4**. Each channel capable of holding one standard glass microscope was circulated with 40 mL of E_3 solution (0.2 mg/L concentration) using a peristaltic pump PFP 5408 (VWR) equipped with silicon tubing at a flow rate of 10 mL.min^{-1}. [7] All heterojunctions were able to degrade the E_3 hormone. However, the difference in their performance is evident. Although, ZnOnw/Cu_2O heterojunction is more efficient than ZnOnr/Cu_2O due to their higher aspect ratio and surface area. In the case of hormone E3, there was no detectable degradation on the clear microscopy slide under UV irradiation.

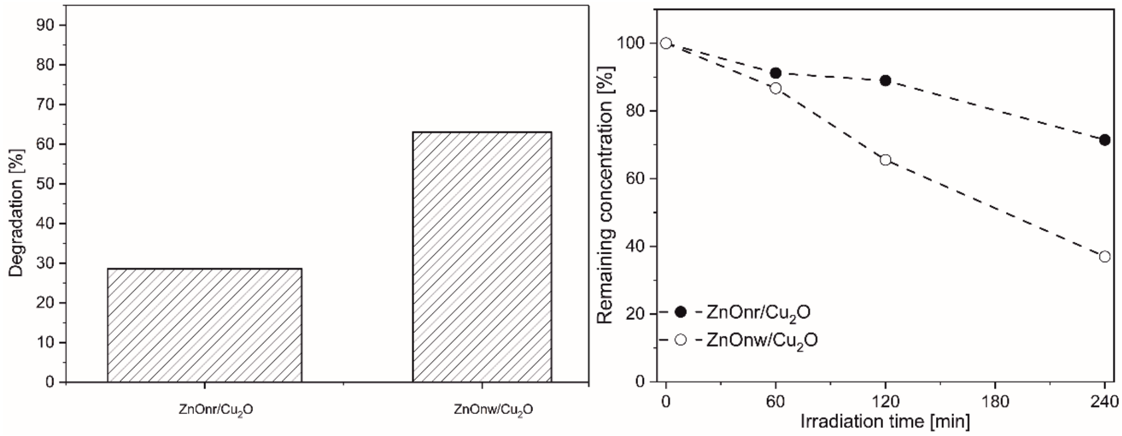

Figure 3 Total degradation efficiency in 240 min and E_3 degradation by ZnOnr/Cu_2O and ZnOnw/Cu_2O heterojunction under UV irradiation in given time intervals.

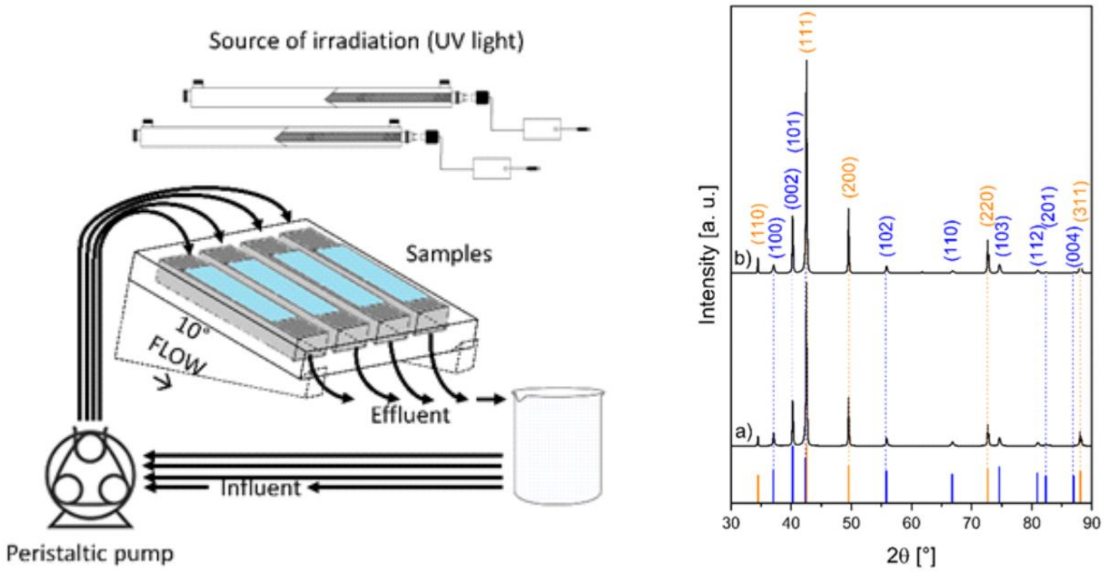

Figure 4 Left part: scheme of the used system for hormone degradation; right part: X-ray diffractogram patterns of ZnOnr/Cu_2O (a) and ZnOnw/Cu_2O heterojunction.

All as-prepared samples exhibit the diffraction peaks of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 1), and (0 0 4) of ZnOnr/Cu_2O and ZnOnw/Cu_2O, which are consistent with wurtzite ZnO hexagonal phase structure (PDF Card No.: 01-073-8765). In the case of nanowires, the dominant diffraction peak for (0 0 2) indicates a high degree of orientation in the c* axis, which means vertical growth to the substrate surface. [10,11] Besides diffraction peaks, (1 1 0), (1 1 1), (2 0 0), (2 2 0), and (3 1 1) were identified for Cu_2O cubic phase structure (PDF Card No.: 01-071-3645). No other phase was detected. Diffractograms of as-grown ZnOnr/Cu_2O and ZnOnw/Cu_2O heterojunctions are shown in **Figure 3** – right part.

The explorer ink color changes from blue to violet for both heterojunctions are visible in **Table 1** after 15 min of UV-light irradiation. These changes indicate significant photocatalytic activities. This color change of the explorer ink resulted from the irreversible reduction of resazurin (Rz) to resofurin (Rf). The explorer ink consists of glycerol and hydroxyethyl cellulose. Glycerol generates electrons to kill photogenerated holes effectively, and hydroxyethyl cellulose is a thickening agent for more effortless electron transfer. [12,13] The color change occurs almost immediately after five minutes of UV irradiation for both samples. The second prepared ink containing *tert*-butyl alcohol and MB was prepared to determine the pollutant's absorption rate onto the surface of the prepared substrates. *Tert*-butyl alcohol is used as a scavenger of free OH radicals. In the case of an untreated microscopy slide, there was no activity to the applied ink on the microscopy slide surface. In contrast, the ink was degraded entirely on surfaces covered with ZnOnr/Cu_2O and ZnOnw/Cu_2O heterojunctions. This phenomenon may indicate the absorption of the prepared heterojunctions, especially Cu_2O. [14]

Table 1 Test of prepared layers under UV irradiation for two different ink

Irradiation time	Tested Ink	ZnOnr/Cu_2O	ZnOnw/$Cu_2$0	Microscopic slide
0 min	*Tert*-butyl alcohol + Methylene Blue			
	Explorer (Resazurin)			
5 min	*Tert*-butyl alcohol + Methylene Blue			
	Explorer (Resazurin)			
10 min	*Tert*-butyl alcohol + Methylene Blue			
	Explorer (Resazurin)			
15 min	*Tert*-butyl alcohol + Methylene Blue			
	Explorer (Resazurin)			

4. CONCLUSION

The ZnO nanorods- and nanowires-based Cu_2O heterojunction were successfully synthesized, characterized, and were compelling enough for the photocatalytic degradation of E_3 hormone with the overall range of efficiencies for nanorods were ~ 30.0 %, and for nanowires 65.0 %. Hence, the as-prepared heterojunctions in this study can be used in a continuous cross-flow closed system to eliminate micro-pollutants such as E_3 from wastewater. In addition, the photocatalytic activity of prepared heterojunctions was assessed by monitoring the rate of resazurin reduction in a motif layer, which may indicate the photocatalytic-induced self-cleaning ability of functionalized glass. Next, using non-commercial prepared ink, an OH radical scavenger, prove the surface structures' absorption.

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