A comparative interlaboratory study on photocatalytic activity of commercial ZnO and CeO₂ nanoparticles

Hong Yin · Takuya Tsuzuki · Keith
R. Millington · Philip S. Casey

Received: 8 May 2014 / Accepted: 4 September 2014 / Published online: 11 September 2014
© Springer Science+Business Media Dordrecht 2014

Abstract Photocatalytic activity (PCA) was one of a number of physicochemical end points identified by the Organisation for Economic Cooperation and Development (OECD) as relevant to environmental safety and human health as part of their *Sponsorship Programme for the Testing of Manufactured Nanomaterial*. Photoactive surfaces can produce reactive oxygen species including free radicals which have the potential to cause oxidative stress in tissue or even oxidative damage to DNA. Here we report a study that involved three laboratories in Australia that independently characterised the PCA of commercially available ZnO and CeO₂ NPs provided by the OECD programme. This inter-laboratory comparison found that PCA is a stable characteristic of NPs which was

insensitive to variations in interlaboratory protocols and with ZnO NPs being more photoactive (by an order of magnitude) than CeO₂ NPs. Comparisons were made between NPs of different sizes and the effect of the presence or absence of a surface coating on PCA. Because the competition between surface and volume effects determined PCA, a critical particle size was found for CeO₂ NPs to achieve maximum PCA. The presence of a surface coating appeared to significantly mitigate, but not eliminate PCA.

Keywords Photocatalytic activity · ZnO · CeO₂ · Nanoparticles

H. Yin (✉) · P. S. Casey
Division of Materials Science and Engineering,
Commonwealth Scientific and Industrial Research
Organisation (CSIRO), Private Bag 33, Clayton,
VIC 3169, Australia
e-mail: Hong.Yin@csiro.au

T. Tsuzuki
Research School of Engineering, College of Engineering
and Computer Science, Australian National University,
Ian Ross Building 31, North Road, Canberra, ACT 0200,
Australia

K. R. Millington
Division of Materials Science and Engineering,
Commonwealth Scientific and Industrial Research
Organisation (CSIRO), Geelong Technology Precinct,
Warrn Ponds, VIC 3216, Australia

Introduction

Manufactured nanomaterials are used in commercial products such as catalysts, cosmetics, microelectronic devices, semiconductors, sensors and additives in textiles and coatings. As a consequence of their small size and large specific surface area, they may exhibit attributes that differ dramatically from those of their bulk counterparts and which may have unforeseen implications for their commercial use. One such attribute is their potential to induce toxicity. In the past decade, the number of published papers studying health and safety issues of nanomaterials has increased significantly (Ostrowski et al. 2009). Most have reported in vitro or in vivo studies examining the

toxicity of various nanomaterials and several studies confirmed that higher toxicity was associated with nano-sized materials compared to the corresponding micro-sized materials (Frohlich et al. 2009; Karlsson et al. 2009; Zhu et al. 2008). Consequently, an improved understanding of the adverse effects of nanomaterials and identifying its physicochemical cause are necessary so that material strategies to reduce or eliminate it can be developed.

Assessing the merits of toxicological studies can be difficult if nanomaterials of interest have been inadequately characterized and/or experimental conditions and/or protocols have been arbitrarily chosen (Bouwmeester et al. 2011). This compromises the rigour by which any causal link between specific physicochemistry and toxicity can be identified, assessed and explained. To improve the relevance of such studies, the Organisation for Economic Cooperation and Development (OECD) initiative adopted a *Sponsorship Programme for the Testing of Manufactured Nanomaterial* part of which was to characterise specific physicochemical properties of a selected range of commercially available nanomaterials that were relevant to environmental safety and human health (OECD 2010a). In the programme, OECD member countries volunteered to undertake physical and chemical testing of specific manufactured nanomaterials. Zinc oxide (ZnO) and cerium dioxide (CeO₂) nanoparticles (NPs) were two such nanomaterials and photocatalytic activity (PCA) was one of seventeen physicochemical parameters of interest (OECD 2010b).

Photocatalysis occurs when a material is irradiated with electromagnetic radiation exceeding its band gap. Electron and hole pairs are generated in the valence and conduction bands (CBs), respectively. The photo-generated charges are available for redox reactions with electron-donor or -acceptor species adsorbed on the surface. Photoactive ZnO and CeO₂ NPs are useful in various applications, such as air purification (Chatterjee and Dasgupta 2005), water splitting for the generation of hydrogen gas (Primo et al. 2011) and photodegradation (Yeber et al. 2000). However, where these are used in coatings or personal care products, PCA needs to be quenched to alleviate the potential for photoactive surfaces to generate reactive oxygen species (ROS), that can cause oxidative stress in tissue or even oxidative damage to DNA (Wang et al. 2007). Sayes et al., for example, highlighted that the

higher toxicity of anatase TiO₂ relative to rutile was associated to its greater PCA (Sayes et al. 2006).

Literature reports on the physicochemical properties of NPs are often based on local laboratory protocols (Krug and Wick 2011). Even if the results of these protocols have been carefully assessed for their intra-laboratory reproducibility, this does not guarantee consistency with test outcomes produced in other laboratories. For example, it has been reported that particle size measurements of polydispersed suspensions of nanoparticle aggregates or agglomerates were not reproducible between laboratories and differences in sample preparation techniques, such as the use of ultrasonication, were observed to further increase variability (Roebben et al. 2011). It is therefore desirable to identify whether reported physicochemical characteristics are reliably consistent across experimental protocols used by different laboratories. Understanding potential sources of variability and validating the relevance of such protocols is of great value for interpreting outcomes of any subsequent (nano) toxicological studies.

For PCA studies of ZnO and CeO₂ NPs, results currently available are mostly based on a single method performed in a single laboratory (Giraldi et al. 2012; Chen et al. 2011). We have been unable to find any reports that specifically focus on testing the same material in different laboratories. In this paper, three laboratories (A, B and C) were involved in characterising the PCA of seven commercially available ZnO and CeO₂ NPs provided by OECD programme. The protocols employed by each laboratory have been accepted by reputable peer reviewed journals (Casey et al. 2006; Tsuzuki et al. 2012; Millington and Maurdev 2004). PCAs of same materials obtained in different laboratories were compared. As the tested NPs varied by supplier and physicochemical properties, the paper also compared PCAs of these NPs, some of various sizes and some with/without surface coatings.

Materials and methods

Materials

Supplier details, product names and other pertinent information regarding the ZnO and CeO₂ NPs used in this paper are presented in Table 1. All samples that

Table 1 Pertinent information about ZnO and CeO₂ NPs used in the test

Material	Supplier	Product name	OECD code	Surface coating	Particle size provided by supplier (nm)
ZnO	BASF, Germany	Z-cote	NM110	None	70–200 mean 100
	BASF, Germany	Z-cote HP1	NM111	Triethoxycaprylsilane (2 %)	90–190 mean 130
	Micronisers, Australia	Nanosun	NM112	None	30–50 nm
	Sigma-Aldrich, UK	Micron	NM113	None	95 % < 3.5 μ m, 50 % < 1 μ m
CeO ₂	Antaria, Australia	Ceria dry	NM211	None	10 nm
	Umicore, Belgium	Nanograin	NM212	None	20–25 nm
	Sigma-Aldrich, UK	Micron	NM213	None	<5 μ m

were supplied were uncoated except one of the ZnO samples (BASF Z-cote HP) which had a silane-based coating (triethoxycaprylsilane) whose purpose was to increase its miscibility in cosmetic and sunscreen formulations. According to the information provided by the suppliers, the four ZnO NPs increased in particle size in the order of Micronisers Nanosun (30–50 nm) < BASF Z-cote (~100 nm) < BASF Z-cote HP1 (~130 nm) < Sigma-Aldrich Micron (<3.5 μ m) whilst CeO₂ NP sizes increased from Antaria Ceria dry (~10 nm), Umicore Nanograin (20–25 nm) to Sigma-Aldrich Micron (<5 μ m). All the tested samples of the same material are from the same batch, but the information on their manufacture processes is unavailable. Master stocks of these batches, initially received by the National Physical Laboratory (NPL) in the United Kingdom, were sub-sampled by the NPL and sent to the National Measurement Institute Australia (NMIA). Then NMIA distributed these samples to three different Australian laboratories involved in PCA analysis.

Materials characterization

Particle size and shape were examined using images taken on a transmission electron microscope (TEM, Tecnai 12, FEI, Eindhoven, The Netherlands) operating at 120 kV. The surfaces of NPs (coated and uncoated) were analysed by X-ray photoelectron spectroscopy (XPS; ESCA LAB 220i-XL Thermo VG Scientific, UK). In the latter, eight wells of a powder sample holder (two wells per sample) were filled with NPs. The sampling depth was less than 10 nm, and the analysis area was approximately 0.5 $\times$ 0.7 mm. XPS data files were processed using the application CasaXPS software (version 2.3.13).

Photoactivity measurement methods

When the irradiation energy exceeds the band gap, electron–hole pairs are generated in the valence and CBs, respectively. The photo-generated electron–hole pairs migrate to the particle surface where they can react with pre-adsorbed species and form free hydroxyl or superoxide radicals. 1,1-diphenyl-2-picrylhydrazyl (DPPH), a stable free-radical molecule, can scavenge these free radicals. A concomitant change of colour occurs with the decrease of DPPH concentration and manifests a reduction in its characteristic absorption at wavelength of 520 nm. Similarly, the photo-reduction of Rhodamine B (RhB) can also be monitored by utilising its characteristic absorption at 554 nm. These two dyes (i.e., DPPH and RhB) were used to measure and compare PCA.

Laboratory A Two dispersions were prepared with 5.2 mg DPPH and 31 mg NPs, respectively in 65 ml Mineral Oil White Light (Aldrich): Caprylic C8/C10 Triglyceride (MOTG) (1:1) and magnetically stirred in a covered beaker (aluminium foil, all sides) for 1.5 h. UV–Vis absorbance spectra of suspensions containing MOTG and NPs (without DPPH) were collected as baseline using Cary 5G UV–Vis NIR spectrophotometer. In the baseline, there was no absorption peak within the range of 400–700 nm due to the presence of MOTG or NPs. Then the two dispersions were combined and poured into a crystallising dish (135 mm inner diameter, 23 mm inner height) and covered (aluminium foil, all sides). The mixture was stirred for 5 min to form a purple colour solution. Before exposure to UV, 3 ml of this solution was withdrawn and placed in a cuvette, its UV–Vis spectrum was measured ($t = 0$) after which it was returned to the mother solution. The solution was then

exposed to UV using a pre-warmed Spectroline UV lamp (BIB150 P/FA, 365 nm, 150 W concentrated spot bulb, diameter = 110 mm) placed at a distance of 12 cm from the solution where the intensity at 365 nm was 45 mW cm^{-2} . The sampling procedure described above was repeated at selected time intervals. PCA is determined by measuring the time it takes for the DPPH radical, (initially purple in colour) to convert to its reduced form (yellow). To quantify the PCA, the value of the absorbance was monitored at a wavelength of 520 nm (the position of a peak in the absorbance spectra due to the purple DPPH radical).

Laboratory B NPs (8 mg) were dispersed in 50 ml of an aqueous RhB solution with a concentration of $0.0096 \text{ mg ml}^{-1}$. The suspension was stirred in the dark for 1 h to ensure the establishment of adsorption and desorption equilibrium of RhB on the particle surface. Subsequently, the suspension was irradiated with simulated sunlight using an Atlas Suntest CPS1 instrument (Atlas Co., Chicago, IL) equipped with 1,500 W xenon lamp and a filter (coated quartz dish). The irradiation intensity was 60 mW cm^{-2} over 300–800 nm. At given intervals, 3 ml of the suspension was extracted and then centrifuged at 6,000 rpm for 10 min to separate particles from supernatant. UV–Vis absorbance spectra of the supernatant were measured with a Varian Cary 3E spectrophotometer (Varian Co., Mulgrave, Australia). The decay of the characteristic optical absorption of RhB at 554 nm was used to monitor PCA in response to UV irradiation.

Laboratory C RhB (23.5 mg) was dissolved in ultrapure water (1 l) in a graduated flask. Small amounts of NPs (20–30 mg) were added to aliquots of this solution (100 ml) and mixed for 5 min in a narrow vessel using a laboratory homogenizer (Model SEV, Kinematica AG, Lucerne) on speed setting four. The suspension was then poured into a flat Petri dish (150 mm diameter) containing a magnetic stirrer bar and tightly covered with PVC cling film. The dish was placed on a magnetic stirrer inside a UVA irradiation cabinet containing an overhead array of eight black light tubes (Philips TLD 36W/08) producing radiation over 340–410 nm with a peak intensity of $270 \mu\text{W cm}^{-2}$ at 365 nm. The suspension was stirred throughout UVA exposure and samples (3 ml) were taken at regular intervals through a single hole in the PVC film using a glass syringe fitted with a stainless steel needle. The samples were placed in small

centrifuge tubes (13 x 51 mm) and spun at 30,000 rpm for 10 min at 10°C using an ultracentrifuge (Beckman TL100 fitted with a TLA100.4 rotor) to remove the NPs. Clear liquor from the centrifuged samples was carefully removed using a Pasteur pipette and placed in a quartz cell and the UV–visible spectrum of the dye was measured over the range 800–200 nm. A set of irradiated RhB samples containing no NPs was used as a control. The main absorbance peak at 554 nm was used to measure the decrease in dye concentration and hence the rate of photocatalysis.

Table 2 summarizes the details of key experimental parameters used in three laboratories.

Results

PCA analysis

Figure 1a presents the typical absorption curves of DPPH in BASF Z-cote ZnO containing dispersions. The characteristic absorption peak of DPPH is found at 520 nm and at $t = 0$, the initial density of the characteristic peak corresponds to the initial concentration of DPPH (c_0). As irradiation time increases, peak density decreases to a lower DPPH concentration (c). The intensity ratio (c/c_0) was plotted versus irradiation time (t) and their dependence is shown in Fig. 1b. Decay time is taken as the time required for the dye to be completely converted to its reduced form, i.e., $c/c_0 = 0$. PCA is determined by the length of the decay time such that the shorter the decay time, the higher the PCA. In addition, as shown in Fig. 1b, the photodegradation of DPPH appears to be a first order reaction indicated by the following linear relationship

$$\ln \frac{c}{c_0} = -A \cdot t$$

where A is the first order rate constant of the radical consumption. Higher rate constant corresponds to higher PCA. Where RhB is used as dye, its characteristic UV absorption peak is found at 554 nm. All other calculations followed the above descriptions.

PCA of ZnO NPs

Table 3 shows decay times and rate constants of ZnO NPs obtained in laboratory A, B and C, respectively.

Table 2 Details of key experimental parameters used in three laboratories

Laboratory	A	B	C
Dye	DPPH	RhB	RhB
Dye concentration (mg ml ⁻¹)	0.04	0.0096	0.0235
Dispersion medium	MOTG	De-ionised water	Ultrapure water
Particle concentration (mg ml ⁻¹)	0.24	0.16	0.20–0.30
Pre-exposure treatment	Particle and dye dispersion was prepared separately and magnetically stirred for 1.5 h before combining. The mixture was further stirred for another 5 min	The suspension containing both particle and dye was stirred in the dark for 1 h	The suspension containing both particle and dye was mixed for 5 min in a narrow vessel using a laboratory homogenizer
Irradiation source	Spectroline UV lamp (BIB150 P/FA, 365 nm, 150 W concentrated spot bulb, diameter = 110 mm) placed at a distance of 12 cm from the solution where the intensity at 365 nm was 45 mW cm ⁻²	Simulated sunlight using an Atlas Suntest CPS1 instrument (Atlas Co., Chicago, IL) equipped with 1500 W xenon lamp and a quartz filter. The irradiation intensity was 60 mW cm ⁻² over 300–800 nm	UVA irradiation cabinet containing an overhead array of eight black light tubes (Philips TLD 36W/08) producing radiation over 340–410 nm with a peak intensity of 270 μW cm ⁻² at 365 nm
Post-exposure treatment	Nil	Centrifuged at 6,000 rpm for 10 min to separate the particles from the supernatant	Centrifuged at 30,000 rpm for 10 min at 10 °C to remove particles

Error data calculated from linear regression for each measurement were also presented. Results for all laboratories indicate that PCA decreases in the following order.

BASF Z-cote ~ Sigma-Aldrich Micron > Micronisers Nanosun > BASF Z-cote HP1. The least variability (in decay times and rate constants) between laboratories was observed in those NPs with the highest PCA (i.e., the shortest decay times). For example, BASF Z-cote decay times varied between 7.7 and 11.3 min (Average = 9.7 min, SD = 1.5 min). Variability increased as PCA lowered such that the least photoactive particles (BASF Z-cote HP1) manifested decay times varying between 12.1 and 45.0 min (Average = 26.7 min; SD = 13.7 min).

PCA of CeO₂ NPs

Decay times and rate constants of CeO₂ NPs with fitting errors calculated from linear regression are shown in Table 4. Results generally indicate that PCA decreases in the following order Umicore

Nanograin > Sigma-Aldrich Micron > Antaria Ceria dry, although there were some slight differences for the less photoactive Antaria Ceria dry and Sigma-Aldrich Micron between DPPH and RhB dye. The least variability between laboratories is observed in the most photoactive Umicore nanograin with decay times varying between 63 and 121 min (Average = 91 min; SD = 29 min). Variability markedly increased as PCA reduced with decay times for the other two samples.

Discussion

Photocatalytic process

The photocatalytic transformation of a dye involves several steps: (1) photo-absorption by the NPs; (2) the generation of electrons and holes; (3) the transfer of charge carriers to the particle surface, and (4) the utilization of the charge carriers by the dyes. The OH radical is recognized as the main reactive

Fig. 1 **a** Typical UV absorption curves of DPPH in BASF Z-cote ZnO containing dispersions, after exposure to UV irradiation, **b** dependence of intensity ratio (c/c_0) on irradiation time (black) and dependence of $\ln(c/c_0)$ on irradiation time (blue). Decay time was determined by the irradiation time where c/c_0 is 0 in black line and rate constant was obtained using the gradient of blue line

species responsible for dye transformation and this can be formed either through reduction induced by electrons or oxidation induced by holes (Bagwasi et al. 2012).

As shown in Fig. 2, CB electrons at the particle surface are scavenged by the ubiquitously present molecular oxygen to yield the superoxide radical anions, $O_2^{\cdot-}$ and when protonated form $HOO^{\cdot}$ radicals which can produce $\cdot OH$ through the following reactions:

At the same time, the valence band (VB) holes (h^+) become trapped as the surface-bound $\cdot OH$ radicals form on oxidation of either the surface OH^- groups and/or the surface H_2O molecules. Photooxidation of the organic dyes (i.e., DPPH and RhB) can take place by reacting with $\cdot OH$ or some other oxidation groups, such as O_2 , $O_2^{\cdot-}$ and $HOO^{\cdot}$.

As indicated in Tables 3 and 4, decay times and rate constants of specific samples varied between different laboratories. This is not surprising as the three laboratories used different methods to characterize PCA (Table 2). Explaining the discrepancy in PCA results between laboratory A and laboratories B, C is not straightforward because the photodegradation kinetics of DPPH are different from that of RhB (Wu et al. 1998; Dransfield et al. 2000). For laboratory B and C using the same dye (RhB), differences in PCA could be related to several reasons. Firstly, laboratory C allowed only 5 min mixing time of particles and dye before light exposure, whilst laboratory B gave 60 min to establish dye-absorption-desorption equilibrium before light exposure. Hence laboratory B's procedure may result in more consistent assessment for samples with different surface areas and pore size/volumes. Secondly, there is a difference in the particle/dye ratio

Table 3 Decay times and rate constants of four ZnO NPs assessed by three laboratories

Sample	Laboratory A		Laboratory B		Laboratory C	
	Decay time (min)	Rate constant (min^{-1})	Decay time (min)	Rate constant (min^{-1})	Decay time (min)	Rate constant (min^{-1})
BASF Z-cote	7.7 ± 1.3	0.35 ± 0.02	10 ± 1	0.53 ± 0.03	11.3 ± 0.9	0.16 ± 0.01
BASF Z-cote HP1	12.1 ± 1.4	0.18 ± 0.01	45 ± 5	0.05 ± 0.01	23.2 ± 2.6	0.13 ± 0.01
Micronisers Nanosun	10.7 ± 0.5	0.23 ± 0.02	20 ± 2	0.14 ± 0.01	17.8 ± 1.4	0.14 ± 0.01
Sigma-Aldrich micron	7.5 ± 1.2	0.32 ± 0.02	10 ± 1	0.46 ± 0.03	10.3 ± 0.6	0.20 ± 0.02

Table 4 Decay times and rate constants of three CeO₂ NPs accessed by three laboratories

Sample	Laboratory A		Laboratory B		Laboratory C	
	Decay time (min)	Rate constant (min ⁻¹)	Decay time (min)	Rate constant (min ⁻¹)	Decay time (min)	Rate constant (min ⁻¹)
Antaria ceria dry	207 ± 10	0.0072 ± 0.0008	202 ± 25	0.0054 ± 0.0017	~2,000	0.0005 ± 0.0001
Umicore nanograin	89 ± 3	0.0141 ± 0.0030	63 ± 17	0.0203 ± 0.0040	121 ± 15	0.0102 ± 0.0020
Sigma-Aldrich micron	237 ± 12	0.0070 ± 0.0020	130 ± 20	0.0087 ± 0.0009	547 ± 35	0.0019 ± 0.0005

Fig. 2 Photocatalytic mechanism of generation of •OH free radicals and some other oxidation groups, such as O₂•⁻ and HOO•

between laboratory B (~16.7) and laboratory C (~10.6), which could also cause various rates of photodegradation. Finally, the radiation sources differed from simulated sunlight (laboratory B) to UVA irradiation cabinet (laboratory C). The former provides a broader band of UV rays with different excitation energy and has much higher intensity (60 mW cm⁻²) than the latter (270 μW cm⁻²).

When comparing the relative PCA order, good consistency was observed between laboratories, i.e., ZnO had an order of magnitude higher PCA than CeO₂. For CeO₂ particles, all laboratories found that Umicore Nanograin (with medium particle size) had the highest PCA whilst for ZnO, BASF Z-cote had the highest activity with its coated counterpart having the lowest. Given this, our inter-laboratory comparison suggests that PCA is a reasonably stable characteristic of NPs and does not appear to be overly sensitive to variations in laboratory protocols. However, as

indicated above there was less variability (for both ZnO and CeO₂) when particles had high PCA and that variability increased as PCA reduced (see Tables 3, 4). On the other hand, PCA is profoundly dependent on particle characteristics such as its material nature, the presence or absence of a surface coating and particle size.

Comparing PCA of ZnO and CeO₂

All three laboratories reported that ZnO NPs had a significantly higher PCA than CeO₂ NPs. Considering that CeO₂ has similar band gap (3.2 eV) as ZnO (3.3 eV), the low PCA of CeO₂ is most likely due to imperfections in the crystal lattice manifested as electron and/or oxygen vacancies. Subsequently photoactivated charge carrier migration to the surface may be too slow or not possible (Bennett and Keller 2011). As shown in XPS spectrum of CeO₂ (Fig. 3), both Ce³⁺ (5–10 at.%) and Ce⁴⁺ (90–95 at.%) oxidation states were detected, although stoichiometry indicates a molecular formula of CeO₂. By changing its oxidation state from Ce³⁺ to Ce⁴⁺, CeO₂ NPs could scavenge the free radicals generated by irradiation (Tarnuzzer et al. 2005). Interestingly, emerging toxicological research has found that CeO₂ NPs can quench free radical generation in vivo at very low concentrations. Hirst and coworkers attributed the quenching ability of nanoceria to the existence of oxygen vacancies in the crystal lattice and the occurrence of Ce³⁺ and Ce⁴⁺ (Hirst et al. 2009).

Comparing PCA of ZnO with or without surface coating

One strategy to reduce PCA is to provide a barrier between the photoactive particle and its environment-

Fig. 3 XPS spectrum of the typical CeO_2 NPs showing the presence of mixed valence states of Ce^{3+} and Ce^{4+} on the surface

preventing direct contact between the two (Wang et al. 2009). BASF Z-cote HP1 ZnO is a coated version of BASF Z-cote and is supplied with a triethoxycaprylsilane coating. The prime purpose of the coating is to make the particle more dispersible in formulated products such as sunscreens and personal care products. XPS survey spectra of this sample confirmed the presence of Si on the particle's surface (spectra not shown). Such surface coating appears to significantly mitigate, but not eliminate, PCA (see Table 3) as in all laboratories BASF Z-cote HP1 was found to be the least photoactive ZnO. It is thought that triethoxycaprylsilane molecules surrounding ZnO NPs restrain, but not completely exclude, the migration or diffusion of charge carried to surface perhaps arising from inconsistencies or discontinuities in the coating. Consequently, a lower charge concentration limits any reaction with surface species such as O_2 , H_2O to produce free radicals and results in reduced PCA. It was noted that the degree to which PCA was reduced varied between laboratories. This was partly attributed to experimental variability and differences in the dye degradation reaction mechanisms (Wu et al. 1998; Dransfield et al. 2000).

Comparing PCA of NPs with different sizes

Particle size is thought to be one of the most important parameters influencing PCA of NPs (Egerton and Tooley 2004; Li et al. 2004) with a smaller particle producing a higher PCA consequent of a higher

specific surface area presenting a larger number of photoactive surface sites. At very small particle sizes some counterproductive processes (such as increased surface recombination, lower utilization of photons and increased defects) may dominate productive processes (increased surface active sites and reduced volume recombination). Consequently, there may be an optimum particle size (critical size) at which a maximum PCA is observed. This critical particle size is well known for nanocrystalline anatase TiO_2 particles. Here, Liu et al. found that 10 nm nanocrystals showed highest photocatalytic efficiency when examining particles with various diameters (4.5, 6.0, 9.1, 9.6, 9.9, 11.7, 12.8 nm) prepared through sol-gel hydrolysis precipitation (Liu et al. 2008). Maira et al. prepared 2.3, 3.8, 7, 11 and 21 nm anatase powders and showed that 7 nm powders exhibited the highest PCA for the gas-phase photo-oxidation of trichloroethylene (Maira et al. 2000). However, there have been few reports on the influence of particle size on NP photo-activity other than TiO_2 (Casey et al. 2004; Dodd et al. 2006) and the effect of physical influences such as agglomeration in the liquid phase has not been deeply studied.

Particle size information provided by the commercial suppliers was limited and non standardised (see Table 1). A microscopic study of size was undertaken to provide a basis on which a size comparison could be made. Figure 4 presents typical TEM images of the four ZnO NPs. BASF Z-cote (uncoated) indicated polyhedral primary particles with a variable morphological and size distribution whilst BASF Z-cote HP1 (coated) showed similar polyhedral particles but with aspect ratios generally larger than BASF Z-cote. Micronisers Nanosun had the smallest particle size with a relatively homogenous size (~ 30 nm) and shape (spherical) distribution. Sigma-Aldrich Micron particles, the largest of the four samples (typically between 100 and 200 nm, with some large aggregates) are also polyhedral.

TEM images of the three commercial CeO_2 NPs are presented in Fig. 5. Antaria Ceria dry has a relatively homogeneous size and shape distribution with particles appearing near spherical and with diameters between 10 and 20 nm. Umicore Nanograin particles are polyhedral with sizes around 30 nm but with some irregular aggregates/agglomerates present. Sigma-Aldrich Micron has a relatively homogeneous distribution of large polyhedral particles (~ 200 nm).

Fig. 4 Typical TEM images of ZnO NPs showing varied particle sizes and shapes

The Feret diameter (D_{Feret}) is widely used in imaging of irregular shaped particles. The D_{Feret} of all seven commercial NPs was determined from TEM images using a semi-automated particle size analysis programme (ImageJ/Fuji). Around 500 particles were analysed to ensure adequate statistical confidence and results are summarized in Table 5 with the calculated D_{Feret} suggesting a particle size order similar to that indicated by the supplier information (Table 1). The least variance between the measured and supplied values was found with smaller particles (Micronisers Nanosun ZnO, Antaria Ceria dry CeO_2 and Umicore Nanograin CeO_2). With larger particles (e.g., BASF Z-cote and BASF Z-cote HP1), however, substantial differences between values were observed. For the largest particles (Sigma-Aldrich Micron ZnO and Sigma-Aldrich Micron CeO_2), microscopic analyses revealed the presence of smaller particles distributed amongst the larger agglomerates.

In previous reports, the size-dependence of PCA was investigated with NPs of different sizes prepared by the same method (Egerton and Tooley 2004; Li et al. 2004; Liu et al. 2008). In this study, the size effects were investigated the first time on commercial samples obtained from different suppliers who produced them by different methods. Decay times and rate constants

obtained from three different laboratories (Table 3), show that BASF Z-cote ($D_{\text{Feret}} = 70$ nm) has the highest PCA of the three uncoated ZnO NPs and its coated counterpart the lowest. There was no clear particle size dependency observed as Sigma Micron ($D_{\text{Feret}} = 143$ nm) showed very similar PCA to BASF Z-cote and surprisingly lower than these was Micronisers Nanosun. Dodd et al. studied PCA of ZnO NPs sized from 28 to 57 nm and found that highest PCA was achieved when the particle size was approximately 33 nm (critical size) (Dodd et al. 2006). In Table 3, no critical size is apparent probably because the four commercial ZnO samples were typically of a larger size and no NPs with a smaller particle size than critical size (around 30 nm) were investigated. Casey et al. found that PCA of ZnO NPs appeared to be independent of particle size at sizes greater than 80 nm (Casey et al. 2004). Our observations here indicated that BASF Z-cote ($D_{\text{Feret}} = 70$ nm) and Sigma Micron ($D_{\text{Feret}} = 143$ nm) had very similar PCA which agreed well with this finding and probably reflect the diminishing influence of the relationship between particle size and specific surface area as particle size increases. In the PCA study of CeO_2 NPs (Table 4), the shortest decay time is consistently observed with Umicore Nanograin CeO_2 ($D_{\text{Feret}} = 30$ nm) rather than with the

Fig. 5 Typical TEM images of CeO₂ NPs showing varied particle sizes and shapes

Table 5 Feret's diameter (D_{Feret}) of ZnO and CeO₂ NPs

	BASF Zcote ZnO	BASF Zcote HP1 ZnO	Micronisers nanosun ZnO	Sigma-Aldrich micron ZnO	Antaria ceria dry CeO ₂	Umicore nanograin CeO ₂	Sigma-Aldrich micron CeO ₂
D_{Feret} (nm)	70 ± 46	82 ± 45	30 ± 9	143 ± 47	12 ± 3	29 ± 19	67 ± 64

smaller Antaria Ceria particles ($D_{\text{Feret}} = 12$ nm) or the larger Sigma-Aldrich Micron particles ($D_{\text{Feret}} = 67$ nm). Based on this, a critical size for maximum PCA may be inferred for CeO₂ NPs.

All the PCA data reported in this paper were measured on particles in their as-received form. The methodologies used were not customised or modified for different particle sizes. One obvious consideration is that PCA measurements using these methods may be sensitive to particle dispersion effects where the measurement of the smallest particle sizes may be most affected given their propensity to agglomerate. To this end, a set of experiments was performed where a variety of dispersion methods (magnetic stirring, high shear mixing, and light ball milling) were used to disperse Micronisers Nanosun ZnO before PCA

testing was performed (Micronisers Nanosun has the smallest and most homogenous size distribution). Here, it was found that these treatments did affect the decay time and could reduce it by up to 30–40 %. This suggests that the degree to which particles (and particularly NPs) are effectively dispersed (i.e., de-agglomerated) will influence empirical outcomes where dispersion is a component of the experimental methodology. At greater degrees of dispersion, the effective surface area is increased, apparent diameter decreased (i.e., agglomerates broken up) with the expectation that PCA would increase, which is what was observed. Clarifying whether surface area or particle size is the key determinant of observed PCA in ZnO is the subject of another study being undertaken by the authors.

Conclusions

The rapidly increasing application of NPs in commercial products requires an improved understanding of any associated potential risks, and in particular, determination of NPs characteristics that may detrimentally affect human health. The OECD initiative has adopted as part of its international sponsorship programme on manufactured nanoparticles characterisation of physicochemical properties of ZnO and CeO₂ NPs. PCA is one of the seventeen physicochemical parameters identified by OECD relevant to environmental safety and human health. This paper measured and compared the PCA of seven commercially available ZnO and CeO₂ NPs provided by OECD programme. These NPs varied by supplier, particle size and surface coating. Three laboratories were involved in the interlaboratory comparison using different methods for PCA testing. We found that although the absolute decay time or rate constant varied from method to method, the PCA comparison within each method between various samples showed consistent results, suggesting that PCA is a stable characteristic of NPs and not sensitive to variations in laboratory protocols. The presence of triethoxycaprylsilane surface coating appeared to significantly mitigate but not eliminate PCA. For commercial CeO₂ NPs, a critical particle size exists for maximum PCA.

Acknowledgments The authors would like to thank Dr. Maxine McCall from CSIRO and Dr. Victoria Coleman from National Measurement Institute (NMI) for coordinating the ZnO and CeO₂ particles distribution within three laboratories. We also thank Mr. Richard Harris, Ms. Lynne Waddington and Dr. Thomas Gengenbach, all from CSIRO, for photocatalytic measurement using DHHP, characterising particle sizes and surface analysis respectively, and Dr Rongliang He and Dr Jinfeng Wang from Deakin University for the photocatalysis measurements using RhB.

References

Bagwasi S, Tian BZ, Chen F, Zhang JL (2012) Synthesis, characterization and application of iodine modified titanium dioxide in photocatalytic reactions under visible light irradiation. *Appl Surf Sci* 258:927–935

Bennett SW, Keller AA (2011) Comparative photoactivity of CeO₂, gamma-Fe₂O₃, TiO₂ and ZnO in various aqueous systems. *Appl Catal B Environ* 102:600–607

Bouwmeester H, Lynch I, Marvin HJP, Dawson KA, Berges M, Braguer D, Byrne HJ, Casey A, Chambers G, Clift MJD, Elia G, Fernandes TF, Fjellsbo LB, Hatto P, Juillerat L,

Klein C, Kreyling WG, Nickel C, Riediker M, Stone V (2011) Minimal analytical characterization of engineered nanomaterials needed for hazard assessment in biological matrices. *Nanotoxicology* 5:1–11

Casey P, Boskovic S, Lawrence K, Turney T (2004) Controlling the photoactivity of nanoparticles (pp 370–374). Nano Science and Technology Institute, Cambridge

Casey PS, Rossouw CJ, Boskovic S, Lawrence KA, Turney TW (2006) Incorporation of dopants into the lattice of ZnO nanoparticles to control photoactivity. *Superlattice Microst* 39:97–106

Chatterjee D, Dasgupta S (2005) Visible light induced photocatalytic degradation of organic pollutants, visible light induced photocatalytic degradation of organic pollutants. *J Photochem Photobiol C* 6:186–205

Chen FJ, Cao YL, Jia DZ (2011) Preparation and photocatalytic property of CeO₂ lamellar. *Appl Surf Sci* 257:9226–9231

Dodd AC, McKinley AJ, Saunders M, Tsuzuki T (2006) Effect of particle size on the photocatalytic activity of nanoparticulate zinc oxide. *J Nanopart Res* 8:43–51

Dransfield G, Guest PJ, Lyth PL, McGarvey DJ, Truscott TG (2000) Photoactivity tests of TiO₂-based inorganic sunscreens—Part 1: non-aqueous dispersions. *J Photochem Photobiol B* 59:147–151

Egerton TA, Tooley IR (2004) Effect of changes in TiO₂ dispersion on its measured photocatalytic activity. *J Phy Chem B* 108:5066–5072

Frohlich E, Samberger C, Kueznik T, Absenger M, Roblegg E, Zimmer A, Pieber TR (2009) Cytotoxicity of nanoparticles independent from oxidative stress. *J Toxicol Sci* 34:363–375

Giraldi TR, Santos GVF, de Mendonca VR, Ribeiro C, Weber IT (2012) Effect of synthesis parameters on the structural characteristics and photocatalytic activity of ZnO. *Mater Chem Phys* 136:505–511

Hirst SM, Karakoti AS, Tyler RD, Sriranganathan N, Seal S, Reilly CM (2009) Anti-inflammatory properties of cerium oxide nanoparticles. *Small* 5:2848–2856

Karlsson HL, Gustafsson J, Cronholm P, Moller L (2009) Size-dependent toxicity of metal oxide particles—a comparison between nano- and micrometer size. *Toxicol Lett* 188:112–118

Krug HF, Wick P (2011) Nanotoxicology: an interdisciplinary challenge. *Angew Chem Int Edit* 50:1260–1278

Li YZ, Lee NH, Hwang DS, Song JS, Lee EG, Kim SJ (2004) Synthesis and characterization of nano titania powder with high photoactivity for gas-phase photo-oxidation of benzene from TiOCl₂ aqueous solution at low temperatures. *Langmuir* 20:10838–10844

Liu S, Jaffrezic N, Guillard C (2008) Size effects in liquid-phase photo-oxidation of phenol using nanometer-sized TiO₂ catalysts. *Appl Surf Sci* 255:2704–2709

Maira AJ, Yeung KL, Lee CY, Yue PL, Chan CK (2000) Size effects in gas-phase photo-oxidation of trichloroethylene using nanometer-sized TiO₂ catalysts. *J Catal* 192:185–196

Millington KR, Maurdev G (2004) The generation of superoxide and hydrogen peroxide by exposure of fluorescent whitening agents to UVA radiation and its relevance to the rapid photoyellowing of whitened wool. *J Photoch Photobiol A* 165:177–185

- OECD (2010a) OECD programme on the safety of manufactured nanomaterials 2009–2012: operational plans of the projects. Series on the safety of manufactured nanomaterials No.22. Environment, health and safety publications
- OECD (2010b) List of manufactured nanomaterials and list of endpoints for phase one of the sponsorship programme for the testing of manufactured nanomaterials: revision. Series on the safety of manufactured nanomaterials No.27. Environment, health and safety publications
- Ostrowski AD, Martin T, Conti J, Hurt I, Harthorn BH (2009) Nanotoxicology: characterizing the scientific literature 2000–2007. *J Nanopart Res* 11:251–257
- Primo A, Marino T, Corma A, Molinari R, García H (2011) Efficient visible-light photocatalytic water splitting by minute amounts of gold supported on nanoparticulate CeO₂ obtained by a biopolymer templating method. *J Am Chem Soc* 133:6930–6933
- Roebben G, Ramirez-Garcia S, Hackley VA, Roesslein M, Klaessig F, Kestens V, Lynch I, Garner CM, Rawle A, Elder A, Colvin VL, Kreyling W, Krug HF, Lewicka ZA, McNeil S, Nel A, Patri A, Wick P, Wiesner M, Xia T, Oberdoerster G, Dawson KA (2011) Interlaboratory comparison of size and surface charge measurements on nanoparticles prior to biological impact assessment. *J Nanopart Res* 13:2675–2687
- Sayes CM, Wahi R, Kurian PA, Liu YP, West JL, Ausman KD, Warheit DB, Colvin VL (2006) Correlating nanoscale titania structure with toxicity: a cytotoxicity and inflammatory response study with human dermal fibroblasts and human lung epithelial cells. *Toxicol Sci* 92:174–185
- Tarnuzzer RW, Colon J, Patil S, Seal S (2005) Vacancy engineered ceria nanostructures for protection from radiation-induced cellular damage. *Nano Lett* 5:2573–2577
- Tsuzuki T, He RL, Wang JF, Sun L, Wang XG, Hocking R (2012) Reduction of the photocatalytic activity of ZnO nanoparticles for UV protection applications. *Int J Nanotechnol* 9:1017–1029
- Wang JJ, Sanderson BJS, Wang H (2007) Cyto- and genotoxicity of ultrafine TiO₂ particles in cultured human lymphoblastoid cells. *Mutat Res Gen Tox En* 628:99–106
- Wang JF, Tsuzuki T, Sun L, Wang XG (2009) Reducing the photocatalytic activity of zinc oxide quantum dots by surface modification. *J Am Ceram Soc* 92:2083–2088
- Wu TX, Liu GM, Zhao JC, Hidaka H, Serpone N (1998) Photoassisted degradation of dye pollutants V Self-photo-sensitized oxidative transformation of Rhodamine B under visible light irradiation in aqueous TiO₂ dispersions. *J Phys Chem B* 102:5845–5851
- Yeber MC, Rodriguez J, Freer J, Duran N, Mansilla HD (2000) Photocatalytic degradation of cellulose bleaching effluent by supported TiO₂ and ZnO. *Chemosphere* 41:1193–1197
- Zhu MT, Feng WY, Wang B, Wang TC, Gu YQ, Wang M, Wang Y, Ouyang H, Zhao YL, Chai ZF (2008) Comparative study of pulmonary responses to nano- and submicron-sized ferric oxide in rats. *Toxicology* 247:102–111