

An evaluation of nanostructured zinc oxide as a fluorescent powder for fingerprint detection

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Abstract Zinc oxide is evaluated as a fluorescent powder for the detection of fingerprints on non-porous surfaces. Pure and lithium-doped nanostructured zinc oxide powders were characterized using scanning electron microscopy, X-ray diffraction, and fluorescence spectroscopy. The zinc oxide powders were applied to fresh and aged fingerprints deposited on non-porous surfaces such as glass, polyethylene and aluminium foil. Zinc oxide was found to produce clear fluorescent impressions of the latent fingerprints when illuminated with long-wave UV light.

Introduction

We report here the results of our investigations into the use of nanostructured zinc oxide (ZnO) particles as fluorescent powders for latent fingerprint detection.

ZnO powder has been used extensively since the end of the 18th century [1], primarily as a white pigment. It has also been used as a base for coloured pigments; for example, with bismuth or cobalt oxide [2, 3]. ZnO is also a wide band gap semiconductor and ZnO particles typically exhibit photoluminescence in the form of a UV band-edge emission [4]. A broad emission band in the visible region of the spectrum is also observed and arises from intrinsic or extrinsic defects in the material [5].

Powder materials are routinely used in the field of forensic fingerprint detection. The conventional powdering technique involves preferential adherence of powder particles to fingerprint residues to provide contrast between the fingerprint features and the background surface [6]. ZnO has been used in white small particle reagents (SPRs) for fingerprint detection [7]. The SPR technique may be regarded as a wet powdering method, where latent fingerprints are visualized using a suspension of fine particles in detergent solution. The technique is effective for the detection of latent fingerprints on wet non-porous surfaces. In each of these applications, the treated fingerprints are visualized using the contrast in colour between the white powder and the background surface.

In the current study, we have explored for the first time the use of the visible luminescence of ZnO materials to provide contrast between fingerprints developed with the oxide and the surface substrate. ZnO powders were prepared and applied to latent fingerprints on non-porous surfaces in the form of a SPR or as a powder. The effect of

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doping the ZnO with lithium ions to enhance the visible luminescence was also investigated.

Experimental

General

The following chemicals were purchased from commercial suppliers and used as received: sodium hydroxide (Chem-Supply), zinc nitrate hexahydrate (Ajax), lithium chloride (Aldrich), *o*-xylene (Fluka), and Tween 20 (Aldrich). MilliQ water ($18 \text{ M}\Omega \text{ cm}^{-1}$) was used in the synthetic procedures. “Black Emerald” and “Blitz Green” fluorescent magnetic powders were purchased from Lightning Powder, USA.

Secondary electron scanning electron microscope (SEM) images were obtained using a Zeiss Supra 55VP SEM using an in-lens detector. An accelerating voltage of either 5 or 10 kV was used (as indicated in the figure captions).

Fluorescence emission spectra of powder samples were recorded on a Varian Cary Eclipse Fluorescence Spectrometer with an excitation slit width of 10 nm and emission slit width of either 5 or 10 nm. Both excitation and emission filters were used to screen higher order wavelengths.

X-ray diffraction experiments of powder samples were performed using a Siemens D5000 powder diffractometer with a graphite post monochromator with the following parameters: wavelength 1.5406 \AA (Cu $K\alpha$), tube power 1.6 kW (40 kV at 40 mA), step size = 0.02° , time per step = 1 s, divergent slit = 1° , receiving slit = 0.02 mm, scan angle range = $15\text{--}75^\circ$.

Synthesis

ZnO particles were prepared by modification of literature procedures [8, 9]. Equal volumes (100 mL) of aqueous zinc nitrate (0.05 M) and sodium hydroxide (0.2 M) solutions were prepared. The sodium hydroxide solution was heated to 70°C on a hotplate stirrer, and the zinc nitrate solution was then added dropwise over 30 min with stirring. The temperature was kept at 70°C and, after 2 h, the white precipitate was collected on a sintered-glass filter and rinsed several times with ethanol and then water. The final product was obtained by centrifugation and dried at room temperature. The particles were characterized using scanning tunnelling microscopy, X-ray diffraction and fluorescence spectroscopy.

Lithium-doped ZnO particles were prepared using the procedure described above except the zinc nitrate solution was replaced with solutions of the following

stoichiometries: (a) 49.5 mM $\text{Zn}(\text{NO}_3)_2/0.5 \text{ mM LiCl}$, (b) 47.5 mM $\text{Zn}(\text{NO}_3)_2/2.5 \text{ mM LiCl}$, (c) 45.0 mM $\text{Zn}(\text{NO}_3)_2/5.0 \text{ mM LiCl}$, and (d) 40.0 mM $\text{Zn}(\text{NO}_3)_2/10.0 \text{ mM LiCl}$.

Development and imaging of fingerprints

All fingerprints were taken from a single donor. Sets of latent fingerprints were deposited in succession after rubbing three fingers over the forehead without recharging with sebum between depositions. For the comparisons on polyethylene and aluminium foil, the centre of the middle fingerprint was cut in half. On glass, the middle fingerprint was deposited across two adjacent glass slides. For each comparison, half of a fingerprint set was treated with one reagent and the other half treated with a second reagent. All deposited fingerprints were stored at room temperature. Each treated sample was imaged using a VSC2000/HR Video Spectral Comparator (Foster and Freeman, UK). The sample was illuminated with long-wavelength UV light and emission was detected by observation through a 570 nm long-pass filter.

Powders were applied using a Lightning No.1-0035 fingerprint brush. For SPR, 0.1 g of ZnO powder was added to 10 mL of distilled water and 0.05 mL of Tween 20 surfactant, then the suspension was sonicated for 5 min. Samples were immersed in the powder suspension for 2–5 min, depending on the type of surface, and washed with distilled water. The samples were then dried at room temperature prior to imaging.

Results and discussion

Synthesis of ZnO particles

ZnO particles were synthesized using adapted literature procedures [8, 9]. Equal volumes of aqueous zinc nitrate (0.05 M) and sodium hydroxide (0.2 M) solutions were mixed and stirred at 70°C for 2 h. Lithium-doped samples were prepared by adding lithium chloride to the zinc solution before mixing with the hydroxide solution. As discussed below, the inclusion of lithium significantly affects the properties of the nanostructured particles. The powders were characterized by X-ray diffraction measurements, fluorescence spectroscopy and scanning electron microscopy.

X-ray diffraction of powders

Powder samples were studied by X-ray diffraction measured in the range between 15 and 75° (see Supporting

Information). The data are in good agreement with the data of hexagonal zincite with respect to the position and relative intensity of the peaks [10]. There were no additional XRD peaks associated with the lithium-doped samples compared to the undoped specimens indicating no new crystal-phase formation. This finding is in agreement with recent work investigating ZnO nanorods doped with lithium up to a concentration of 10% [11]. The structural agreement between the doped and pure ZnO patterns indicates that each of the dopant atoms do not significantly alter the packing structure of the parent ZnO lattice, although as shown below, some interesting morphological differences between doped and undoped are observed in the SEM images.

Scanning electron microscopy

The micro- and nanostructure of the ZnO particles was investigated using a SEM. Figure 1a shows an SEM image of undoped-ZnO particles. The images reveal flower-like ZnO particles that are generally in the size range 1–3 μm with a reasonably uniform size distribution.

Figure 1b,c shows higher magnification images that reveal the nanostructure of the micron-sized particles. Well-oriented, flower-like structures are evident with each “petal” composed of many small nanoparticles. A similar morphology of ZnO has been previously reported [12–14].

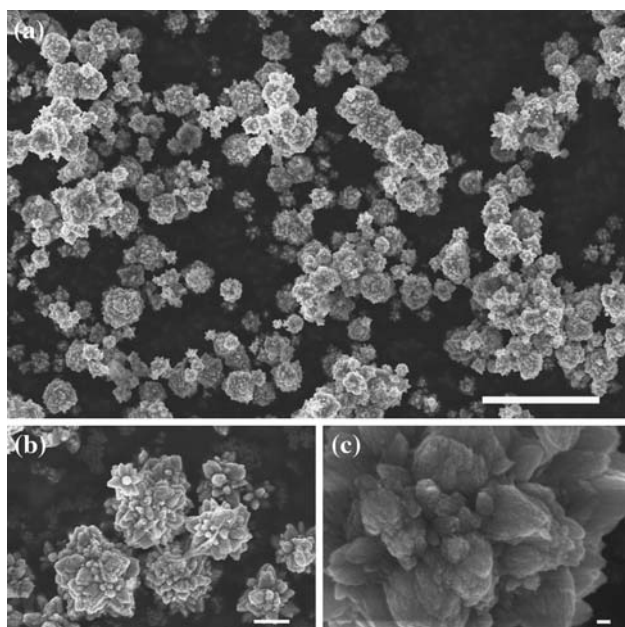


Fig. 1 (a) SEM image of undoped ZnO particles (5,000 \times magnification, accelerating voltage = 10 kV). Scale bar = 10 μm . (b) Image at 31,200 \times magnification, scale bar = 1 μm (accelerating voltage = 5 kV). (c) Image at 100,000 \times magnification, scale bar = 200 nm (accelerating voltage = 10 kV)

When lithium ions were added to the reaction mixture, more plate-like “petal” structures were observed in the SEM images. The mean diameter of the particles obtained from addition of 1% lithium (relative to zinc) is approximately 1–2 μm , similar to the undoped samples. Upon increasing the ratio of lithium to zinc in the reaction mixture, more needle-like structures were observed on the surfaces of the isolated powders. Figure 2 shows SEM images of lithium-doped ZnO particles from reactions, where a 10% Li:Zn ratio was used (Fig. 2a, b) and a 20% Li:Zn ratio (Fig. 2c). In each case, the particle diameter was approximately 1–2 μm . Recently, Zhu et al. [15] proposed that the presence of lithium dopants in zinc lattice sites would decrease the number of inherent oxygen vacancies. This in turn should promote the growth of more ordered structures. This effect is observed in the images shown in Fig. 2, where an increase in well-oriented growth occurs with increasing lithium concentration. In general, it is apparent that the addition of lithium ions has a significant effect on the morphology of the resultant nanostructured

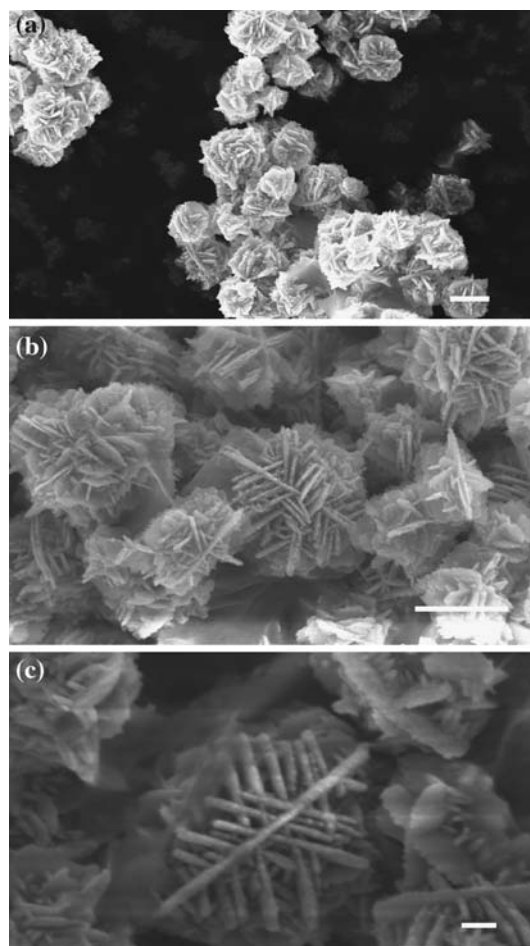


Fig. 2 SEM images of lithium-doped ZnO particles. (a, b) 10% Li-doped; scale bar = 1 μm (accelerating voltage = 10 kV). (c) 20% Li-doped; scale bar = 200 nm (accelerating voltage = 5 kV)

ZnO particles, although as mentioned above, this is not directly evident from powder XRD data.

Fluorescence spectroscopy

Figure 3 shows the fluorescence spectrum obtained from undoped, dried ZnO powder. It is typical of ZnO powder with a relatively intense emission at 388 nm and a broad emission band centred at ~ 587 nm. The peak at 388 nm is the near band-edge emission (NBE) and corresponds to the band-gap energy of this compound (3.3 eV at room temperature). The green emission band at ~ 587 nm is attributed to defects such as oxygen vacancies [5].

In this work, we sought to exploit the visible luminescence of ZnO to enable detection of latent fingerprints on various surfaces. It was anticipated that incorporation of lithium ions into the material would increase the intensity of the luminescence band in the visible region by introducing more surface defect sites [16]. As described above, the inclusion of different amounts of lithium ions in the reaction mixtures had an observable effect on the particle surface morphology by SEM analysis. Figure 4 shows the effect of lithium ion concentration on the fluorescence emission spectra of lithium-doped ZnO samples. These data suggest that a dopant concentration of $\sim 10\%$ (relative to zinc) is optimal to enhance the visible emission.

Because the luminescence properties of nanosized ZnO particles depend greatly on their surface properties [17], experiments were performed to investigate the effect of mechanical grinding on the fluorescence of the particles. It is apparent from the fluorescence emission spectra of 10% lithium-doped ZnO particles before and after grinding (see Supporting Information) that the defect fluorescence band at ~ 587 nm decreases after grinding of the sample while the intrinsic emission band at ~ 380 nm increases. Similar behaviour was observed for undoped ZnO powders, indicating that the inclusion of lithium ions is not responsible

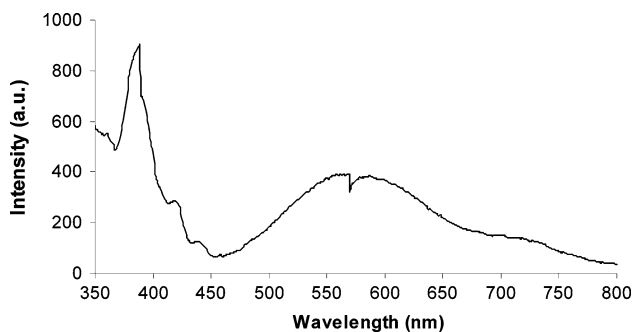


Fig. 3 Fluorescence emission spectrum of ZnO powder. Excitation wavelength = 320 nm, excitation slit width = 10 nm (features at 460 and 570 nm are artefacts arising from filter changes)

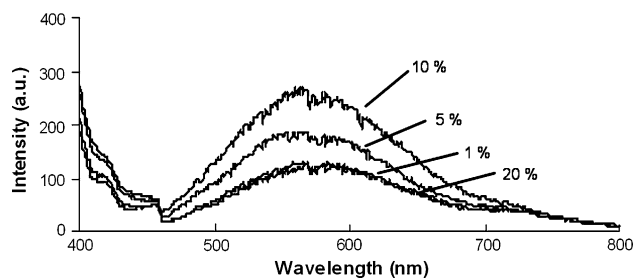


Fig. 4 Fluorescence emission spectra for ZnO doped with 1–20% Li. Excitation wavelength = 360 nm, excitation slit width = 5 nm

for the spectroscopic changes upon mechanical grinding. A recent study [18] reported a similar decrease in the visible luminescence excited by UV light after grinding experiments and suggested that mechanical grinding induces changes in the defect structure of the ZnO crystal lattice. Our results are consistent with these findings, but in addition to the decrease in defect emission, we note the concomitant increase in the band gap emission intensity.

From the fluorescence emission spectroscopy, we conclude that the powders are fluorescent in a region suitable for use in latent fingerprint detection. Doping with lithium ions somewhat enhances the intensity of the visible emission band, while mechanical grinding has the opposite effect.

Application to latent fingerprint detection

ZnO powders were applied to fingerprints on non-porous surfaces such as glass, polyethylene and aluminium foil. The powders were applied by the conventional powder and brush technique and as a SPR. In the SPR method, ZnO powder was dispersed in distilled water containing a surfactant (Tween 20). The specimens were immersed in the suspension, washed with distilled water, and then dried at room temperature before imaging.

Figure 5 shows a 10-day-old fingerprint deposited on glass that has been developed with undoped ZnO using the powder and brush technique. The specimen was illuminated at 350 nm and it is apparent that the luminescence of the ZnO provides good contrast between the fingerprint ridges and the background.

Figure 6 shows a comparison of fingerprints on polyethylene developed using ZnO by two different techniques. The left half of this fingerprint set shows the results of treatment using the powder and brush technique, while the right half shows fingerprints developed using SPR. It was found that SPR consistently yielded well-developed fingerprints even from older prints. The powder and brush technique often resulted in significant background staining. A comparison of the two techniques on aluminium foil



Fig. 5 A 10-day-old fingerprint on glass developed with nanostructured ZnO using the powder and brush technique and detected using a 570 nm long-pass filter with 350 nm illumination

showed that both powdering and SPR yielded excellent results on this surface. We suggest that an electrostatic effect exists with dry powder on plastic, but this does not occur with SPR or on aluminium foil.

Figure 7 shows a comparison of fingerprints treated with undoped ZnO and with 10% Li-doped ZnO powders using the SPR technique. Although the doped ZnO powder yields slightly more intense images, we generally observed little significant difference in intensity or detail between the two treatments, suggesting that the benefits of doping with lithium may be minimal in a practical sense. The handling properties of the Li-doped ZnO powder were similar to the undoped powder.



Fig. 6 Three-week-old fingerprints on polyethylene, developed using powdering (left) and SPR (right); illumination at 350 nm and detection using a 570 nm long-pass filter

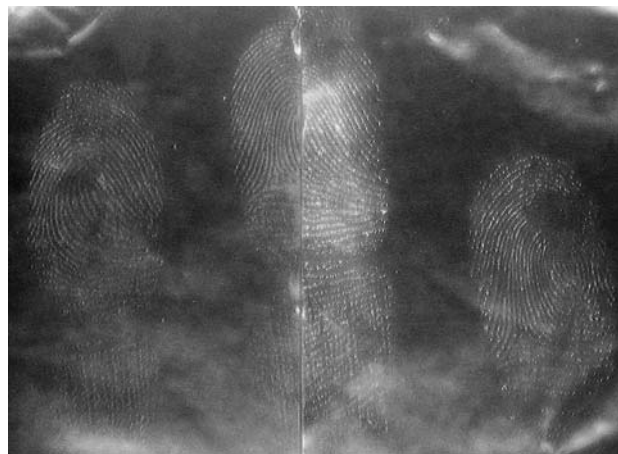


Fig. 7 Fresh fingerprints on aluminium foil treated with ZnO (left) and ZnO:Li 10% (right); illumination at 350 nm and detection using a 570 nm long-pass filter

Development of fingerprints using the powder and brush technique generally deposited more ZnO material on fresh fingerprints on all the tested surfaces. On polyethylene surfaces, the powder and brush technique often resulted in background staining. SPR using ZnO pigment gave excellent results in all cases.

Experiments were performed to compare ZnO with some commercial fingerprint powders on aluminium surfaces. “Black Emerald” and “Blitz Green” fluorescent magnetic powders were used in a comparison with 10% Li-doped ZnO particles (see Supporting Information for images). When observed under white light, very similar development of fingerprints was observed. With UV illumination, the ZnO particles yielded significantly less fluorescence intensity than the commercial powders, although the fingerprints developed with ZnO still showed excellent ridge detail with minimal background staining.

In summary, the ZnO particles applied to latent fingerprints produced clear fluorescent impressions when illuminated with long-wave UV light. In comparison with some commercially available fluorescent fingerprint powders, the fluorescence intensity was somewhat lower for the ZnO powders described here, but it produced less background development, which may lead to a better overall contrast. Other advantages include a straightforward synthesis from relatively cheap starting materials, low toxicity and the utility of using the material as a dry powder or as a wet SPR.

Conclusion

Nano-structured ZnO powders can provide sharp and clear development of latent fingerprints with minimal background staining on non-porous surfaces. SEM images

showed that the nanostructure of these particles is affected by the addition of lithium ions to the reaction mixture. The synthesized ZnO exhibited emission peaks centred at approximately 380 and 587 nm.

ZnO applied to fingermarks produced fluorescent fingermarks under long-wave UV illumination and could be used as a powder or SPR. The SPR was significantly more effective on polyethylene and on aged prints than the dry powder technique. A comparison between pure ZnO and Li-doped ZnO showed no significant differences under either UV or white light illumination, even though fluorescence spectroscopy showed the Li-doped material to be somewhat more fluorescent.

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