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Abstract

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Na-doped ZnO UV filters with reduced photocatalytic activity for sunscreen application

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Abstract

Due to its physical and chemical stability in addition to its transparency in the visible region with ultraviolet protective activity, ZnO can be used in sunscreen applications. In our article, Na doped zinc oxide nanoparticles were prepared in different concentrations by sol-gel and Solvothermal techniques to reduce their photocatalytic activity. The photocatalytic activity of the doped samples was suppressed effectively at a concentration of 0.03 at% Na doping up to 90% by conducting the sol-gel process rather than the Solvothermal process which resulted in about 70% photocatalytic reduction in a period of time from (0-30 min) when exposed to ultra violet and visible light. In addition the nanoparticles resulted by Sol-gel route shows a reduction in photoactivity under solar simulation about 98% rather than those resulted via Solvothermal process which shows a reduction around 92% for 30 min which is the same period of time used for the photocatalytic degradation test . The particle size was around 64.6- 84.6 nm for samples prepared by both methods.

Keywords: UV filters; ZnO; Photodegradation; sunscreens; ROS

1. Introduction

In the past two decades, the concern for skin protection from ultraviolet (UV) radiation has attracted considerable attention due to the increased intensity of UV rays that can reach the Earth's surface as a result of the breakdown of the ozone layer[1, 2]. There are a number of reports on the risks from exposure to UV rays from sunlight[3, 4], such as skin aging[5-8], sunburn and sun-tanning phototoxicity, and skin cancer[1, 3, 9-12]. Most of them relate to the risks from the generation of reactive oxygen species (ROS), which are created during UV exposure. For this reason, the demand for efficient UV-protection has become very urgent [3, 12]. Most of the UV radiation that reaches the earth consists of UVA (around 95-99 %) and UVB (around 1-5 %) [11]. UVB is well known for its carcinogenic effects and causes erythema. Recently, UVA has also attracted attention, since, in comparison to UVB, it can penetrate deeply into the skin, which can result in significant health concerns [4, 6, 8]. Modern sunscreen products must diminish the radiation ranges of both UVA and UVB, since they both can cause health problems [13]. Therefore, the sunscreen agents represent one of the significant tools to protect the skin from UV irradiation. There are both organic and inorganic UV blockers in sunscreen products [1, 2, 4, 14-18]. Because of the partial degradation of sunscreen organic filters by UV irradiation, which is suspected to increase UV-absorbent allergy and photoallergy, developing novel inorganic UV blockers that provide efficient UV protection over a wide spectrum, good comfort, and high safety when applied on the human skin is necessary [2, 19-21]. Inorganic materials can absorb, reflect, or scatter the ultraviolet radiation, depending on their particle size, unlike the organic blockers, which absorb the UV irradiation[1, 3, 8, 10, 11, 13, 15, 22-25] . Nowadays, most inorganic UV-blocking filters are based on titanium dioxide (TiO₂) and zinc oxide (ZnO) [1, 11, 13, 14, 24-26]. ZnO can provide protection in the UVA range, which is also dangerous solar radiation, since its harmful effects are not reflected in the current Sun Protection Factor (SPF) measurement technique, which is based on the erythema caused by UVB alone [8, 22, 26]. Indeed, ZnO is attractive for sunscreen formulization, and this relates to many advantages, such as its modest refractive index (2.0), its absorption of the small fraction of solar radiation in the UV range which is equal to or less than 385 nm, its high probable recombination of photogenerated carriers (electrons and holes), large direct band gap, high exciton binding energy, non-risky nature, and high tendency towards chemical and physical stability. These advantages make the ZnO nanoparticles transparent in the visible region with UV protective activity, and therefore, the UV blocking ability of ZnO has been important [6, 15-17, 27, 28]. A significant issue for ZnO use in sunscreens is that it can generate ROS in the presence of UV light because of its photocatalytic

activity. Therefore it is essential to make a non-photocatalytic ZnO material through doping with other metals[3, 15].

Several efforts have been made to deactivate the photocatalytic activity of ZnO by using inorganic surface modifiers. The doping of ZnO with different metals is another way to modify its photocatalytic activity [15, 29, 30]. Recently, successful doping of ZnO with different metals such as Ce, La, Co, Mn, Al, Li, Na, K, and Cr by various procedures, such as a simple and facile one-pot water bath, co-precipitation, and hydrothermal, Solvothermal, combustion, and sol gel methods has been reported. These materials exhibit greater performance than undoped ZnO towards decreasing the photocatalytic activity of ZnO in visible light. Therefore, metal doping can be an effective technique to modify the ZnO photocatalytic activity [15, 31-37]. In several papers, however, the photocatalytic activity of ZnO has been reduced successfully by doping with Mn, Ni, N, and Co prepared by sol-gel, Solvothermal, and co-precipitation processes, respectively[30, 38-41]. These reports demonstrate that suitable doping and synthesis strategies have the potential to modify the photocatalytic properties of ZnO in the UVA range, and they can be used to create ZnO UV filters with reduced photocatalytic activity. In the current article, we report reduction of the UV photocatalytic activity of Na doped ZnO fabricated through sol-gel and hydrothermal methods.

2. Experimental section

2.1. Chemicals

Zinc acetate dehydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.999% used as the source of Zn, sodium nitrate, NaNO_3 , purity $\geq 99.0\%$ as the source of Na, commercial ZnO nanopowder, ethanol amine ($\text{C}_2\text{H}_7\text{NO}$, purity $\geq 99.5\%$), and methanol, were purchased from SIGMA ALDRICH and used to synthesize Na doped ZnO.

2.2. Sample preparation

We have emphasized cost-effective methods that can be scaled up for industrial application. In this report, commercial ZnO nanoparticles and Na doped ZnO nanoparticles produced by sol-gel and Solvothermal methods were used.

2.2.1. Sol-gel method

Firstly, 0.25 M of each starting material was prepared, and then they were separately stirred and dissolved in ethanolamine (10.975 g of zinc acetate dehydrate in 200 ml of ethanolamine and 0.424 g of NaNO_3 in 20 ml of ethanolamine). Secondly, specific quantities of the two resulting solutions were mixed in a beaker, so as to achieve Na doping levels of 0.03 and 0.05 at%, and stirred using a magnetic stirrer at temperatures ranging from 60-80°C for 120 - 190

min. Finally, the gelatine product obtained was calcined for two hours at 500°, and then the samples were ground for characterisation.

2.2.2. Solvothermal method

Initially, 0.25 M each of the prepared materials was separately stirred and dissolved in methanol, whereas the same amounts of zinc acetate dehydrate and sodium nitrate as listed above were also used for the preparation in 200 ml and 20 ml of ethanol, respectively, and the same doping levels were used. Then, the Solvothermal process was conducted thermally in a stainless steel vessel in a vacuum drying oven (VDO-30 CH), and the samples were held at 150° overnight and cooled down to room temperature. Finally, the milky solution was centrifuged and washed three times with water and ethanol, then dried at 80° overnight and ground into powder for characterisation. Table 1 shows the preparation conditions for the resultant samples produced by the sol-gel and Solvothermal approaches.

Table 1 Preparation conditions for samples produced by the sol-gel and Solvothermal methods.

Method	Sample Label	Zn (at %)	Na (at %)	Oven temperature (C°)	Annealing temperature (°C)	Annealing time (h)
Sol-gel	Sg1	9.97	0.03	-	500	2
Sol-gel	Sg2	9.95	0.05	-	500	2
Solvothermal	Sv1	9.97	0.03	180	500	2
Solvothermal	Sv2	9.95	0.05	180	500	2

2.3. Characterisation

The purity and crystallinity of the as-prepared samples were characterized by X-ray diffraction (XRD, GBC, MMA) at room temperature. The X-ray diffraction (XRD) measurements on powder samples were performed on an XPERT-PRO 9 9PW 3050/60 equipped with Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$) operated at 40 kV and 30 mA. Samples were scanned within the angular range of 20- 80 degrees with a scanning rate of 0.2 degree / min. Morphologies of the synthesized samples were characterized with a scanning electron microscope (SEM, JEOL JSM-7500FA) and a transmission electron microscope (TEM, JOEL ARM-200F). The photocatalytic properties of the samples were tested in a Rayonet Photochemical Chamber Reactor (RPR) providing radiation in the UVB + UVA range using crystal violet dye. Simulated sun irradiation of the synthesized samples was conducted in a LCS - 100™ solar simulator. The UV absorption and dye photodegradation were tested in a Shimadzu UV-3600. Diffuse reflectance spectroscopy was used to calculate the band gaps of the pure and prepared

1 samples. X-ray photoelectron spectroscopy (XPS) was conducted using a SPECS PHOIBOS
2 100 Analyser installed in a high-vacuum chamber with the base pressure below 10–8 mbar.
3 XPS was used to analyse the valence state of Zn and provide information on the surface
4 chemical composition of the materials. X-ray excitation was provided by Al K α radiation with
5 photon energy, $h\nu = 1486.6$ eV at the high voltage of 12 kV and power of 120 W. The XPS
6 binding energy spectra were recorded at the pass energy of 20 eV in the fixed analyser
7 transmission mode. Analysis of the XPS data was carried out using the commercial CasaXPS
8 2.3.15 software package.

14 **2.4. Photocatalytic and sun simulator tests**

16 The pure ZnO and Na doped ZnO were used as photocatalysts and crystal violet as an
17 evaluating agent. The test was carried out as follows: 5 mg of pure and Na doped ZnO was
18 dispersed and magnetically stirred in 100 ml of crystal violet, respectively, for 30 min in the
19 dark. Next, the prepared suspensions were irradiated in an RPR reactor under an Hg lamp with
20 wavelengths fixed at 300 nm and 350 nm, and located 20 cm away from the 150 ml beaker.
21 Different time periods of exposure were recorded from 0-30 min, with an aliquot taken each
22 five min. Finally, the UV-visible (UV vis) spectra of the irradiated suspensions were collected
23 on a UV-3600 Shimadzu. The same method was carried out for the sun simulator, but the final
24 suspension was irradiated by an LCS - 100TM solar simulator with 1 sun solar irradiation.

33 **3. Results and discussion**

34 **3.1 X-ray diffraction (XRD)**

36 The XRD analysis shows that all the as-prepared ZnO samples have a polycrystalline structure
37 and very good crystallinity. Figure 1 and 2 presents the XRD spectra of the undoped and Na-
38 doped ZnO nanoparticles synthesized by the sol-gel and Solvothermal methods respectively.
39 All peaks can be well indexed to hexagonal wurtzite ZnO [(space group P6₃mc or (186)/amd,
40 JCPDS No. 96-230-0114] zinc oxide, indicating high purity and good crystallinity. It can be
41 observed in the figure that the samples are polycrystalline in nature, possessing the hexagonal
42 wurtzite structure. It is also observed that there is no impurity phase corresponding to Na. The
43 most intensive diffraction peaks of zincite, the (100) and (101) peaks, were selected to calculate
44 the cell parameters. Tables 2 and 3 show the cell parameters, average crystallite size, d -spacing,
45 amount of Na, identifications of peaks, and the corresponding phase angles.

Fig 1 XRD patterns of commercial and Na-doped ZnO nanoparticles of Sg1- 0.03 and Sg2- 0.05 were prepared by the sol-gel method.

Fig 2 XRD patterns of commercial and Na-doped ZnO nanoparticles of Sv1- 0.03 and Sv2- 0.05 prepared via Solvothermal method.

Table 2 Cell parameters, average crystallite size, d-spacing, amount of Na, and peaks and their phase angles for samples grown by the sol-gel process.

Na (at%)	Sample	Peak	<i>d</i> -spacing (nm)	θ (°)	<i>a</i> (Å)	<i>c</i> (Å)	Crystallite size (nm)
0	Commercial ZnO	100	2.777	32.20	3.207	5.18	98.8
		101	2.448	36.68			
0.03	Sg1	100	2.8014	31.92	3.235	5.19	86.6
		101	2.4650	36.42			
0.05	Sg2	100	2.8143	31.77	3.253	5.19	72.6
		101	2.4748	36.27			

Table 3 Cell parameters, average crystallite size, d-spacing, amount of Na, and peaks and their phase angles for the solvothermal process.

Na (at%)	Sample	Peak	<i>d</i> -spacing (nm)	θ (°)	<i>a</i> (Å)	<i>c</i> (Å)	Crystallite size (nm)
0	Commercial ZnO	100	2.777	32.20	3.207	5.184	98.8
		101	2.448	36.68			
0.03	Sv1	100	2.7946	31.95	3.227	5.191	64.6
		101	2.4610	36.48			
0.05	Sv2	100	2.8117	31.80	3.253	5.198	34.7
		101	2.4722	36.31			

3.2 Morphologies

Figures (3-7) show SEM, TEM, and high resolution TEM (HRTEM) images, with the corresponding selected area electron diffraction (SAED) patterns of the commercial and Na-doped commercial ZnO nanoparticles. The samples resulted from Sol-gel route noted by A nearly spherical type of nanoparticle morphology was observed, and the particle sizes were, on average, less than for the commercial ZnO (Tables 2 and 3). They also show images of nanoparticles obtained by both the sol-gel and the solvothermal methods, which clearly demonstrate that both types of nanoparticles possess nearly spherical morphology. Both *a* and *c* lattice parameters were clearly increased, which led to an increase in unit cell volume for the as-prepared samples synthesised by both methods. The platelet particles of pure ZnO mostly vanished when doped with Na in different amounts, and their particle size was greatly reduced, ranging between 72.6-86.6 nm for the nanocrystals produced by sol-gel approach and 34.7-64.6 nm for the nanoparticles resulting from the solvothermal process. For more details of the pure and doped ZnO, TEM images and SAED patterns were collected, and they indicated very

good crystallinity for the as-prepared samples, as clearly shown in the lattice fringes, which are also consistent with the XRD patterns. The lattice spacings of the pure ZnO and prepared samples are 0.2447, 0.2470, 0.2603, 0.2467, and 0.2807 nm, which correspond to the (101), (101), (002), (101), and (100) planes for the pure ZnO, Sg1, Sg2, Sv1, and Sv2 samples, respectively.

Fig 3 SEM, TEM, and HRTEM images, and SAED patterns for Commercial ZnO.

Fig 4 SEM, TEM, and HRTEM images, and SAED patterns for Sg1 from the Sol-gel process- 0.03 doping.

Fig 5 SEM, TEM, and HRTEM images, and SAED patterns for Sg2 from the Sol-gel process- 0.05 doping.

Fig 6 SEM, TEM, and HRTEM images, and SAED patterns for Sv1 from the Solvothermal process- 0.03 doping.

Fig 7 SEM, TEM, and HRTEM images, and SAED patterns for Sv2 from the Solvothermal process- 0.05 doping.

3.3 UV-visible spectroscopy

UV-visible spectra of the prepared samples are shown in Figures 8 and 9 which were recorded in the range of 200 - 800 nm for optical band-gap calculations. Samples of Na doped ZnO, Sg1 from the sol-gel method and Sv1 from the Solvothermal method, showed less absorption compared to undoped commercial ZnO, but they exhibited less degradation compared with commercial ZnO regarding the dye, especially Sg1, which showed a lack of photocatalytic activity towards the dye.

Fig 8 UV–visible spectra of the commercial and Na-doped ZnO nanoparticle of Sg1-0.03, Sg2- 0.05 samples prepared by the sol-gel method.

Fig 9 UV–visible spectra of the commercial and Na-doped ZnO of Sv1-0.03, Sv2- 0.05 prepared by the Solvothermal method.

3.4 Band gap measurements

By using diffuse reflectance spectroscopy to investigate the pure commercial ZnO and the doped samples (Sg1, Sg2, Sv1, Sv2) that resulted from the sol-gel and Solvothermal methods, respectively, the band gaps for the samples have been calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$

in (eV), where α is the absorption coefficient, h is Planck's constant, and ν is the frequency, as shown in Figures 10 and 11. The extrapolation of the linear portion of the curve to $\alpha = 0$ gives the band-gap value (E_g), as shown in Table 3. The data show that doping with Na has shifted the band gap of ZnO to UVA. Note that the samples prepared by the sol-gel route show higher shifting towards UVA, up to 387.5 nm, compared to those prepared by the Solvothermal method, which reached 381.53 nm, as illustrated in Table 4.

Table 4 Band-gap energy (E_g) for photocatalysis of the commercial and Na-doped ZnO nanoparticle samples of Sg1- 0.03, Sg2- 0.05 prepared by the sol-gel route and Sv1-0.03 Sv2- 0.05 prepared by Solvothermal method.

Samples	E_g (eV)	λ (nm)
Commercial ZnO	3.33	372.37
Sg1	3.20	387.5
Sg2	3.25	381.53
Sv1	3.25	381.53
Sv2	3.29	376.89

Fig 10 Plot of $(\alpha h\nu)^2$ as a function of energy ($h\nu$) for commercial and Na-doped ZnO nanoparticle of Sg1- 0.03, Sg2- 0.05 samples prepared by the sol-gel method and (Sv1- 0.03, Sv2- 0.05) prepared by the Solvothermal method.

Fig 11 Plot of $(\alpha h\nu)^2$ as a function of energy ($h\nu$) for commercial and Na-doped ZnO nanoparticle of Sv1- 0.03, Sv2- 0.05 prepared by the Solvothermal method.

3.5 Photocatalytic activity

The photocatalytic activity of the synthesized materials was recorded for time periods from 0 to 30 min on a Rayonet Photochemical Chamber Reactor (RPR), operating from 120-277 V, 50-60 Hz. Figures 12 and 13 show their degradation properties compared to commercial ZnO.

Fig 12 Photocatalytic activity towards crystal violet dye (CV) of commercial and Na-doped ZnO nanoparticles in terms of relative dye degradation over time for the samples Sg1- 0.03, Sg2- 0.05 synthesised via sol-gel process.

Fig 13 Photocatalytic activity towards crystal violet dye (CV) of commercial and Na-doped ZnO nanoparticles in terms of relative dye degradation over time of the samples Sv1- 0.03, Sv2- 0.05 synthesised by Solvothermal process.

From the above, we can see that the samples fabricated by the sol-gel process clearly show higher performance towards suppression of the degradation compared to the Solvothermal route. This may be due to the effects of the synthesis conditions, which create surface oxygen

vacancies during the decomposition of organic species containing carbon at high temperature, because such conditions do not exist in the Solvothermal synthesis. Therefore, the sol-gel method is more suitable for UV sunscreen applications than the Solvothermal.

3.6 Solar simulation

Figures 14 and 15 show the solar simulation properties of our samples compared to commercial ZnO. The solar simulation properties of the synthesized nanoparticles were recorded from 0 to 30 min using an LCS - 100™ solar simulator with simulated 1 sun solar irradiation.

Fig 14 Degradation of crystal violet dye (CV) over time with exposure to simulated 1 sun solar irradiation in conjunction with commercial and Na-doped ZnO nanoparticles of Sg1- 0.03, Sg2- 0.05 produced by the sol-gel Solvothermal (Sv1- 0.03, Sv2- 0.05) method.

Fig 15 Degradation of crystal violet dye (CV) over time with exposure to simulated 1 sun solar irradiation in conjunction with commercial and Na-doped ZnO nanoparticles of Sv1- 0.03, Sv2- 0.05 produced by the Solvothermal method.

3.7 X-ray photoelectron spectroscopy (XPS)

Typical XPS survey spectra of the undoped and Na-doped ZnO nanoparticles can be seen in Figures 16 and 17. High resolution scans for C, O, Zn, and Na were also performed. The survey spectra demonstrate that the main peaks correspond to Zn 2p_{1/2} and 2p_{3/2}, O 1s, Na 1s, and C 1s orbitals for the pure ZnO and the prepared samples synthesized by both the sol-gel (Sg1, Sg2) and Solvothermal (Sv1, Sv2) methods.

According to the XPS curves and typical studies the Zn and O peaks were prominent, and the curves of the prepared samples (Sg1, Sg2, Sv1, and Sv2) show that the doping process was successfully done, although the peaks that are related to Na are very weak. Generally, the peaks at 1022.79 and 1045.86 eV are respectively related to the core lines of the Zn 2p_{3/2} and 2p_{1/2} states. The difference in binding energy between the two peaks was around 23.07 eV, which is consistent with the standard reference values for ZnO. The predictable values of the binding energies and the difference in binding energy in the Zn 2p spectrum show that Zn is in the +2 oxidation state. The core level O 1s peaks for Na-doped ZnO, centred at 531.30 and 533.15 eV, might be shaped in two ways: firstly, from the oxygen of ZnO, and secondly, from partial Na–O–Na bonding. The low binding energy peak (531.30 eV) can be referred to the O–Zn bond, which is related to the O²⁻ ions in the wurtzite structure of the hexagonal Zn²⁺ ion group. Furthermore, the higher energy peak (533.15 eV) is commonly attributed to the presence of the

Zn(OH)_2 phase, so that the formation of this peak may be attributed to the absorption of atmospheric moisture. Na and C peaks were observed for Na 1s (1071.39 eV) and C 1s (287.92 eV). The positions of C, O, and Zn peaks in Sg1, Sg2, Sv1, and Sv2 are the same as for the reference commercial ZnO. All of the measurements related to Zn 2p, Na 1s, and O 1s represent the perfect samples (Sg1 and Sv1) for each synthesis (sol-gel and Solvothermal) method, and the other samples Sg2 and Sv2 are included as well for comparison.

Fig 16 Typical XPS (a) survey spectra and higher resolution (b) Zn 2p, (c) Na 1s, and (d) C 1s peaks for the commercial and Na-doped ZnO nanoparticles of Sg1-0.03, Sg2-0.05 synthesized by the sol-gel method.

Fig 17 Typical XPS (a) survey spectra and higher resolution (b) Zn 2p, (c) Na 1s, and (d) C 1s peaks for the commercial and Na-doped ZnO nanoparticles of Sv1-0.03, Sv2-0.05 synthesized by the Solvothermal method.

4. Conclusions

In conclusion, we employed cost effective nanotechnologies to fabricate sodium-doped zinc oxide nanoparticles with super-low photoactivity that would be suitable for UVA filters in sunscreens. Zinc acetate dehydrate was doped by sodium in different doping concentrations using the sol-gel and Solvothermal routes. The experimental results show an increase in the cell parameters and decreased particle size as a function of doping concentration. These modifications may lead to a significant modification in the photocatalytic activity of ZnO towards deactivation under UV and visible light, especially at the doping level of 0.03 at% for the samples prepared by the sol-gel which was around 90% rather than the Solvothermal method that shows deactivation about 70% for 30 min. In addition, the photoactivity of the ZnO has been reduced up to 98% for samples resulted by Sol-gel method and 92% for those resulted via Solvothermal route under solar simulation also in 30 min. Furthermore, at the same doping level, the band gap was increased to reach the UVA region.

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