Growth of wurtzite ZnO nanorods using different capping agents: Characterization, morphology, and investigation the catalytic activity in some oxindoles and indolyl organics

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ABSTRACT

ZnO nanorods have been prepared through chemical deposition of Zn(OAc)_2.2H_2O by employing different capping agents, (PEG, MW=2000 and PEG, MW=5000). The fabricated catalyst was characterized by scanning electron microscope (SEM) images and XRD pattern. The results show the one dimensional growth of ZnO nano-rods. The capping agents can control the shape and growth of nano-sized crystals. The vertically aligned ZnO was fabricated by PEG 2000, but PEG 5000 changes the ZnO nano-rods to elbow shape. The synthesized nano-rodopes have been utilized as highly efficient catalyst to promote some one-pot multicomponent reactions (MCRs) of indoles consist of symmetrical and unsymmetrical 3,3-di(indolyl)indoline-2-ones and tris(indolyl)methanes synthesis under mild reaction conditions, respectively. Comparison of the catalytic power of these two kinds of synthetic ZnO NRs (2000 & 5000) has also been investigated. Importantly, the catalysts can be recovered from the reaction media and reused for four runs without any activity loss.

INTRODUCTION

Nano-size materials with high surface area ratio can alter chemical and physical properties and have been considered more in recent decade [1,2]. Metal nano-oxids have been gained attention in recent years due to their new exciting industrial applications as photocatalysts, semiconductors, gas sensors, thermal conductive nano-particles and solar energy convertors [3-8]. They have been developed as proper candidate as catalyst due their unique properties [9-12]. It has been shown that material properties such as energy bond gap and thermal conductivity are size dependent [13,14]. Among the various nano-materials, zinc oxides (ZnO) have been applied as photocatalysts, antibacterial materials, and optoelectronic devices [15-17]. Currently, the optoelectronic application of ZnO nano-sized particles were widespread owing to high exciting energy (60 meV) and wide energy band gap (3.37 eV) [18]. Up to now, various ZnO nano-structures with different morphologies have been synthesized such as nano-particles [19], nano-tubes [20], nano-wires [21], nano-flowers [22], nano-belts [23] and nano-rods [24].

Some synthesis methods are based on the use of toxic capping gents and solvents. Therefore many efforts have been devoted to substitute green approaches using non-toxic materials. Tragacanth as a biotemplate was carried out for metal oxide nanoparticle synthesis and ferrite nanocomposites [25-27]. However, the sol-gel using tragacanth is a simple and cost effective method for preparation of nanomagnetic NiFe\textsubscript{2}O\textsubscript{4}@ZnO [28]. As an
alternative, the oak fruit hull and Arabic gum have been introduced as convenient and low cost biomaterials for synthesis of the bimetallic nano oxides and nickel oxide [29-31]. In continuation Arabic gum was proposed for magnesium oxide and zinc oxide nanoparticles over sol-gel method [32, 33]. It was found that magnesium ferrite with attractive catalytic properties such as degradation of dyes can be prepared using sol-gel method over tragacanth gum [34, 25]. In addition, ferulago angulate and black tea extract were proposed as convenient biomaterial for ZnO nano particles [35, 36].

In the past few years, diverse preparation methods have been proposed for the synthesis of ZnO nano-crystals. Moreover, various physical, electrochemical and chemical deposition methods have been developed for the synthesis of 1D vertically aligned ZnO NRs. The sol-gel precipitation method in alcoholic solution is commonly used for simple obtaining of ZnO NRs [37]. In addition, hydrothermal method [38], sputtering [39], electrochemical reaction [40], and molecular beam epitaxy [41] have been reported and applied in different studies. Most of these techniques are expensive and difficult, especially to control the size and crystal uniformity [1]. Pulsed laser ablation is one of the precise methods for ZnO nano-sized obtained in recent years [42, 43]. Although this technique is a controlled fabrication method, but it is more expensive. Chemical deposition method is an important, applied and efficient technique. Different synthesis routes have been proposed with different capping agents and by adjusting various parameters such as pH value, temperature and reflux time.

Multi-component reactions (MCRs) have attracted for organic chemists recently because of their highlighted advantages such as atom economy, convergence, high productivity, ease of implementation, excellent products yields, and large-range of application in organic and medicinal chemistry. N-containing heterocyclic MCRs have gained in great interest because of the importance of nitrogen in drugs as well of natural products branches [44-46].

In this research, a chemical precipitation method was used and modified for ZnO NR fabrication. The self-assembly nano-rods were obtained in the presence of PEG 2000 & 5000. The one dimensional structure of ZnO NR was characterized and studied for two aforementioned surfactants. In the other word, the effect of different capping agents on the shape and size of nano-rods were studied and compared. The experiments show different chemical routes affect crystalline size and structure. It was found that catalytic activity of some organic transformations can be improved by using ZnO NRs.

EXPERIMENTAL

Materials and methods

Zinc acetate dehydrate Zn(OA)₂.2H₂O, PEG 2000, PEG 5000, and all other chemicals and solvents were purchased from Merck company. In the present work, deionized water and NH₃ (Merck, 25%) were used. Nano-crystal characteristics were observed and performed by X-ray diffractometer (Philips, with CuKα1 radiation, cobalt anode with wave length 1.7889, 40 kV, 40 mA), and scanning electron microscope (SEM, model EM 3200, kyky). ¹H-NMR spectra were recorded in CDCl₃ solvent on a Brucker 400 MHz spectrometer. Melting points were determined using a Stuart Scientific SMP2 capillary apparatus and are uncorrected.

Procedure for the synthesis of ZnO NRs

A typical and simple chemical deposition method was employed for the synthesis of ZnO NRs [47]. Briefly, Zn(OA)₂.2H₂O (1g) and PEG 2000 (0.3g) were dissolved in 140 mL double distilled water to obtain a clear and transparent solution. 1.5 mL NH₃ (25%) was added drop wise to form an alkaline solution. The solution was stirred and refluxed for 6 h at 80. It was cooled, centrifuged and washed with distilled water and ethanol for more times. The precipitant was stirred with 90 mL double distilled water and refluxed for 9 h to complete the reaction. The solution was cooled again, centrifuged and washed with absolute ethanol. Then, the participant was dried in an oven at 100. The ZnO NRs have been prepared and studied in the next section. Surface clean nano-rods were obtained by capping agent removal.

General procedure for preparation of symmetrical and unsymmetrical 3,3-di(indolyl)indoline-2-ones

A mixture of indoles 1a-e or pyrrole (2 mmol), isatins 2a-d (1 mmol), H₂O (5 mL), and ZnO NRs (15 mol%) were added to a 25 mL flask equipped with a condenser and refluxed by constant stirring for appropriate time as shown in Table 3. The progress of the reactions monitored by thin layer chromatography (TLC) technique. After reaction completion, the mixture was diluted with EtOAc (10 mL) and centrifuged to remove the catalyst.
The filtrate was extracted with water and further EtOAc (2×10 mL), the organic layer dried over anhydrous MgSO₄ and evaporated under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel to afford the pure symmetrical products 3a-k. In the case of unsymmetrical 3,3-di(indolyl) indoline-2-ones, in the first step of the domino-MCR, appropriate indoles 1a-d (1 mmol), isatins 2a-b (1 mmol), H₂O (5 mL), and ZnO NRs (15 mol%) were refluxed in a vessel equipped with condenser to provide the 3-hydroxy-3-(indolyl) indolin-2-ones as intermediate compounds. The reaction conversion was checked by TLC. Then 1 mmol of an appropriate indole was added to the flask and refluxed to perform their corresponding unsymmetrical 3,3-di(indolyl)indoline-2-ones 3l-r. The work-up procedure is the same as symmetrical analogs. All the products were known and characterized by comparison of their melting points and ¹H-NMR data with those of the authentic samples in literature.

General procedure for tris(indolyl)methanes synthesis

A mixture of indoles 1a-d (3 mmol), triethylorthoformate 4 (3 mmol), and ZnO NRs (15 mol%) heated by vigorous magnetic stirring at 110°C for the appropriate time needed for completion that was monitored by TLC method (Table 4). The solid residue diluted with EtOAc (10 mL) and centrifuged to remove ZnO. Extraction the filtrate with EtOAc, drying over anhydrous MgSO₄ and evaporation the solvent followed by purification through column chromatography on silica-gel lead to the correspondence tris(indolyl)methanes 5a-d.

Recycling of ZnO NRs

Upon the completion of compounds 3a and 6a, the ZnO NRs that were separated via centrifuging, washed with EtOAc (2×10 mL), dried and reused for the similar reactions. The recovery and catalyst usage was repeated within four runs without noteworthy loss of catalytic activity.

RESULTS AND DISCUSSION

Morphology of ZnO NRs

In this section, the structure and morphology of ZnO nano-rods were obtained and considered. The XRD pattern of obtained nano-rods is shown in Fig. 1 that angles were reported for cobalt anode with wave length 1.7889 Å. The 2θ values were multiplied in 0.86 for Cu anode. The peaks values in the presence of PEG 2000, were observed at the following scattering angels (2θ) 31.8, 34.5, 36.4, 47.9, 57.3, 64.1, 67.8, 69.5 and 70.8. These peaks correspond to the reflection from 100, 002, 101, 102, 110, 103, 200, 112 and 201 crystal planes, respectively and identified the hexagonal Wurtzite unit cell (according to JCPDS No. 36-1451 for ZnO). XRD figures show non central symmetry and polar surfaces [48-50]. Furthermore, no significant shifts of peaks are recorded, which indicates that there are any impurities such as capping agents or other solvents and other ZnO nano-structures.

Figs. 2 and 3 show the XRD pattern for products (by PEG 2000 & PEG 5000). X-ray diffraction plot of ZnO NRs fabricated using PEG 5000, is shown in Fig. 3. The peaks for this case were observed at the angels (2θ) 31.8, 34.5, 36.4, 48.03, 57.5, 64, 67.9, 69.5 and 70.8. In the other hand, the peaks correspond to Wurtzite nano-crystal planes precisely for both cases.

Fig. 1. XRD of ZnO NRs were obtained by PEG 2000 (The angles are reported for Cobalt anode λ=1.78Å).
In continue, the average diameter of ZnO NRs has been estimated using Scherrer formula [51]:

\[ d = \frac{k \lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda \) is wavelength of the X-ray (\( \lambda=1.54 \text{ Å for Cu anode} \) & \( \lambda=1.78 \text{ Å for Co anode} \)), \( \beta \) is FWHM (full width at half maximum in radians) of the diffraction peak, \( \theta \) is the Bragg's diffraction angle, and \( k \) is a constant between 0.89 and 1. This formula represents a simple relationship between crystal size and peak broadening. Peak broadening is due to the size of nano-crystal, strain and instrumental broadening. Then, \( \beta \) is defined by following formula:

\[ \beta = \beta_{\text{size}} + \beta_{\text{ins}} + \beta_{\text{strain}} \]  

(2)

\( \beta_{\text{strain}} \) expresses micro strain that have been observed by stocks and Wilson in 1944 [52]. This term emerges due to imperfect crystals. Also, an accurate equation must be account instrumental broadening effect \( (\beta_{\text{ins}}) \). In this work, strain malfunction on XRD pattern was neglected but \( \beta_{\text{ins}} \) was accounted by XRD pattern of instrument. This allows us to accurate calculation of nano-rods diameter. Particle size of ZnO nano-rods were calculated in the presence of PEG 2000 and PEG 5000. The estimated crystallite size using Scherrer's formula is of the same order in SEM images. Mean particle diameter was calculated 21 nm in the presence of PEG 2000 as capping agent and 36 nm for PEG 5000. For this case, \( \beta_{\text{ins}} \) was estimated 0.0033 radians based on instrumental XRD pattern.

Capping agents are frequently used in nanoparticle synthesis to prevent overgrowth and aggregation as well as to control the size of nanoparticle in a precise way. Capping agents
could be stopped the nanoparticles and nano-rods growth. Stabilizing agents were added to the initial solution to prevent agglomeration of the nano-rods. The above mentioned materials play different roles which result various products. Here too, dispersing agent helps to prevent agglomeration, but the final product must be a liquid or suspension [53].

PEG could serve all of the three aforementioned roles that were commonly used by different researchers. In this work, the effects of two different capping agents (PEG 2000 & PEG 5000) on ZnO NRs growth were studied and analyzed. The residual capping agents have adverse and favorable behaviors in catalytic applications of ZnO NRs. The capping agents usually act as a physical barrier to restrict the free access of reactant to catalytic nano-powders; they can also be utilized to promote heterogeneous catalytic performance of nano-crystals. Due to the complexity of these opposite effects, a general and complete survey of capping agents in nano-catalysis is therefore necessary. The adverse impact on heterogeneous catalytic reactions has been not studied precisely which is therefore necessary. The characteristics, shape, size, growth manner and catalytic performance of ZnO NRs were studied in this research. The SEM images of ZnO nano-rods are cylindrical in morphology that were shown in Fig. 4. S5 is ZnO NRs which were prepared by PEG 2000. SEM images confirm vertically aligned growth of ZnO nano-rods. The diameter of S5 (by PEG 2000) nano rods is in the range of 35-50 nm that can be seen in Fig. 4(a). It is apparent from SEM images that diverse shapes of nano-crystals were obtained using PEG 5000. The SEM micrograph of S6 (by PEG 5000) shows an elbow in the presence of PEG 5000. Both S5 and S6 have homogeneous morphology.

PEG 5000 changes the growth habit of ZnO nano-rods and can control the shape of their lattices. Although XRD pattern shows Wurtzite nano-structure, the fabricated ZnO was bow and have not been vertically aligned. Interestingly, this shape is being reported for the first time whereas for different capping agent. In the other word, PEG can control the crystal shape by changing the orientation of rods.

**Investigation the catalytic activity of synthesized ZnO NRs**

The catalytic activities of synthesized ZnO NRs (Fabricated by PEG 2000 & PEG 5000) have been evaluated in some MCRs on the basis of

![Fig. 4. The SEM images of ZnO NRs 2000 (a, b) & ZnO NRs 5000 (c, d).](image-url)
indole ring. Indole moiety is featured in variety of pharmacologically and biologically active compounds [54]. Among a wide range of substituted indole-based heterocycles, 3,3-di(indolyl)indoline-2-ones and tris(indolyl)methanes (TIMs) possess special position. The former contains anticancer [55], antimicrobial [56], and antiinflammatory [57]. TIMs serves bacterial metabolites and cytotoxic agents [58].

Due to strategic situation of these classes in organic and biological chemistry, herein we focus on their synthesis utilizing newly synthesized ZnO NRs. In the first step, some reactions have been schematized using model substrates to optimize the reaction conditions using ZnO 2000 nanoparticles as catalyst. Results are summarized in Table 1 for 3,3-di(indolyl)indoline-2-ones, and Table 2 for TIMs. As expected in Table 1 the typical production of compound 3a, obtained in H2O as solvent under reflux conditions are at the highest yield (entry 3). Performing the model reaction at ambient temperature 70 (entry 2) and room temperature (entry 4) caused moderate yields. Comparing the data of entry 3 and 5 confirms that decreasing the ZnO mole ratio leads to increasing the reaction time. Also, the experiments show that increasing temperature and catalyst mole ratio don't affect the reaction progress considerably.

Perceiving data of Table 2, the model reaction of TIM synthesis was the condensation of indole

Table 1. Screening the optimized reaction condition for the synthesis of 3a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions (1a/2a mole ratio/ ZnO NR amount/ solvent/ temperature)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2/1/ 15 mol%/ solvent-free/ 110℃</td>
<td>1</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>2/1/ 15 mol%/ H2O/ 70℃</td>
<td>1</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>2/1/ 15 mol%/ H2O/ reflux</td>
<td>1</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>2/1/ 15 mol%/ H2O/ r.t.</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>2/1/ 10 mol%/ H2O/ reflux</td>
<td>1.5</td>
<td>85</td>
</tr>
</tbody>
</table>

Table 2. Optimizing the reaction conditions for 5a preparation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions (1a/4 mole ratio/ ZnO NR amount/ solvent/ temperature)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3/3/ 15 mol%/ solvent-free/ 110℃</td>
<td>1</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>3/3/ 15 mol%/ H2O/ reflux</td>
<td>5</td>
<td>&lt;20</td>
</tr>
<tr>
<td>3</td>
<td>3/3/ 15 mol%/ MeOH/ reflux</td>
<td>2.5</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>3/3/ 15 mol%/ solvent-free/ 90℃</td>
<td>1</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>3/3/ 15 mol%/ solvent-free/ r.t</td>
<td>5</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>3/2/ 15 mol%/ solvent-free/ 110℃</td>
<td>1</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>3/3/ 10 mol%/ solvent-free/ 110℃</td>
<td>1</td>
<td>68</td>
</tr>
</tbody>
</table>
with triethylorthoformate that accomplished under solvent-free conditions at 110 (entry 1). Diminution the temperature to 90, declines the reaction yield (entry 4). Decreasing the amount of 4 (entry 6) or ZnO NRs mole ratio (entry 7), discounted the reaction yield.

After denotation the optimized conditions for the synthesis of these two classes of compounds, in the second step, different derivatives of 3,3-di(indolyl)indoline-2-ones have been prepared (Table 3). Attending the whole results in Table 3, demonstrated the ZnO NRs (2000) efficacy in the synthesis of symmetrical 3,3-di(indolyl)indoline-2-ones via the condensation reaction of various electron-deficient and electron-rich indoles and isatins (entries 1-9). Condensation of 3-metylindole with isatin at its 2-position, is another noteworthy potential of the catalyst (entry 10). To illustrate the widespread applicability of the catalyst, condensation of pyrrole and isatin occurred on its C-2 position to create product 3k (entry 11). Moreover ZnO NRs (2000) catalyzed preparation variety of unsymmetrical 3,3-di(indolyl)indoline-2-ones prosperously (entry 12-18).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Indole</th>
<th>Isatin</th>
<th>Product</th>
<th>ZnO NRs (2000)</th>
<th>ZnO NRs (5000)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Time (h)</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>1</td>
<td>1a</td>
<td>2a</td>
<td>3a</td>
<td>1.45</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>2b</td>
<td>3b</td>
<td>0.45</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>2c</td>
<td>3c</td>
<td>1</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>2d</td>
<td>3d</td>
<td>3</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>2a</td>
<td>3e</td>
<td>6</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>1b</td>
<td>2b</td>
<td>3f</td>
<td>5</td>
<td>83</td>
</tr>
<tr>
<td>7</td>
<td>1b</td>
<td>2c</td>
<td>3g</td>
<td>2</td>
<td>77</td>
</tr>
<tr>
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<td>9</td>
<td>1c</td>
<td>2d</td>
<td>3i</td>
<td>5</td>
<td>68</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>2a</td>
<td>3j</td>
<td>5</td>
<td>65</td>
</tr>
<tr>
<td>11</td>
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<td>2a</td>
<td>3k</td>
<td>6</td>
<td>68</td>
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<tr>
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<td>1a, 1b</td>
<td>2a</td>
<td>3l</td>
<td>2.5</td>
<td>88</td>
</tr>
<tr>
<td>13</td>
<td>1a, 1c</td>
<td>2a</td>
<td>3m</td>
<td>2.5</td>
<td>85</td>
</tr>
<tr>
<td>14</td>
<td>1a, 1d</td>
<td>2a</td>
<td>3n</td>
<td>3</td>
<td>86</td>
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<tr>
<td>15</td>
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<tr>
<td>16</td>
<td>1b, 1d</td>
<td>2a</td>
<td>3p</td>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>17</td>
<td>1a, 1b</td>
<td>2b</td>
<td>3q</td>
<td>2.45</td>
<td>89</td>
</tr>
<tr>
<td>18</td>
<td>1a, 1d</td>
<td>2b</td>
<td>3r</td>
<td>3.45</td>
<td>84</td>
</tr>
</tbody>
</table>
Continuously ZnO NRs (2000) catalyzed different TIMs’ synthesis successfully (Table 4, entries 1-4). In the subsequent stage, in order to comprise the ZnO NR (5000) efficacy with its 2000 analog, all the mentioned reactions have been accomplished alternatively. Surprisingly, applying the same reaction conditions, ZnO NRs 5000 displayed better results in time and yield (Tables 3 and 4). These observations can be due to the major surface area of ZnO NRs 5000 than 2000.

Kong et al. reported that ZnO NR has Lewis acid sites (Zn\(^{2+}\)) and Lewis basic sites (O\(^{2-}\)) [59].
As shown in Scheme 1, initially, a Lewis basic moiety on ZnO NRs reacts with indole and the Lewis acid sites (Zn2+) activate the carbonyl group of isatin and also the oxygen moiety of triethylorthoformate, so the formation of the products is occurred. So, based on this explanation, the larger surface area of ZnO NR (5000) relative to its 2000 analog could be the proof of its more efficient catalytic activity.

Since the recycling and reusability of heterogeneous catalysts, is one of the important items in practical application, the recycling tests of ZnO NRs 2000 & 5000 have been investigated in product 3a synthesis. The recycled catalyst, subjected to another catalytic reaction under the same reaction conditions. As shown in Fig. 5, the reused catalyst displayed consistent reactivity within 4 runs.

CONCLUSION

ZnO nano-rods were fabricated through a chemical deposition method. Two different capping agents, PEG 2000 & PEG 5000, were applied via this technique. Morphology and nano-structure of obtained crystals were studied with SEM images and XRD patterns. The Wurtzite structure of obtained crystals were studied with SEM images and XRD patterns. The Wurtzite structure of ZnO NRs 2000 & 5000 have been investigated this technique. Morphology and nano-structure of obtained crystals were studied with SEM images and XRD patterns. The Wurtzite structure of ZnO NRs 2000 & 5000 have been investigated this technique. Morphology and nano-structure of obtained crystals were studied with SEM images and XRD patterns. The Wurtzite structure of obtained crystals were studied with SEM images and XRD patterns. The Wurtzite structure of obtained crystals were studied with SEM images and XRD patterns. The Wurtzite structure of obtained crystals were studied with SEM images and XRD patterns. The Wurtzite structure of obtained crystals were studied with SEM images and XRD patterns.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

16. Zhang L, Ding Y, Povey M, York D. ZnO nanofluids – A
37. Hosseinzadeh Z, Ramazani A, Hosseinzadeh K, Razaghi-


