Cadmium oxide: green synthesis, characterization and H 2 storage performance

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Abstract

This study aims to green synthesize and full characterize CdO nanoparticles by means of an environmentally friendly synthesis using Crocus sativus in its reaction with cadmium ions. The CdO nanoparticles were characterized and their purity was confirmed by XRD and UV.-Vis. spectroscopy. Moreover, scanning electron microscopy (SEM) showed that the prepared cadmium oxide nanoparticles were polymorphic. Furthermore, cadmium oxide nanoparticles were cast in the gas storage (H $_2$) study. The hydrogen storage results prove that the maximum H $_2$ uptake was equal to 2.85 Wt.%H $_2$ at a pressure of 69 bar at 77 K with [?]H=0.62607 KJ/mol H $_2$ and [?]S=3.35697 J/mol H $_2$. K. Moreover, the thermodynamic studies under four different temperatures proves that the maximum H $_2$ uptake could be recorded at a pressure limit of 69-86.2 bar.

1-Introduction

Nanotechnology encompasses processes that manipulate matter to achieve atomic-scale sizes, leading to materials with novel properties. Advanced techniques have emerged for manufacturing highly efficient nanomaterials. Green synthesis, a simpler alternative to traditional methods, aims to reduce harsh processing conditions. This approach involves the use of bacteria, fungi, and human cells as viable systems for green synthesis [1-6]. Metal oxides are highly significant nanomaterials with versatile applications in various fields such as environment, health, and industry. Cadmium oxide, in particular, has been extensively studied and utilized. However, the toxicity of cadmium salts restricts its widespread use, despite its excellent reactivity and effectiveness in many applications. To address this issue, researchers have explored eco-friendly approaches for synthesizing cadmium oxide nanoparticles using aqueous plant extracts, providing a more sustainable and environmentally conscious method of preparation [1-3]. From plant extracts for this purpose, for example, citrus limitta peels were used to prepare cadmium oxide nanoparticles of approximately 51 nanometers and irregular shapes [7]. Agathosma betulina was also used in the preparation of this oxide in the form of irregular sphere-like structures with a size not exceeding 50 nanometers [8]. Studies remained directed for this purpose in order to obtain cadmium oxide in a regular nanoscale form, and indeed most studies have achieved this. For example, andrographis paniculata[9], green tea[10], and leucaena leucocephala[11] were used, in which the particle size ranged between 5 and 57 nm. In the pursuit of environmentally friendly alternatives and to mitigate pollution risks, our focus shifted towards utilizing cadmium oxide in hydrogen storage applications. As hydrogen plays a vital role in the new era of clean science, extensive research has been dedicated to finding cost-effective materials with superior hydrogen storage capabilities. Cadmium oxide emerges as a favorable option due to its potential. Several oxides, such as nickel oxide with added metals, have demonstrated hydrogen storage capacities of approximately 0.7 wt.%[12]. In contrast, zinc oxide exhibited a lower hydrogen storage capacity of around 1 wt.%[13]. These studies contribute to the exploration of optimal materials for hydrogen storage purposes. The pure cadmium oxide was not used until now, as only

the composite Cd/CdO was used. However, the storage value reached 1.3 Wt.% [14]. Therefore, this study aims to prepare and characterize cadmium oxide nanoparticles and then complete the lack of information about the ability to store hydrogen in metal oxides.

2. Experimental

2.1. Synthesis of crocus sativus extract

1 g of crocus sativus plant was immersed in 100 ml of deionized water and refluxed at f 75°C for 2 minutes. The mixture was then passed from cotton filter to remove the big cellulose particles and the then centrifuged to collect the extract.

2.2. Synthesis of CdO NPs

Cadmium nitrate (100 ml, 0.5 M) was heated under stirring at a temperature 80°C. Thereafter 100 ml of freshly prepared extract was added drop by drop and left on a hot plate for an hour at a temperature of 160°C under continuous stirring and finally off-white precipitate was formed which was then collected by centrifuge, washed thoroughly with hot deionized water and calcined at 500°C for 2 hour.

3. Results and Discussion

3.1. Characterization of the synthesized CdO NPs

3.1.1. XRD pattern

Scherrer equation that illustrated in equation 1, was used to determine the average particle size of cadmium oxide nanoparticles.

$D = (094\ \lambda)\ /\ (\beta\ \cos\vartheta)$..... (1)

Where $\lambda = 1.542$ Å, β FWHM in radians and ϑ is the diffraction position. The (111), (200), (220), (311) and (222) reflections were determined in the XRD measurement and the result are in agreement with reference patterns of CdO (JCPDS file No. 05-0640) [15]. See Figure 1.

Figure 1: X-ray diffraction of the as-prepared CdO

3.1.2. Scanning electron microscope (SEM) and transmission electron microscopy (TEM)

SEM measurement which was shown in Figure 2 shows a homogeneous distribution of the prepared CdO polymorphic, with a median particle size of 64.58 nm. The TEM measurement showed very well separated particles with irregular sphere like structure of 45-67 nm. Furthermore, the measurement showed a rhombic shape-like structure of 50 nm, as shown in Figure 3. However, the particle size distribution in Figure 3 confirmed that the mean particle size was 55 nm which is in consistence with XRD and SEM.

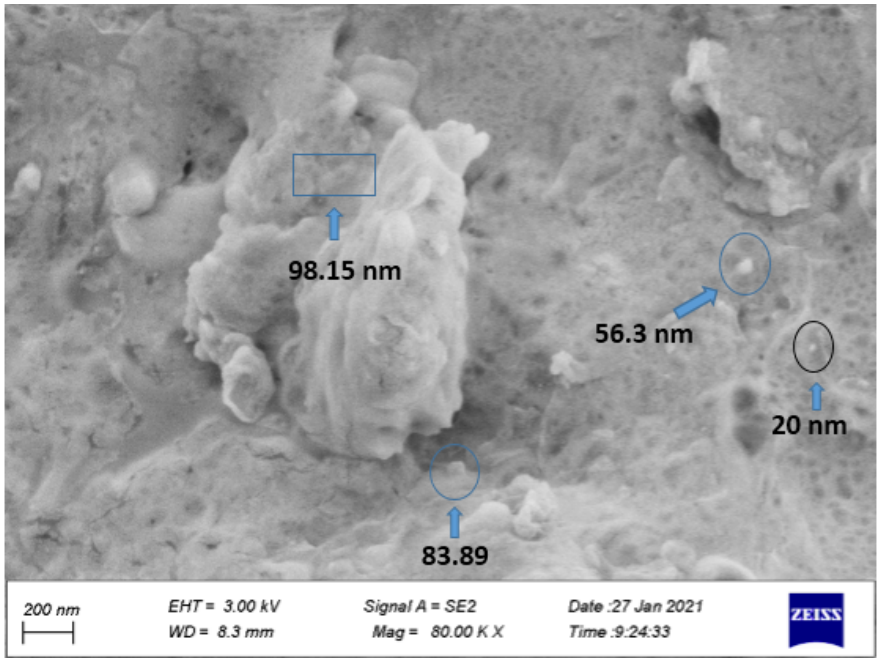

Figure 2: SEM image of CdO nanoparticles and particle size distribution

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Figure 3: TEM image of CdO nanoparticles and particle size distribution

3.1.1.3. Ultra Violet-Visible (UV-Vis) spectrum

The UV-Vis spectrum was illustrated in Figure 4 which representing the absorbance spectrum of as-prepared cadmium oxide at the wavelength range of 190 – 600 nm. The measurement proves that the absorption peak was found at 302 nm. This peak proves the formation of CdO nanparticles [14].

Figure 4: Wavelength vs Absorption of CdO nanoparticles

The energy band gap is measured with the help of absorption spectra and a graph of $(\ ?h?)^{\mathbf{2}}$ versus energy is plotted. The energy band gap of cadmium oxide nanoparticle is 4.65 eV that the value of band gaps increased due to quantum size effect.

3.1.1.4. Fourier transformation infrared spectroscopy (FTIR)

The measurement showed low-intensity broad band centered at 3533 cm^{-1}, which usually appears in nanomaterials due to water adsorption on their surfaces. This band is due to the stretching vibration of hydroxyl in water which is proven by the presence of the bending stretching band of hydroxyl in water at 1620 cm^{-1} [16].

The band at 1448 cm^{-1} indicates the presence of the C=C bond, which is present after the combustion of organic compounds and the transformation into an skeletal carbonic structure only [17]. The distinctive bands of cadmium oxide appeared in the spectrum as follows: a band at 1049 cm^{-1} and a band at 540 cm^{-1} and a band at 1311 cm^{-1}, which are attributed to the stretching vibration of Cd-O [18-20]. See Figure 5.

Figure 5: FTIR of the CdO nanoparticles

3.2. Hydrogen storage of CdO nanoperticles

As shown in Figure 6, the measurement proved that cadmium oxide has the ability to store hydrogen at a pressure of 20 bar, with a value of 0.132 Wt.%H_2. After that, the storage continued to increase by increasing the pressure until it reached the highest storage value, which amounted to 2.85 Wt.%H_2 at a pressure of 80 bar, after which the increase in pressure did not have any effect on the ability to store [21].

The Van't Hoff equation proves that the storage process has a regression coefficient value of 0.97. Through the slope and intercept, the enthalpy value reached 0.62607 KJ/mol H_2, while the entropy value reached 3.35697 J/mol H_2, which means that the adsorption is of the physical type [21-24]. In any case, the temperature change did not have an effect on the weight value, because the pressure change was relatively small, which means that it is possible to reach the highest storage without the need for a low temperature. See Figure 7 and Table 1.

Figure 6: Hydrogen storage isotherm in CdO nanoparticles at 223 K

Figure 7: Vant Hoff plot (1/T Vs. Ln P) of equilibrium pressures and the linear fit to the data

Table 1: Thermodynamic properties of H_2 storage in CdO NPs

T (K)	1/T	P (bar)	ln (P)	[?]H	[?]S
	(K^{-1})			(KJ/mol H_2)	(J/mol H_2. K)
77	12.987	69	4.343805	0.62607	
173	5.78	77	5.153292		3.35697
223	4.4843	80	5.407172		
273	3.663	86.2	5.609472		

Conclusions

From this study, we concluded the successful synthesis of CdO using the green method which is easy, cost-effective, and short technique. Furthermore, the study proved the formation of CdO nanoparticles with irregular sphere like structures of 55 nm particle size. Regarding the hydrogen storage, the results prove that the maximum H_2uptake was equal to 2.85 Wt.%H_2 at a pressure of 69 bar at 77 K with [?]H=0.62607 KJ/mol H_2 and [?]S=3.35697 J/mol H_2. K. Moreover, the thermodynamic studies at four different temperatures proves that the maximum H_2 uptake could be recorded at a pressure limit of 69-86.2 bar. Meaning that, the temperature change did not have an effect on the weight value, because the pressure change was relatively small, which means that it is possible to reach the highest storage without the need for a low temperature.

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None

Conflict of interest statement

The authors declare no financial conflict of interest statement

References

1. Kelsall, R.W.; Hamley, I.W. and Geoghegan, M. 2005. Nanoscale science and technology. John Wiley and Sons Ltd, 473p.

2. Seabra, A. B. and Durán, N. 2015. Metals, 5: 934-975.

3. Ingale, A. G. and Chaudhari, A. N. 2013. Journal of Nanomedicine and Nanotechnology, 4(2).

4. Plaza, D. O.; Gallardo, C.; Straub, Y. D.; Bravo, D. and Pérez-Donoso, J. M. 2016. Microbial. Cell Factories, 15:76. DOI: 10.1186/s12934-016- 0477-8.

5. Kalyani, P.; Vineela, K. C.; Geetha, S.; and Hemalatha, K.P.J. 2016. Int. J. Curr. Microbiol. App. Sci., 5(10): 50-56.

6. El-Said, W.A.; Cho, H.; Yea, C. and Choi, J. 2014. Advanced Materials. 26 (6): 910–918.

7. Pagar, K., Chavan, K., Kasav, S., Basnet, P., Rahdar, A., Kataria, N. Ghotekar, S. (2023). *Journal of Drug Delivery Science and Technology* , 104373.

8. Thema, F. T., Beukes, P., Gurib-Fakim, A., & Maaza, M. (2015).*Journal of Alloys and Compounds* , *646* , 1043-1048.

9. Karthik, K., Dhanuskodi, S., Gobinath, C., Prabukumar, S., & Sivaramakrishnan, S. (2017). *Journal of Materials Science: Materials in Electronics* , *28* , 7991-8001.

10. Nagabhushana, H., Basavaraj, R. B., Prasad, B. D., Sharma, S. C., Premkumar, H. B., & Vijayakumar, G. R. (2016). *Journal of Alloys and Compounds* , *669* , 232-239.

11. Savale, A., Ghotekar, S., Pansambal, S., & Pardeshi, O. (2017). *J. Bacteriol. Mycol. Open Access* , *5* (5), 00148.

12. Guo ZP, Yuan L, Konstantinov K, Huang ZG, Liu HK. Mater Lett 2006;60: 3891e4.

13. Wan Q, Lin CL, Yu XB, Wang TH. Appl Phys Lett 2004;84:124e6.

14. Khan, W. S., Cao, C., Butt, F. K., Ali, Z., Usman, Z., Nabi, G., Hussain, S. (2013). *international journal of hydrogen energy* , *38* (5), 2332-2336.

[15] H.P. Klug, and L.E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, New York (1954).

[16] N.C.S. Selvam, R.T. Kumar, K. Yogeenth, L.J. Kennedy, G. Sekaran, J.J. Vijaya, Powder Technol. 211 (2011) 250–255.

[17]A. Askarinejad, A. Morsali, Mater. Lett. 62 (2008) 478–482.

[18] K. Kaviyarasu, E. Manikandan, P. Paulraj, S.B. Mohamed, J. Kennedy, J. Alloys Compd. 593 (2014) 67–70.

[19] L.A. Saghatforoush, S. Sanati, R. Mehdizadeh, M. Hasanzadeh, Superlattices Microstruct. 52 (2012) 885–893.

[20] M. Mazaheritehrani, J. Asghari, R.L. Orimi, S. Pahlavan, Asian J. Chem. 22 (2010) 2554–2564.

[21] Salih, B. D., Alheety, M. A., Mahmood, A. R., Karadag, A., & Hashim, D. J. (2019). *Inorganic Chemistry Communications* , *103* , 100-106.

[22] Majeed, A. H., Hussain, D. H., Al-Tikrity, E. T. B., & Alheety, M. A. (2020). *Chemical Data Collections* , *28* , 100450.

[23] Alheety, M. A., Al-Jibori, S. A., Mahmood, A. R., Chaurasiya, P. K., Karadag, A., Verma, T. N., & Tiwari, D. (2023).*International Journal of Hydrogen Energy* , *48* (23), 8549-8562.

[24] Al-Isawi, A. A., Al-Jibori, S. A., Al-Janabi, A. S., & Alheety, M. A. (2022, February). In *Macromolecular Symposia* (Vol. 401, No. 1, p. 2100388).