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ZnO/CdO nanocomposites for textile effluent degradation and electrochemical detection

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ABSTRACT

In this report, the photocatalytic and electrochemical activity of ZnO and ZnO/CdO nanocomposites were determined. Pure ZnO and nanocomposite ZnO/CdO were prepared by a vapor to solid mechanism and were characterized by different physical and chemical techniques. The CdO-modified ZnO possessed high efficiency to degrade textile effluent. It also showed high efficiency of degradation, such as 98% for methylene blue and 93% for methyl orange. Cadmium oxide (impurity) plays an important role in achieving zinc oxide materials that exhibit UV to visible light degradation of textile effluent. Additionally, uric acid sensing performed to study the electrochemical activity revealed that ZnO/CdO (90:10) nanocomposite produced high anodic currents, and these results were in agreement with the cyclic voltammetry reports.

1. Introduction

Nanomaterial-based biosensors and photocatalysts have gained tremendous importance in recent years, with respect to their application in the highly sensitive detection of various enzymes and the degradation of industrial pollutants. They have significant impact on human health and the ecosystem [1–13]. Metal oxide nano semiconductors have been extensively investigated in the past decade for properties that are suitable for photocatalytic and biosensing applications [1–13]. Among all semiconductors, zinc oxide is one of the hardest polar inorganic materials with a large bandgap and is non-hazardous in nature. The low-cost and high thermal stability of ZnO enable its use in versatile applications.

Industrial wastewater treatment is a major issue of social concern due to the direct release of industrial effluents into nearby water resources, which leads to contamination of the entire resource. Efforts are being made to develop simpler and inexpensive technologies for the sustenance of a green atmosphere [14]. Heterogeneous catalytic activity is one such green technology that has received greater attention for wastewater treatment and is highly efficient in the complete elimination of toxic chemicals in the environment [15,16]. As discussed in our previous work, the photocatalytic activity of ZnO modified with CdO (95:5 weight ratio) effectively degraded methylene blue under visible light [17]. Zhou et al. reported that the presence of an increased amount of chemisorbed oxygen on the surface of CdO/ZnO nanocomposite materials makes them suitable for gas sensing devices, which are extremely sensitive in the detection of ethanol and carbon monoxide [18,19].

Nanosemiconductor-based biosensors are used in the detection of innumerable enzymes, among which uric acid (UA) detection is of utmost importance because it plays a significant role in human health. The blood plasma of a normal person contains 3.4–7.2 mg/dL (for men) and 2.4-6.1 mg/dL (for women) UA. A slight increase or decrease in the UA level is found to antagonize people with medical conditions such as hyperuricemia, gout, Lesch–Nyhan syndrome, arthritis and kidney stones [20,21]. Therefore, for the early stage detection of the related diseases, an accurate estimation of the UA levels in the body is mandatory. Therefore, it is of clinical significance to develop simple and

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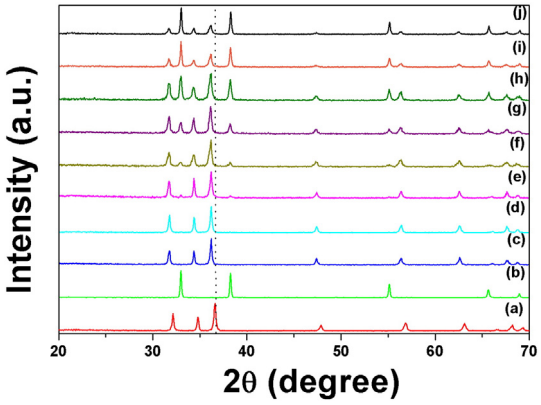

Fig. 1. XRD pattern of (a) ZnO, (b) CdO, (c) ZnO/CdO (99:01), (d) ZnO/CdO (97:03), ZnO/CdO (95:05), (f) ZnO/CdO (90:10), (g) ZnO/CdO (80:20), (h) ZnO/CdO (70:30), (i) ZnO/CdO (60:40) and (j) ZnO/CdO (50:50).

effective methods for UA estimation. Among the various analytical methods, electrochemical analysis has proved to be a promising approach for UA detection. Ahmad et al. described the effective determination of uric acid with a detection limit of 0.05–2 mM using ZnO nanosheets, which provided high electron flow, favoring enhanced sensitivity [22]. In the case of other enzymes, such as glucose, the incorporated hollow nanosphere of ZnO on Nafion and GOD showed effective detection [23]. Xia et al. proposed GCE electrodes incorporated with ZnO nanoflowers for the electrochemical detection of dopamine. This hierarchical arrangement of the nanomaterial resulted in enhanced sensitivity with a very low detection limit for DA [24].

The main aim of this study is to reduce the degradation time by optimizing the ratio of ZnO/CdO (99:01, 97:03, 95:05, 90:10, 80:20, 70:30, 60:40 and 50:50) catalyst. These materials were prepared by the thermal decomposition method and were characterized using techniques such as XRD, FE-SEM, HR-TEM, HR-XPS, UV–vis and BET analysis, and the results are discussed in detail. To the best of our knowledge, no research reports have been published on the UA detection of ZnO/CdO nanocomposites. Therefore, the prepared materials were subjected to electrochemical detection of uric acid. The photocatalytic degradation of model dyes and real textile effluent was also investigated.

2. Experimental

2.1. Materials

Zinc acetate dihydrate, cadmium acetate and uric acid (UA) were purchased from Sigma-Aldrich. Methyl orange (MO) and methylene blue (MB) were procured from Rankem Chemicals, India and were used without further purification. All of the aqueous solutions were prepared using double distilled water.

2.2. Methods

2.2.1. Synthesis of different photocatalysts

Preparation of ZnO, CdO and ZnO/CdO composites was based on the vapor to solid mechanism [25]. Raising the temperature of the raw material results in the production of its vapor, which upon cooling, is deposited on the crucible. At the beginning of condensation, defects on the surface of the substrate (crucible) act as favorable sites for nucleation of the oxide vapor [25]. Further, condensation allows nuclei to grow into nanoparticles. Pure ZnO nanomaterial was synthesized as per our procedure reported previously [17,26]. A 3.0 g sample of the raw material (zinc acetate dihydrate), weighed using an unbiased four digit weighing balance, was ground for 3 h in a mortar. The ground material taken in an alumina crucible was calcined at 350 °C for 3 h in a muffle furnace. Similarly, CdO nanomaterial was also prepared with cadmium acetate as the raw material under the same temperature conditions. Various weight percentages of ZnO/CdO nanocomposites were synthesized by mixing various weight percentages of zinc acetate dihydrate and cadmium acetate (at weight ratios of 99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50). The mixture was ground for 3 h and calcined at 350 °C for the same time period.

2.2.2. Photocatalytic experiment

Visible light irradiation was conducted using a projection lamp (7748XHP 250 W, Philips) in a photoreactor without any external source. UV protection was provided using a 600 mL cylindrical beaker covered by 0.5% aqueous $K_2Cr_2O_7$ solution circulating in a glass jacket. Model water soluble dyes, such as methylene blue (MB) and methyl orange (MO), were prepared by the procedure described in our previous reports [27,28]. The optimized catalyst with the highest degradation was further used to study the decoloration of industrial effluent.

2.2.3. Electrochemical experiment

All electrochemical measurements were performed on a PGSTAT-12 electrochemical work station (AUTOLAB, The Netherlands BV). The measurements were based on a three electrode system: with a glassy carbon (GC) electrode (0.07 cm^2) as a working electrode, a Pt wire (~20 cm^2) as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Prior to each experiment, the GCE surface was polished with fine grade alumina powders to a mirror polish, sonicated for approximately 15 min in DD water, degreased with acetone and washed with copious amounts of DD water. The solutions were purged with nitrogen (99.99%) for at least 30 min prior to each electrochemical measurement, and a nitrogen environment was maintained throughout the experiments. Pristine ZnO and ZnO/CdO were analyzed at the modified glassy carbon electrode (GCE) as follows: 3 mg of pristine ZnO and ZnO/CdO were suspended in 3 mL of ethanol and subjected to ultrasonic agitation for 30 min to obtain a homogeneous suspension. The polished GCE was coated with 5 μL of the above suspension to obtain pristine ZnO and binary-modified GCE.

Table 1
Lattice parameter and crystallite size (D) of all the prepared samples.

Sample	ZnO hexagonal 79-0208		CdO cubic 73-2245	ZnO D (nm)	CdO D (nm)	Bandgap value (eV)
	a (Å)	c (Å)	a (Å)			
ZnO	3.262 (9)	5.206 (3)		24	–	3.20
CdO			4.709 (6)		49	2.53
ZnO/CdO (1)	3.265 (7)	5.214 (3)	–	39	–	3.12
ZnO/CdO (3)	3.263 (6)	5.211 (3)	–	38	–	3.03
ZnO/CdO (5)	3.264 (6)	5.213 (2)	4.696 (2)	30	38	2.99
ZnO/CdO (10)	3.263 (3)	5.221 (2)	4.698 (2)	26	25	2.90
ZnO/CdO (20)	3.269 (6)	5.221 (3)	4.707 (6)	30	31	2.86
ZnO/CdO (30)	3.266 (6)	5.222 (3)	4.709 (4)	32	34	2.82
ZnO/CdO (40)	3.266 (1)	5.218 (3)	4.706 (6)	33	49	2.79
ZnO/CdO (50)	3.267 (6)	5.219 (2)	4.706 (6)	35	54	2.75