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Zinc oxide functionalized human hair: A potential water decontaminating agent

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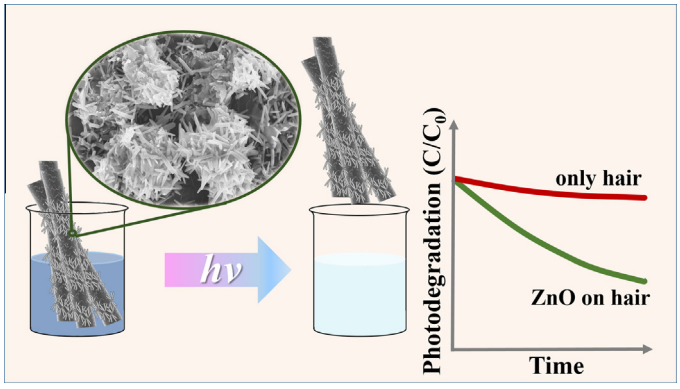
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Nano-ZnO is an efficient photocatalyst that can be employed for water purification but its separation from water is difficult. Immobilization of nano-ZnO on a fibrous material is expected to add practicality to its application.
Experiments: We synthesized ZnO nanostructures on a natural waste, human hair, via a cost-effective process, characterized the system and tested the efficacy of the composite for photo-decomposition of a few toxic materials in water.
Findings: Layers of well crystalline ZnO nanostructures grew homogeneously on hair strands, initially as thin plates that slowly turned with time into nanorods (length 400–600 nm, width 28–30 nm), converting the mildly hydrophobic hair (water contact angle 104°) surface into superhydrophobic (water contact angle 149°). The composite was found to effectively photodecompose toxic dyes like methylene blue, direct red, alizarin red S and aromatics (toluene), for multiple cycles without losing much efficacy.

1. Introduction

Contamination of water bodies by toxic compounds generated as industrial wastes has posed serious threat to the environment. Remediation, recycling and sanitisation of the waste water is essential for maintaining sustainability and balancing the natural resource scarcity. Decontamination techniques include both physical and chemical interventions during waste water treatments. The former is the most commonly used technique for removal of particulates and water insoluble compounds such as oils from large spills through adsorptions. Various factors such as surface area and

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specificity govern the adsorbing capacity of materials, and their practical applications requires them to be environmentally benign. In principle, any hydrophobic and oleophilic material can be used for such purpose including inorganic compounds like hydrophobically modified clays, calcium carbonate, silica and cross linked polymers [1–13]. However, they lack ability to chemically purify water from contaminants.

Many water soluble toxic constituents being organic in nature can be photochemically degraded in presence of suitable catalysts. Photocatalytic degradation processes for destroying organic pollutants in wastewater have been exhaustively studied with inorganic semiconductor materials like TiO_2, ZnO and SnO_2 [14–18]. Recently there are reports of using functionalized clays and layered double hydroxides (LDH) as efficient photocatalysts [7,38]. Often ZnO is used as an alternate photocatalyst to TiO_2, owing to the similarity in band gap [16]. Photocatalytic activities of the metal oxides are affected by various factors like chemical composition, phase structures, surface hydroxyl groups, particle size, crystallinity and surface defects. The efficacy of such inorganic compounds is a function of their particle size, which restricts their widespread use since it is often difficult to remove small sized particles from contaminated water and at very low particle sizes, they are possibly toxic to environment [19,20].

A better way could be to immobilize these particles on benign substrates, to achieve functional benefits without affecting their release to the environment [21,22]. Immobilization of these functional materials on surfaces of cheap and possibly waste materials for degradation of toxic wastes without appreciable cost and resource deployment is an interesting area of research.

ZnO is a versatile inorganic semiconductor oxide that has been proven to be a potential candidate for detoxification of wastes by photocatalytic degradation. Its optical, catalytic and sensing properties can be tuned easily by controlling its size and morphology [23–26]. The photocatalytic activity of nanoparticulate ZnO has been demonstrated in a few recent studies, where it has been shown that its efficacy significantly increases with decrease in size [22]. Making ZnO more hydrophobic makes it a potent adsorbent for non-polar organic compounds, however, its photocatalytic activity might be affected by the hydrophobic coating. Thus, it is pertinent to develop a three pronged strategy to (a) immobilize ZnO on benign surface, (b) develop structural hierarchy of ZnO particles, so that hydrophobicity arises from the induced roughness alone without further coating and (c) control the particle size through in-situ synthesis.

One such benign substrate for immobilization is human hair. It has comparatively less natural oil content compared to animal furs, making the former suitable adsorbent for water insoluble organics. But it lacks the ability to 'decompose' any toxic ingredients contaminated in the waste water. We became curious to know what might happen if we combined the adsorption capability of human hair and the ability of nanoparticulate ZnO to provide surfaces for photo catalytic decomposition of potentially toxic organics, not merely as a mixture but by growing the ZnO hierarchically on human hair.

In this paper, we report a facile, cost-effective and rapid synthetic route of making ZnO nanostructures on human hair surface with varying wettability and its successful demonstration as surface bound photo-catalyst for degradation of a few harmful chemicals from oil-contaminated water.

2. Experimental details

2.1. Materials

Natural white hair of Caucasian origin was obtained from International Hair Importers, USA. Zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$, AR grade] and hexamethylenetetramine (HMTA) [$C_6H_{12}N_4$, AR grade] were procured from Aldrich and used without further purification. Methylene Blue, Direct Red 23, Alizarin Red S, Crystal violet, Nile Red dyes were procured from Aldrich; Quinzarine Green SS dye was procured from Dyechem Pvt. Ltd. Deionised water was used in all reactions and had the following characteristics: pH 6.95, electrical conductance 2×10^{-6} S cm^{-1}, total dissolved salt <0.4 mg L^{-1}, and turbidity <0.1 NTU.

2.2. Methods

2.2.1. Synthesis of ZnO particles on hair

ZnO was grown on hair strands by hydrothermal reaction using aqueous solutions of zinc nitrate with HMTA by a process reported earlier [17]. In a typical reaction, 50 mM zinc nitrate and 50 mM HMTA were mixed together in sealed autoclavable containers and to it 100 mg of hair strands tied to a Teflon thread were immersed. The containers were stoppered and kept at 95 °C in an air oven for 0.5–8 h. After the specified time of hydrothermal treatment, the containers were taken out and cooled to room temperature. The hair strands were washed thoroughly with de-ionized water followed by copious amount of ethanol and dried in air. The different sets of reactions are described in Table 1.

2.2.2. Material characterization

The morphology evolution of as-grown ZnO particles on hair strands was characterized by a field emission source scanning electron microscope (FESEM) Ultra-55, Zeiss NTS GmbH equipped with an energy dispersive X-ray (EDX) spectrometer at an accelerating voltage of 10 kV. The crystallinity of the ZnO particles was examined by powder X-ray diffraction (XRD) using Siemens-D5000 X-ray diffractometer. Analysis was done using Cu K_α radiation with a nickel filter and a zero background sample cell operating at $\lambda = 0.154$ nm, 40 kV and 30 mA. All samples were measured in the continuous scan mode at 25°–70° (2θ) with a scanning rate of 0.025° (2θ) s^{-1}. Peak positions and relative intensities of products were characterized by comparing to values from the Joint Committee for Powder Diffraction Standards (JCPDS, card number 36-1451). Thermogravimetric analysis (TGA) was performed on a Pyris 1 TGA (Perkin Elmer Corp.) under nitrogen atmosphere at a scanning rate of 10 °C min^{-1} from 25 °C to 700 °C.

2.2.3. Photocatalytic efficacy

Photocatalytic activity of the ZnO functionalized hair was measured by SAIC MVL series instrument equipped with UV light from a mercury lamp source (60 W, 365 nm), by following the degradation pattern of various synthetic dyes.

(a) *Dye degradation:* Methylene Blue ($C_{16}H1_8ClN_3S{\cdot}3H_2O$, λ_{max}: 664 nm), Direct Red 23 ($C_{35}H_{25}N_7NaO_{10}S_2$, λ_{max}: 509 nm) and Alizarin Red S ($C_{14}H_7NaO_7S$, λ_{max}: 425 nm) dyes were used for the experiment. Either of 100 mL of 20 μM Methylene Blue, 25 μM Direct Red 23 or 100 μM Alizarin Red S dye was taken, to it 25 mg of the ZnO functionalized hair were added and stirred for 30 min at 400 rpm and 25 °C in dark to establish adsorption–desorption equilibrium between

Table 1
Compositions of reactants and time intervals at which ZnO were synthesized.

Sample	$Zn(NO_3)_2{\cdot}6H_2O$ (mM)	HMTA (mM)	Reaction time (h)
ZnO-0.5	50	50	0.5
ZnO-1	50	50	1.0
ZnO-2	50	50	2.0
ZnO-4	50	50	4.0
ZnO-6	50	50	6.0
ZnO-8	50	50	8.0