Worked in different universities/institutions in various capacities as follows:

From the SelectedWorks of Dr. Mohammad Mansoob Khan

June 12, 2015

ZnO/CdO nanocomposites for textile effluent degradation and electrochemical detection

Mohammad Mansoob Khan, Dr

Available at: https://works.bepress.com/mmansoob_khan/60/
ZnO/CdO nanocomposites for textile effluent degradation and electrochemical detection

R. Saravanan a,*, F. Gracia a, Mohammad Mansoob Khan b, V. Poornima c, Vinod Kumar Gupta d,e,f, V. Narayanan g, A. Stephen h,i

a Department of Chemical Engineering and Biotechnology, FCFM, University of Chile, Beauchef 850, Santiago Chile
b Chemical Sciences, Faculty of Science, Universiti Brunei Darussalam, Jalan Tunku Link, BE1410, Brunei Darussalam
c Faculty of Applied Health Sciences, Chettinad Academy of Research and Education, Kelambakkam, India
d Center for Environment and Water, The Research Institute, King Fahd University of Petroleum and Minerals Dhahran, Saudi Arabia
e Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa
f Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India
g Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India
h a Department of Chemical Engineering and Biotechnology, FCFM, University of Chile, Beauchef 850, Santiago Chile

ARTICLE INFO

Article history:
Received 28 March 2015
Received in revised form 18 May 2015
Accepted 21 May 2015
Available online xxxx

Keywords:
Textile effluent
Nanocomposite
ZnO/CdO
Uric acid
Visible light

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.

© 2015 Elsevier B.V. All rights reserved.

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 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, arthralgia 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
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 transfer. Lattice parameter and crystallite size (D) of all the prepared samples.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO hexagonal 79-0208</th>
<th>CdO cubic 73-2245</th>
<th>ZnO D (nm)</th>
<th>CdO D (nm)</th>
<th>Bandgap value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.262 (9)</td>
<td>5.206 (3)</td>
<td>4.709 (6)</td>
<td>–</td>
<td>3.20</td>
</tr>
<tr>
<td>CdO</td>
<td>3.265 (7)</td>
<td>5.214 (3)</td>
<td>–</td>
<td>39</td>
<td>2.53</td>
</tr>
<tr>
<td>ZnO/CdO (1)</td>
<td>3.263 (6)</td>
<td>5.211 (3)</td>
<td>–</td>
<td>38</td>
<td>3.12</td>
</tr>
<tr>
<td>ZnO/CdO (3)</td>
<td>3.264 (6)</td>
<td>5.212 (3)</td>
<td>4.696 (2)</td>
<td>30</td>
<td>3.03</td>
</tr>
<tr>
<td>ZnO/CdO (5)</td>
<td>3.263 (3)</td>
<td>5.221 (2)</td>
<td>4.698 (2)</td>
<td>26</td>
<td>2.99</td>
</tr>
<tr>
<td>ZnO/CdO (10)</td>
<td>3.269 (6)</td>
<td>5.221 (3)</td>
<td>4.707 (6)</td>
<td>30</td>
<td>2.90</td>
</tr>
<tr>
<td>ZnO/CdO (20)</td>
<td>3.268 (6)</td>
<td>5.222 (3)</td>
<td>4.709 (4)</td>
<td>32</td>
<td>2.86</td>
</tr>
<tr>
<td>ZnO/CdO (30)</td>
<td>3.266 (1)</td>
<td>5.218 (2)</td>
<td>4.706 (6)</td>
<td>33</td>
<td>2.79</td>
</tr>
<tr>
<td>ZnO/CdO (50)</td>
<td>3.267 (6)</td>
<td>5.219 (2)</td>
<td>4.706 (6)</td>
<td>35</td>
<td>2.75</td>
</tr>
</tbody>
</table>

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 photo reactor without any external source. UV protection was provided using a 600 mL cylindrical beaker covered by 0.5% aqueous K2Cr2O7 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 cm2) as a working electrode, a Pt wire (−20 cm2) 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 (99.999%) 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.
2.2.4. Characterization details

The crystal structures of the synthesized materials were determined by an X-ray diffractometer (Rich Seifert 3000, Germany) using Cu Kα1 radiation with \( \lambda = 1.5406 \ \text{Å} \). Transmission electron microscopy (TEM, Mark II, JEOL 2000FX, Tokyo, Japan), operated at 200 kV, was used for the microstructure analysis of the nanomaterials. The oxidation states of the catalysts were examined using X-ray photoelectron spectroscopy (XPS, DRA 400 — XM1000 OMICRON, ESCA+, Opmicron Nanotechnology, Germany). The specific surface area was calculated from the Brunauer–Emmett–Teller (Micromeritics ASAP 2020, USA) equation. The surface morphology, elemental analysis and energy dispersive X-ray spectroscopy (EDS) analysis were determined using a field emission scanning electron microscope (FE-SEM, HITACHI-SU6600, Hitachi, Japan). The optical bandgap and the photocatalytic activity measurement were performed using a UV–visible spectrophotometer (RX1, PerkinElmer, USA).

3. Results and discussion

The structures of pure zinc oxide (ZnO), cadmium oxide (CdO) and composite materials (with different weight percentages of ZnO/CdO) were studied using X-ray diffraction analysis. Fig. 1 reveals the diffraction pattern of all samples and their corresponding data indexed using XRDA 3.1 and Origin 8 software. Fig. 1 (a) shows the diffraction peaks of the 2θ values 32.1, 34.7, 36.6, 47.8 and 56.8 corresponding to the (h k l) planes (100), (002), (101), (102) and (110), respectively, of ZnO. We concluded that ZnO has a hexagonal structure (JCPDS No: 79-0208) without impurities. The diffraction pattern of the CdO sample is depicted in Fig. 1(b) with peaks (111), (200) and (220) indicative of the cubic structure of CdO, which coincides with the JCPDS No: 73-2245. The ZnO/CdO (99:01, 97:03) diffraction patterns are shown in Fig. 1(c) and (d). In these patterns, the CdO peaks are invisible because the percentage of CdO in the composite is very low (1% and 3%). The appearance of the CdO peaks in Fig. 1(e) and (j) is due to the increased CdO weight percentage in the sample. The crystallite sizes of the prepared samples were calculated using the Scherrer formula. The lattice parameters and crystallite sizes (D) are shown in Table 1.

The composite (ZnO/CdO) peaks are shifted towards a lower angle compared with the pure ZnO peaks. The shift towards the lower angle is attributed to the incorporation of Cd\(^{2+}\) with a larger ionic radius into the Zn\(^{2+}\) with a smaller atomic radius. This is similar to the observation reported by Ziabari et al. [29]. However, the addition of the impurity (CdO) does not affect the structure of ZnO. The broadened diffraction pattern of all samples and their corresponding data indexed using XRDA 3.1 and Origin 8 software. Fig. 1 (a) shows the diffraction peaks of the 2θ values 32.1, 34.7, 36.6, 47.8 and 56.8 corresponding to the (h k l) planes (100), (002), (101), (102) and (110), respectively, of ZnO. We concluded that ZnO has a hexagonal structure (JCPDS No: 79-0208) without impurities. The diffraction pattern of the CdO sample is depicted in Fig. 1(b) with peaks (111), (200) and (220) indicative of the cubic structure of CdO, which coincides with the JCPDS No: 73-2245. The ZnO/CdO (99:01, 97:03) diffraction patterns are shown in Fig. 1(c) and (d). In these patterns, the CdO peaks are invisible because the percentage of CdO in the composite is very low (1% and 3%). The appearance of the CdO peaks in Fig. 1(e) and (j) is due to the increased CdO weight percentage in the sample. The crystallite sizes of the prepared samples were calculated using the Scherrer formula. The lattice parameters and crystallite sizes (D) are shown in Table 1.

The composite (ZnO/CdO) peaks are shifted towards a lower angle compared with the pure ZnO peaks. The shift towards the lower angle is attributed to the incorporation of Cd\(^{2+}\) with a larger ionic radius into the Zn\(^{2+}\) with a smaller atomic radius. This is similar to the observation reported by Ziabari et al. [29]. However, the addition of the impurity (CdO) does not affect the structure of ZnO. The broadened
The diffraction peaks of the composite material are indicative of their smaller size, whereas the sharper peaks of pure ZnO are due to the larger crystal size. The increased surface area due to the decreasing size is confirmed by the BET analysis. The surface area of pure ZnO is 8.7 m²/g. Increasing the concentration of CdO (1%, 3%, 5% and 10%) resulted in an increase in the surface area of the composite (ZnO/CdO) (10.1 m²/g, 11.5 m²/g, 12.4 m²/g and 13.2 m²/g). The surface area value of the composite (11.4 m²/g, 10.5 m²/g, 9.4 m²/g and 7.4 m²/g), corresponding to 20 wt.% to 50 wt.% of CdO, decreased. This decrease in the surface area is reasonable because of the excess crystalline CdO on the surface of ZnO. These results agree with those reported by Akurati et al. [30].

The surface morphologies of the prepared pure ZnO, CdO and ZnO/CdO (different weight percentages) were studied using FE-SEM (Fig. 2). The image of pure ZnO exhibits randomly distributed nanorods and is shown in Fig. 2(a). The diameters of the ZnO nanorods are 40 nm, and the lengths are in micrometers. Fig. 2(b) represents pyramid-shaped CdO. It is evident from Fig. 2 (c to j) that an increase in the wt.% of the CdO decreased the length of the nanorods. In the case of higher concentration (above 10%) of CdO, the nanocomposites are highly agglomerated (Fig. 2(g to j)). A close observation of the nanocomposites reveals the presence of spherical particles along with the nanorods. The addition of impurities (CdO) overrules the process of nucleation and growth, which in turn results in increased agglomeration and a change in the morphology of ZnO [31].

Elemental analysis of the sample was performed by energy dispersive X-ray spectroscopy. Fig. S1 depicts the EDS spectra of ZnO, CdO and ZnO/CdO (different weight percentages) were studied using FE-SEM (Fig. 2). The image of pure ZnO exhibits randomly distributed nanorods and is shown in Fig. 2(a). The diameters of the ZnO nanorods are 40 nm, and the lengths are in micrometers. Fig. 2(b) represents pyramid-shaped CdO. It is evident from Fig. 2 (c to j) that an increase in the wt.% of the CdO decreased the length of the nanorods. In the case of higher concentration (above 10%) of CdO, the nanocomposites are highly agglomerated (Fig. 2(g to j)). A close observation of the nanocomposites reveals the presence of spherical particles along with the nanorods. The addition of impurities (CdO) overrules the process of nucleation and growth, which in turn results in increased agglomeration and a change in the morphology of ZnO [31].

Additional information about the shape and structure were obtained using TEM and HR-TEM images. The TEM image (Fig. 3(a)) of ZnO/CdO (90:10) composite material exhibits nanorod agglomeration with closely packed spherical nanoparticles, which agrees with the FE-SEM analysis. The fringe pattern of the composite material (Fig. 3(b)) indicates the presence of parallel planes. Planes are indexed, and the measured ‘d’ value reveals that the (002) plane matched the hexagonal structure of ZnO (JCPDS No: 79-0208), whereas the (200) plane corresponds to the cubic structure of CdO (JCPDS No: 73-2245). The HR-TEM image confirms the formation of the composite material, which agrees with our XRD result.

The oxidation states of the elements present in the ZnO/CdO composite material (90:10) comprising of zinc (Zn), cadmium (Cd) and oxygen (O) were determined using X-ray photoelectron spectroscopic (XPS). All of the HR-XPS spectra were calibrated using carbon C 1s (284.6 eV) as reference. The HR-XPS spectrum of zinc shown in Fig. 4 (a) has a binding energy of approximately 1021.2 eV and 1044.2 eV for the 2p3/2 and 2p1/2 states, respectively, which is in agreement with the literature [32–34]. Similarly, in Fig. 4(b), the binding energies of 405.3 eV in the 3d5/2 state and 412.1 eV in the 3d3/2 state correspond to cadmium, which is evident from previous reports [32–34]. From Fig. 4(c), it is evident that oxygen is present in three different states, which correspond to CdO, ZnO and the surface hydroxyl groups [35], whose binding energies are 529.8 eV, 532.4 eV and 534.9 eV, respectively. There is no formation of metallic Zn and Cd. Therefore, the XPS spectra confirmed that the composite material consists of Zn²⁺ and Cd²⁺ states, and the results resemble the XRD observation.

The absorption spectra of the ZnO, CdO and ZnO/CdO (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) at room temperature are shown in Fig. 5. The ZnO absorption edge is ~360 nm, which corresponds to the UV region. The absorption edge of pure CdO is ~490 nm, which is in the visible region. The absorption edge of the composite material was extended to the red region, whereas that of pure ZnO was

---

**Fig. 2 (continued).**
found to lie in the blue region. The bandgap energies calculated using Tauc’s plot are presented in Table 1, which shows that there is a decrease in the bandgap with increasing weight percentage of cadmium. Wang et al. reported that the bandgap value of coupled oxide (ZnO/ SnO₂) is lower than that of pure ZnO because of its synergistic effect. Because the bandgap of SnO₂ is low (2.6 eV), the bandgap energy of the composite decreases [36]. A similar phenomenon could arise in the present photocatalyst system; the CdO bandgap is low when compared with ZnO. Hence, the UV–vis absorption results indicate that the prepared binary catalysts have absorption bands in the visible region.

3.1. Photocatalytic degradation under visible light illumination

3.1.1. MB and MO degradation

The photocatalytic degradation activity of ZnO, CdO and ZnO/CdO (99:1, 97:3, 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50) samples was studied using model organic dyes. The time course degradation curves for MB and MO are shown in Figs. 6 and 7. MB and MO decoloration occurs with the CdO and ZnO/CdO samples. Pure ZnO, due to its large bandgap, does not cause decoloration, whereas a pure CdO sample brought approximately 13% and 11% degradation of MB and MO because the lower bandgap exhibits faster electron–hole recombination. Among the samples, ZnO/CdO (90:10) showed the highest degradation efficiency (98% of MB and 93% of MO) when irradiated for 3 h. This concentration degrades the model dye twice as fast as in our earlier report, which is a significant improvement [17]. The corresponding optical absorption spectra of MB and MO by ZnO/CdO (90:10) catalyst under visible light irradiation for different time intervals are given in Fig. S2. The recycling ability is an essential factor to identify the long term chemical stability of the catalyst. Therefore, the optimized high efficiency catalyst ZnO/CdO (90:10) was used for the degradation of methyl orange solution under visible light, and this process was repeated 7 times. Fig. S3 represents the recycling ability of the catalyst. After 7 times degradation, there is no significant variation in the efficiency, which suggests that the optimized catalyst is stable and reusable.

In conclusion, the close proximity of the conduction bands of CdO and ZnO retards the back reaction from the conduction band to the valence band. The electrons from the conduction band of CdO hop into the conduction band of the ZnO nanoparticles [17]. This mechanism effectively prevents the electron–hole recombination due to its synergic effect between CdO and ZnO. Thus, the efficiency of the photogenerated electron-holes in ZnO/CdO is higher than in pure ZnO and CdO. Additionally, the ZnO/CdO photocatalyst shows a red shift in the absorption spectrum (Fig. 5) compared to ZnO, which improves its photocatalytic activity in the visible region of the spectrum. The ZnO/CdO (90:10) nanocomposites demonstrated faster degradation rates than reported...
previously [32,33]. ZnO/CdO also had a lower degradation rate compared to previous reports [37,38]. The photocatalytic activity is influenced by various parameters, such as the synthesis method, the availability of surface hydroxyl groups, the size of the particle, the extent of agglomeration, the crystallinity of the catalyst and the dopant concentration. After thorough consideration, we come to the conclusion that the thermal decomposition method provides an efficient and cost effective route for the production of efficient photocatalytic material.

3.1.2. Degradation of textile effluent
Among the prepared samples, the ZnO/CdO (90:10) showed the best photocatalytic degradation efficiency for the two common dyes under visible light irradiation. Therefore, ZnO/CdO (90:10) was used to study the decoloration of industrial effluent under visible light irradiation. Fig. 8 represents the change in the absorption of the industrial effluent solution. An increase in irradiation time caused a decrease in the absorption band, as evident from Fig. 8. Most of the textile effluents have been degraded within 7 h using ZnO/CdO (90:10) photocatalyst under visible light irradiation. More than 85% catalytic activity was obtained using the selected catalyst.

3.2. Electrochemical studies
Uric acid (UA) sensing was performed to study electrochemical activity. Fig. 9 shows the cyclic voltammetry response of 3 mM uric acid for bare, pure ZnO and ZnO/CdO nanocomposite material-modified GCE at a scan rate of 50 mV/s. The ZnO/CdO (90:10) samples had higher anodic peak currents compared with the other samples. Fig. 10 shows the CV results of ZnO and ZnO/CdO (90:10) for the comparative study. The high availability of surface hydroxide and low agglomeration enable the ZnO/CdO (90:10) composite to exhibit higher...
current with lower potential than do the ZnO nanorods. These results are in agreement with the BET, FE-SEM and TEM analyses. Composite samples with CdO weight percentage greater than 10% and with increased agglomeration resulted in low current response. These results are in agreement with recent literature reported by Choi et al. [39]. Therefore, we conclude that (ZnO/CdO) composites with high surface area and low agglomeration exhibit high sensitivity.

4. Conclusion

ZnO/CdO nanocomposites prepared by vapor to solid mechanisms are good catalysts. The photocatalytic degradation activity of the nanocomposites with greater efficiencies and the high degradation effect on the industrial effluents (dyes) enable their use in wastewater treatment. CdO-modified ZnO has also been proved to have higher enzyme (in this case UA) sensing activity. Thus, the developed nanocomposites are among the most efficient catalysts in wastewater treatment and in the degradation of industrial pollutants that have been reported. Low cost synthesis and high efficiency and sensitivity make the catalysts a suitable material for the degradation of pollutants and enable us to move a step further towards a greener environment.

Acknowledgment

We acknowledge the National Center for Nanoscience and Nanotechnology, University of Madras, Chennai, India for the XPS and TEM characterizations. The authors (R.S., F.G.) acknowledge the support of CONICYT through the project CONICYT/FONDAP/15110019 and the postdoctoral fellowship granted to R.S.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2015.05.040.

References