

Please cite the Published Version

Southworth, Jamie S, Kohler, Sven and Pimblott, Simon M (2018) Gas Production from the Radiolysis of Water Adsorbed on ZnO Nanoparticles. *Journal of Physical Chemistry C*, 122 (44). pp. 25158-25164. ISSN 1932-7447

DOI: <https://doi.org/10.1021/acs.jpcc.8b04276>

Publisher: American Chemical Society

Version: Accepted Version

Downloaded from: <https://e-space.mmu.ac.uk/621820/>

Usage rights: © In Copyright

Additional Information: Accepted manuscript published by and copyright American Chemical Society.

Enquiries:

If you have questions about this document, contact openresearch@mmu.ac.uk. Please include the URL of the record in e-space. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from <https://www.mmu.ac.uk/library/using-the-library/policies-and-guidelines>)

Gas Production from the Radiolysis of Water Adsorbed on ZnO Nano-Particles

Jamie S. Southworth^{a, b}, Sven P. K. Koehler^{a, b, c, d} and Simon M. Pimblott^{a, b, e *}

^a School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK

^b Dalton Cumbrian Facility, The University of Manchester, Westlakes Science & Technology Park, Moor Row, CA24 3HA, UK

^c Photon Science Institute, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK

^d Current address: School of Science & the Environment, Manchester Metropolitan University, Chester Street, Manchester, M1 5GD, UK

^e Current address: Idaho National Laboratory, Nuclear Science User Facilities, 995 University Boulevard, Idaho Falls, ID 83401-0355, USA.

* Corresponding author: Jamie.southworth@postgrad.manchester.ac.uk

Abstract

The presence of a metal oxide surface can significantly alter the product yield distribution during the radiolysis of water. Some metal oxides such as ZrO₂ or CeO₂ have been shown to increase the yield of H₂ during the irradiation of water adsorbed on the oxide as compared to liquid water, while other oxides such as PuO₂ exhibit lower H₂ yields. In this study, the γ -ray radiolysis of the ZnO/H₂O system was investigated. Surprisingly, both O₂ and H₂ were produced in similar quantities. The production of O₂ is unexpected as no, or negligible, amounts of O₂ have been observed for the radiolysis of water adsorbed on other oxides. Molecular oxygen production is observed during the radiolysis of both wet and dry ZnO, indicating that the source of at least some of the O₂ is the bulk oxide. The production of H₂ due to the radiolysis of water adsorbed on ZnO is an order of magnitude greater than for pure water. This increase is likely due to an energy transfer process from the oxide to the adsorbed water molecules. However, the radiolysis of aqueous suspensions of ZnO resulted in lower radiolytic H₂ yields than for pure water.

Introduction

The interaction of ionizing radiation with water adsorbed on the surface of metal oxides has been the subject of intense study in recent years,^{1,2,3,4,5,6} and the presence of certain metal oxides has been observed to have pronounced effects upon the yields of some important species produced during irradiation.^{7,8} While the radiation chemistry of pure water is well understood and the yields of radiolysis products are reliably established, the mechanisms underpinning radiolysis of water in the presence of a ceramic interface are not universally agreed.^{9,10}

The radiolysis of water adsorbed on ZrO_2 and CeO_2 particles has been observed to increase the yield of H_2 by up to four orders of magnitude compared to the yield for pure water.¹¹ Conversely, it has been documented that certain metal oxides decrease the radiolytic yield of H_2 relative to the radiolysis of pure water.⁸ An important example of an oxide which appears to decrease the yield of H_2 is PuO_2 , a product of the reprocessing of spent nuclear fuel.¹²

Attempts to ascertain the oxidising products formed in the radiolytic splitting of water at an oxide surface have been inconclusive. For instance, when molecular oxygen (O_2) is detected from the radiolysis of water in the presence of metal oxides, it is in almost negligible volumes as O_2 is a highly efficient scavenger of the H atom and the hydrated electron.¹³ This renders the detection of any quantities of O_2 novel and worthy of further investigations.¹⁴

Phenomena such as the enhancement of the radiolytic yield of H_2 or the radiolytic production of O_2 in the presence of oxides common to the nuclear industry could give rise to operational and safety concerns.^{15,16} These include the pressurisation of waste containers, alteration of coolant water chemistry and hydriding of fuel cladding in reactor cores. For these reasons, the investigation of the radiation-induced chemistry, including the production of H_2 and other species, of water in contact with metal oxides is of utmost importance, and understanding the mechanism of H_2 production and common trends amongst various oxides are valuable. The exact mechanism behind the increased H_2 yield during the radiolysis of water adsorbed on oxide surfaces is not known, but it must involve

energy or charge transfer from the solid oxide to adsorbed water molecules leading to altered yields of molecular products, or changes of surface structure or morphology.¹⁷

The Zn cation is an important additive in the primary circuit coolant chemistry of light water reactors. It is added to reduce the build-up of radiation fields away from the reactor by replacing and limiting the incorporation of gamma emitting Co in oxide films.¹⁸ Petrik *et al.* have suggested that the presence of a zinc oxide, ZnO, surface does not increase the radiolytic yield of H₂.⁸ It has also been reported that dry ZnO thermally releases O₂ when heated to above ca. 400°C.¹⁹ The oxide subsequently enters a sub-stoichiometric state, which is accompanied by a colour change from white to green/yellow. After cooling in an O₂ rich atmosphere, the colour change is quickly reversed as the oxide re-absorbs O₂. The sub-stoichiometry is documented as Zn_(1+x)O where $x = 7.0 \times 10^{-4}$.²⁰ It has also been reported that the radiation tolerance of ZnO can be tuned by engineering specific defects into the lattice for increased stability in radiative environments.²¹

In this study, the effects of γ -irradiation on the water–ZnO system are investigated. First, the structure of the ZnO powder was determined by X-ray Diffraction (XRD) and the surface moieties were characterised by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. The surface area and porosity of the oxide particles were determined by the Brunauer-Emmett-Teller (BET) method. Irradiations were performed using 1.173 MeV and 1.332 MeV γ -rays from a 60-Co source. The radiolysis of water adsorbed on the surface of ZnO particles and of water – ZnO slurries was examined by characterising and quantifying the gaseous products. The dependence of radiation dose upon the yield of H₂ and O₂ was also investigated, as was the variation of both products as a function of water loading on the oxide surface.

H₂ and O₂ were both detected, but not in stoichiometric quantities: Most interestingly, O₂ was also detected from the irradiation of nominally dry ZnO particles, i.e. the interaction of ionising radiation with the ZnO powder seems to have a similar effect as compared to thermal treatment.

Experimental

Zinc oxide (99.9%) was purchased from Sigma Aldrich and used without further purification. The surface area and the estimated particle size were determined by the Brunauer-Emmett-Teller (BET) method using a Micromeritics TriStar II surface area analyser. Analysis of water and other contaminants on the surface of the powder was conducted using temperature dependent Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. DRIFT spectra were measured *in situ* with a Bruker Vortex 60 FT-IR spectrometer employing a Harrick Praying Mantis high temperature cell. X-Ray diffraction (XRD) measurements were taken using a Bruker D8 Powder X-ray Diffractometer. Scans were taken over 2θ values between 20° and 85° with a step size of 0.05° . Samples were kept static during measurements.

Prior to preparation by humidity control, samples were heated to 500°C for up to 36 h to remove adsorbed water and any residual organic contaminants from production. Heating to this temperature was not found to alter the specific surface area (determined by BET). The oxide was cooled and stored under vacuum, then weighed in sample tubes and finally placed in a constant humidity chamber. Sample tubes consist of 10 mm diameter Pyrex tubes 10 cm in length. The humidity of the chamber was controlled using saturated salt solutions and the percent relative humidity (%RH) measured using Testo 174H data loggers.²² After uptake of water, samples were re-weighed, followed by the sample tubes being purged with a positive pressure of argon (99.999% procured from BOC) and before being flame sealed. We also performed control experiments in which we irradiated empty, purged sample tubes, which did not generate a detectable amount of either H_2 or O_2 .

Gamma-irradiation was performed using a Foss Therapy Services Inc. 812 self-contained ^{60}Co source. In July 2017, the dose rate was measured by Fricke dosimetry to be 442.7 Gy/min. Samples were irradiated with up to 36.5 kGy. The gases produced were measured (after cracking open the glass sample tubes under argon flow) using an SRI 8610C Gas Chromatograph (GC) equipped with a Thermal Conductivity Detector (TCD). Argon carrier gas was passed through a constant flow

regulator, an injection loop connected to a four-way valve and into a column containing a molecular sieve.

The carrier gas selection determines the sensitivity of the TCD to the analyte gasses. In order for the TCD to have high sensitivity to a specific gas the thermal conductivity of the analyte must be significantly different to that of the carrier gas.²³ There is a large difference in the thermal conductivities of H₂ and Ar, hence Ar was used as the carrier gas in the detection H₂. In contrast, Ar has a similar thermal conductivity to O₂, hence in this instance, He was selected as the carrier gas to increase O₂ sensitivity.²⁴

GC calibration was performed for each gas by injecting known quantities of either pre-mixed 5% H₂ in Ar or 5% O₂ in Ar calibration gases (Scientific and Technical Gases Ltd). Injections were performed using a Sample-Lok A2 gas tight microliter syringe (Sigma-Aldrich). The lower limit of detection of the GC is 1 µL, determined by injecting progressively smaller volumes until no signal was observed. H₂ and O₂ volumes were calculated from the GC output using the ideal gas law.

Results and Discussion

The diffraction pattern of ZnO powder used in this study was recorded both pre and post exposure to gamma irradiation. Comparison of the measured spectrum for the unirradiated powder with known XRD data²⁵ suggests the crystal structure of the nano-particles is hexagonal (0001) wurtzite. γ -irradiation did not noticeably alter the crystal structure even at the maximum dose used in this study, 36.5 kGy. The figure is included in the supplementary information (Figure S1).

To compare the radiolytic H₂ yields from water adsorbed on metal oxides for different measurements, and more importantly for a range of metal oxides, it is crucial to correctly quantify the amount of water adsorbed on the ZnO surface; here this parameter will be expressed as the average number of monolayers of water on the oxide surface. In order to calculate this quantity, the specific surface area (SSA) of the particles was determined by the BET method (4.121 ± 0.1 m²/g) and it is assumed that there are 10¹⁹ adsorption sites per m². The shape of the isotherm (included in the supplementary data,

Figure S2) indicates that the particles are non-porous. Making the assumption that the particles are spherical and non-porous, then based on the surface area, the average particle diameter is ~270 nm.

Figure 1 shows the increase in mass as a function of %RH of the humidity chamber. Even when left for an extended period at 99.9% relative humidity, the maximum water coverage achieved is only 8 monolayers. In contrast, ZrO_2 has been observed to adsorb three to four times that amount in the same time.¹¹

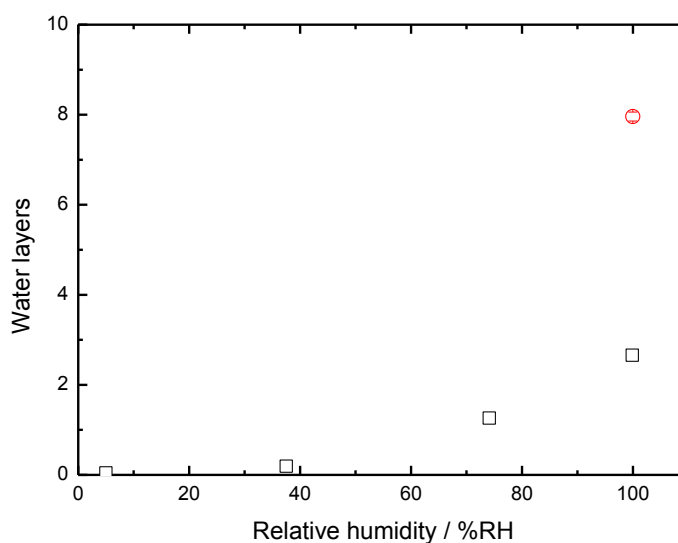


Figure 1 - Number of water layers adsorbed after 24 hours (□) by ~1.0 g samples of ZnO as a function of relative humidity. After 14 days the coverage reaches a maximum of approximately 8 monolayers (○). Error bars included however, they are hidden by the data points.

The number of monolayers is calculated from the difference in mass between the dry powder and the powder post exposure to water vapour in the relative humidity chamber. The uptake of water on the surface of dry ZnO is a slow process with several days required to achieve more than two to three monolayers coverage.

DRIFT spectra of ZnO particles that had been left in a relative humidity chamber for 14 days at 99.9%RH were recorded as a function of temperature to analyse the amount of intact water molecules

present, shown in Figure 2. The spectra were recorded at 25°C, 100°C, up to 500°C in incremental steps of 100°C. The spectrum was then re-recorded once the sample had cooled to 25°C.

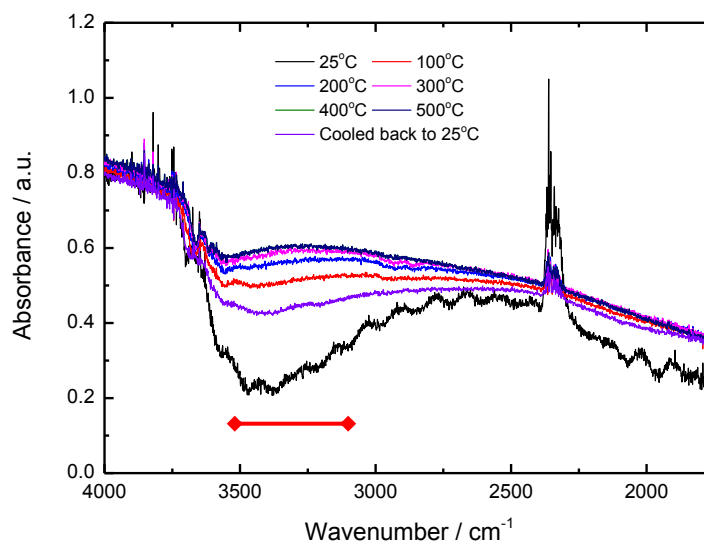


Figure 2 - DRIFT measurements taken at temperatures of 25°C, 100°C, and in 100°C intervals until 500°C. The spectrum was recorded again after the sample had cooled back to 25°C. Free OH bond stretching vibrational frequency range is visible below 3500 cm^{-1} , taken from Ref. [26] shown as the red bar under the spectrum.

The OH bond stretching vibrations between 3000 cm^{-1} and 3500 cm^{-1} (indicated by the red bar in Figure 2) are characteristic of undissociated water.²⁶ The absorbance is strongest at 25°C and decreases in magnitude until at 500°C where it disappears. After allowing the sample to cool down to ambient temperature, the water absorbance does not re-appear. These data suggest heating the oxide sample to above 400°C will remove intact water molecules from the surface of the oxide down to surface coverages below the detection sensitivity of the spectrometer. We hence concluded that following heat treatment, coverages with undissociated water are expected to be well below one monolayer, although there may also be species from dissociatively chemisorbed water (such as OH groups) present on the surface. The feature at around 2250 cm^{-1} is due to the presence of gas phase CO_2 in the headspace above the sample in the Harrick cell.

In radiation chemistry, the yield of a species produced by ionizing radiation is usually expressed by the G value, which denotes the number of molecules of a species produced per 100 eV of radiation energy deposited into the system. The G(H₂) value for pure water with a small quantity of a hydroxyl radical scavenger (typically 0.1 mmol KBr) to prevent recombination chemistry is well documented to be 0.45 molecules/100 eV. This quantity translates to $\sim 0.45 \times 10^{-7} \text{ mol J}^{-1}$ in SI units.²⁷

When assessing radiation effects in multiphase systems (such as water/metal oxide systems), two options exist for quantifying the radiation dose received by a sample; the first approach is to calculate the dose received by the water-metal oxide system as a whole. The second approach is to only consider the dose received by the water adsorbed on the oxide. In this case, calculating the dose received with respect to adsorbed water *only* means any deviation from the yield for pure water can be attributed to processes caused by the presence of the oxide, such as the transfer of energy from the metal oxide to the water.¹⁰ In the following discussion, the dose of radiation received is calculated with respect to the *mass of the adsorbed water* only, as this allows identification of any effect due to the metal oxide. For instance, an increased yield might signify energy is transferred to the adsorbed water from the oxide while a decreased yield might suggest enhance recombination chemistry on the oxide surface.

The effect of the γ -radiation dose on the number of molecules of H₂ produced by radiolysis of 1.2 monolayers of water adsorbed on ZnO nanoparticles is shown in Figure 3. The production of H₂ increases linearly with radiation dose, over the dose range investigated. No H₂ was observed for an unirradiated sample of wet ZnO powder, indicating that the production of H₂ is a radiation effect, not a catalytic effect of the oxide alone. In addition, the irradiation of dry ZnO also yields no H₂, indicating that the source of H₂ is the adsorbed water.

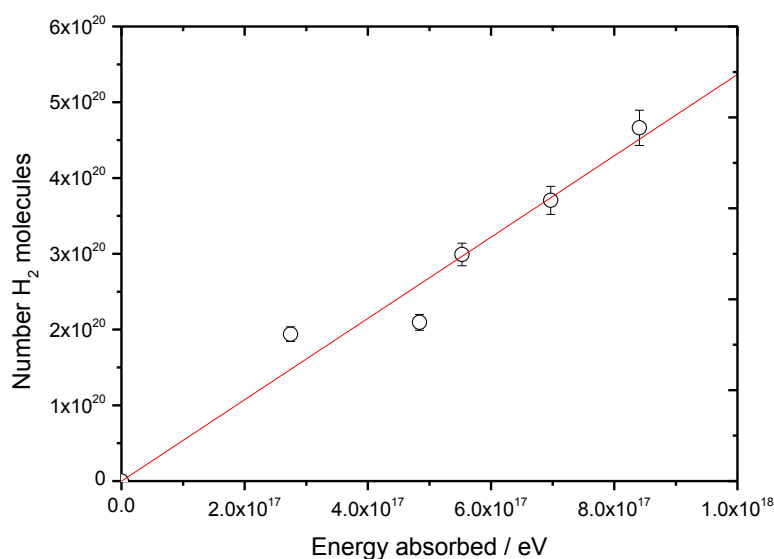


Figure 3 – Effect of dose absorbed by the water on H₂ production from the γ -radiolysis of water adsorbed on ZnO particles with a surface area of 4.121 m²/g. Water coverage is estimated to be 1.2 monolayers and $G(\text{H}_2) = 5.56$ molecules/100 eV from the slope of the plot.

The yield of H₂ produced, $G(\text{H}_2)$, is obtained from the slope of the best fit line to the experimental data in Figure 3. At 5.56 molecules/100 eV, the value from 1.2 monolayers of water adsorbed on ZnO is more than an order of magnitude greater than is observed for the radiolysis of pure water, 0.45 molecules/100 eV. This result is in contrast to results by Petrik *et al.*, who suggested that ZnO is part of the group of oxides which do not enhance the production of H₂ from adsorbed water. The increase suggests that energy is transferred from the oxide to adsorbed water molecules. While the exact mechanism is not known, Petrik *et al.* have suggested that the enhanced production of H₂ at water-oxide interfaces could be attributed to exciton (electrostatically bound electron-hole pair) formation in the bulk oxide due to the irradiation and subsequent exciton migration to the oxide/water interface.⁸ At the interface, exciton annihilation causes dissociation of the water molecules leading to the formation of H₂.²⁸ Petrik *et al.* also postulate that the band gap of the oxide plays a role in determining the magnitude of enhancement in the H₂ yield with the maximum enhancement being observed for oxides with a band gap of ~5 eV (such as ZrO₂)²⁹ which is close to the bond dissociation

energy of the H-OH bond of (adsorbed) water.⁸ Thus annihilation of a surface exciton at the water-oxide interface is postulated to lead to H-OH bond breakage. In the case of ZnO, the band gap is 3.3 eV, which is significantly less than H-OH bond energy, yet the enhancement in the yield of H₂ is considerable.³⁰ LaVerne and co-workers have also observed significantly enhanced H₂ production from water adsorbed on a variety of oxides including CeO₂, TiO₂ and SiO₂ with band gaps different from 5 eV.^{1,2,11,17,28}

The amount of O₂ produced from the radiolysis of 1.2 monolayers of water adsorbed to the surface of ZnO nanoparticles as a function of radiation dose to the water is shown in Figure 4. No O₂ was detected from unirradiated ZnO samples, nor does water left in contact with ZnO without irradiation yield a detectable quantity of O₂. The quantity of O₂ produced radiolytically increases linearly with dose. The only previous observation of radiolytic production of O₂ from water adsorbed on an oxide was made by LaVerne and Tandon, who detected O₂ in amounts at least an order of magnitude lower than H₂ production during their work on the radiolysis of water adsorbed on UO₂.³¹ This work on the radiolysis of water adsorbed on ZnO observes O₂ production in similar yields to H₂.

The yield of O₂, G(O₂), from the radiolysis of 1.2 monolayers of water adsorbed on ZnO determined from the gradient of the best fit to the data in Figure 4 is 2.067 molecules/100 eV. The stable oxidising products typically detected during the radiolysis of water are H₂O₂ and HO₂, while O₂ is generally not observed.¹⁰ O₂ is efficient scavenger of hydrogen atoms and the hydrated electron and its precursors, and O₂ molecules will readily react with these species to form either the hydroperoxyl radical or the superoxide radical anion. These secondary radical species will then further react to form H₂O₂ and re-form O₂.

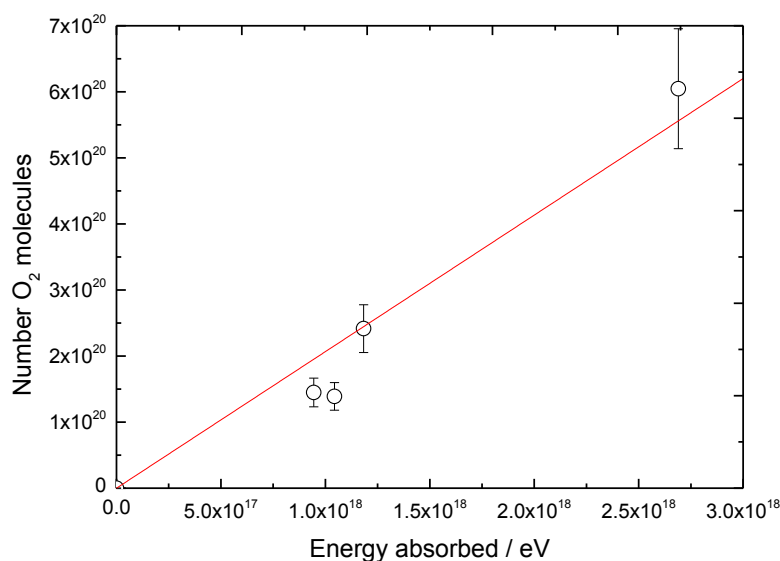


Figure 4- Dose dependence of O₂ produced from the radiolysis of 1.2 monolayers of water adsorbed to the surface of ZnO nanoparticles. Dose calculated for energy absorbed by the adsorbed water only. Here, $G(\text{O}_2) = 2.067$ molecules/100 eV.

While the amounts of O₂ and H₂ detected from the radiolysis of 1.2 monolayers of water adsorbed on ZnO nanoparticles are similar, they are not stoichiometric. The yield of O₂ is about four times that of H₂ rather than the “expected” 2:1 ratio. This difference indicates that the source of O₂ may not be the adsorbed water, but the ZnO itself. Furthermore, O₂ is not produced unless the oxide is irradiated suggesting that the production of O₂ is not a catalytic effect of the oxide alone, but due to the interaction of radiation with the oxide. When the dose is calculated with respect to the energy absorbed by the mass of the oxide and water, $G(\text{O}_2) = 2.067$ molecules/100 eV.

Figure 5 shows the volume of O₂ produced from irradiation of ~1.0 g of dry ZnO as a function of dose to the oxide. Even dry samples of ZnO, which were not exposed to water vapor in a relative humidity chamber, generated O₂ when irradiated, with the rate of production increasing linearly with dose. The yield of O₂ determined from Figure 5 is $G(\text{O}_2) = 8.34 \times 10^{-3}$ molecules/100 eV (with the absorbed energy calculated with respect to the mass of the oxide).

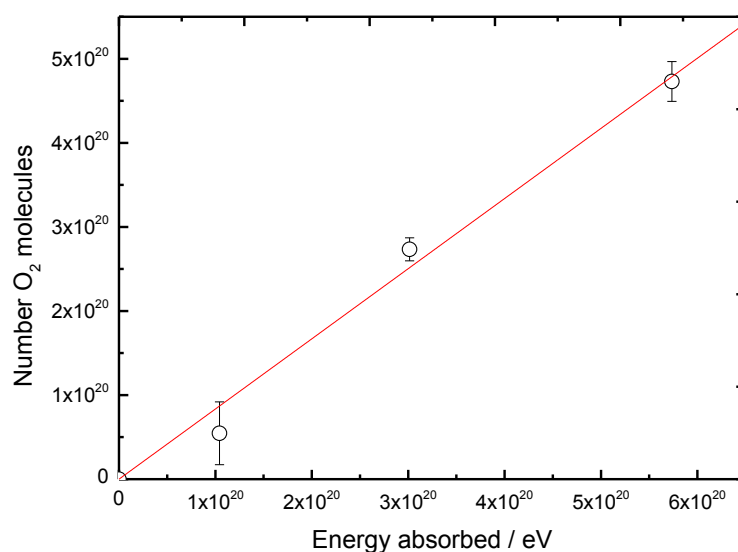


Figure 5 – Number of molecules of O₂ produced as a function energy absorbed from the radiolysis of 1.0 g dry ZnO nano-powder. $G(\text{O}_2) = 8.34 \times 10^{-3}$ molecules/100 eV for dry ZnO, with the dose calculated with respect to the mass of the oxide.

Observing O₂, but not H₂, during the irradiation of the dry oxide samples clearly demonstrates that the source of O₂ is the oxide, and it is not produced due to the decomposition of physisorbed water molecules. However, it is not possible to rule out dissociatively chemisorbed water/OH groups as the potential source of O₂.

As briefly mentioned previously, it is known that *thermal* treatment of ZnO can lead to a reduction of the oxide; the sub-stoichiometry that arises from the *thermal* treatment of ZnO to above 400°C is reported to be Zn_(1+x)O where $x = 7.0 \times 10^{-4}$.^{20,20} Based on this stoichiometry, heating 1.0 g of ZnO should produce about 87 μL of O₂. This value is of the same magnitude as the volumes measured in this work, which strongly suggests that γ-irradiation reduces ZnO in a similar vein as thermal treatment of ZnO. This colour change is also observed during gamma irradiation, which is quickly reversed upon exposure to an O₂ rich atmosphere.

While the previous discussion was centred around H_2 production from 1.2 adsorbed monolayers of water on ZnO nanoparticles, we have repeated these experiments for further coverages to extract $G(\text{H}_2)$ values as a function of the average number of water layers, see Figure 6.

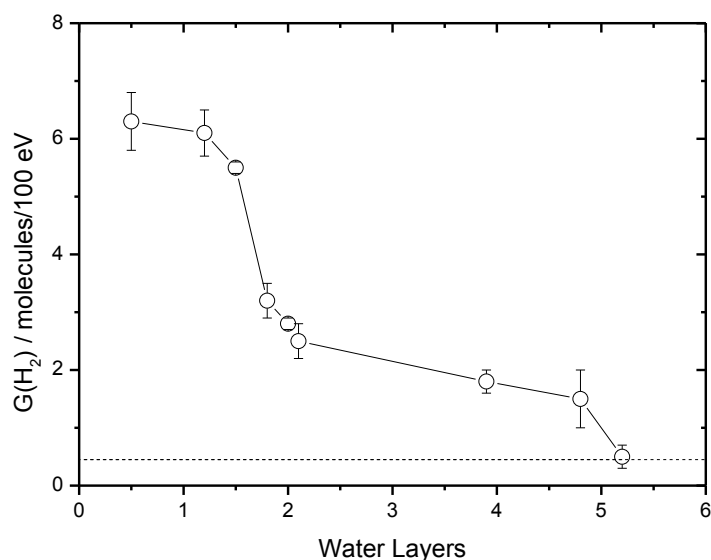


Figure 6 – Yield of H_2 as a function of the number of water layers adsorbed on ZnO. The $G(\text{H}_2)$ value for the radiolysis of pure water is 0.45 molecules/100 eV, shown as a dashed line for comparison. A colour change of white to yellow/green was also observed during γ -irradiation.

In order to explain these experimental results, it is worth comparing the observed G-values for H_2 production with those for other metal oxides. Experiments investigating the radiolysis of water adsorbed on ZrO_2 and CeO_2 particles found $G(\text{H}_2)$ values of 150 molecules/100 eV and 20 molecules/100 eV, respectively.¹¹ The radiation-catalytic activity of ZnO towards H_2 production is much less than for ZrO_2 . This discrepancy may be explained in part by the (larger) difference between the band gap for ZnO and the H-OH bond strengths as compared to ZrO_2 . However, some form of energy transfer must still take place, as otherwise $G(\text{H}_2)$ values similar to deaerated water (0.45 molecules/100 eV) would be expected.

The $G(\text{H}_2)$ values in the experiments ZrO_2 and CeO_2 show a sharp rise in $G(\text{H}_2)$ as the water loading is decreased,¹¹ which is not observed for ZnO. The yields for all oxides, however, should decrease to

the value for deaerated water as the water loading on the oxide increases; this is because the influence of the substrate is felt less and less as the water coverages increases, and outer water layers are further removed from the oxide interface. Since it is reasonable to assume that the propagation of excitons through the adsorbed water layers is independent of the metal substrate, it seems that the lower $G(H_2)$ values for ZnO are due to a less efficient energy transfer from the oxide to the adsorbed water.

H_2 production from the radiolysis of aqueous suspensions of ZnO in water has also been investigated. The amount of ZnO present (in terms of weight percent) was varied from 1% to 90%, shown in Figures 7(a) and (b).

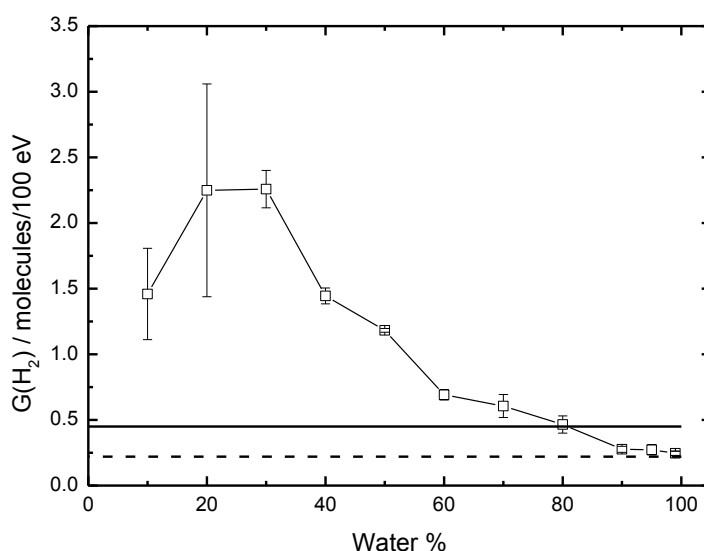


Figure 7a- Yield of H_2 as a function of the weight percentage of water when $G(H_2)$ calculated with respect to dose absorbed by H_2O *only*. Solid horizontal line indicates the value for 0.1 mmol KBr (~ 0.45 molecules/100 eV), dashed line indicates pure water (~ 0.22 molecules/100 eV).

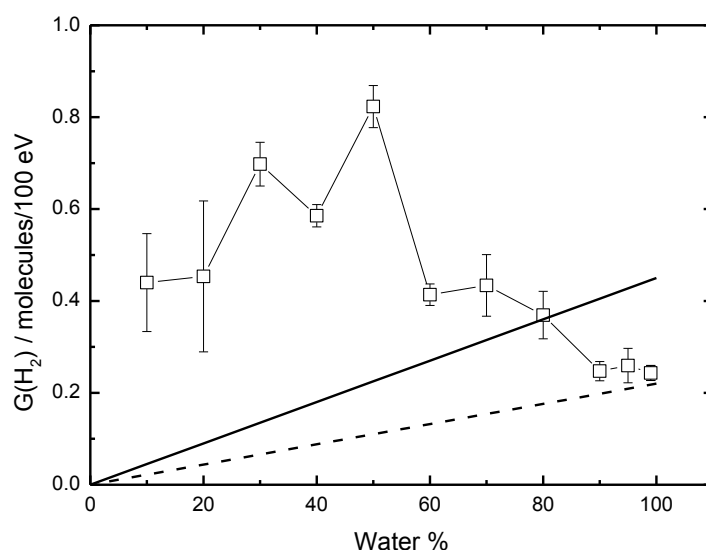


Figure 7b- Yield of H_2 as a function of the weight percentage of water when $G(H_2)$ calculated with respect to dose absorbed by ZnO and H_2O . Solid line indicates the value for 0.1 mmol KBr (~0.45 molecules/100 eV), dashed line indicates pure water (~0.22 molecules/100 eV).

Figure 7(a) and (b) shows the variation in $G(H_2)$ with weight percent water with the G-value calculated relative to the amount of energy deposited in the water only in Figure 7a and relative to the amount of energy deposited in the water *and* the oxide (Figure 7b). The figures also include lines showing the expected G-value for H_2 that would be expected if it was produced solely from the radiolysis of water (deaerated or with 0.1 mmol KBr). The energy deposited to the two phases is calculated according to the “mixture law” which states that the fraction of the total energy initially deposited into a multicomponent mixture is proportional to the electron density (or the mean mass collision stopping power) of each component.³²

At 20% water, the samples can be more accurately described as a damp powder or a paste than an aqueous suspension/slurry. Water is not evenly distributed about the oxide powder, which is thought to give rise to the error associated with this measurement.

These data show that as the weight% of water increases, $G(H_2)$ decreases. One would expect this as the influence of energy transfer processes occurring from the oxide to the water phase becomes less

pronounced as the amount of water approaches 100%. Interestingly, as the percentage water present reaches 100%, $G(H_2)$ tends towards the value observed for the radiolysis of pure water *alone* (measured as 0.22 molecules/100 eV - dashed lines in Figure 7a and 7b). This is at odds with work done on other water/oxide systems – namely aqueous suspensions of ZrO_2 and Al_2O_3 .^{28,33} $G(H_2)$ for zirconia and alumina slurries falls to approximately the value for deaerated water with a radical scavenger (0.45 molecules/100 eV), indicating that oxide particles scavenge OH radicals. In this case, it appears that ZnO is unreactive towards radiation-produced radicals and therefore, it does not break the reaction chain and is inert.

Conclusion

The γ -radiolysis of dry ZnO and water adsorbed on ZnO powder was examined. Following irradiation, no change in the bulk crystal structure was detected by XRD up to a dose of 36.5 kGy, nor was there any change in surface area as measured by the BET method.

Most strikingly, the production of O₂ was observed in comparable amounts to H₂ during the radiolysis of water adsorbed to ZnO. The volume of O₂ was observed to increase linearly with dose, and O₂ was even observed after irradiation of dry ZnO powder. O₂ has never previously been observed in similar quantities to H₂ during irradiation experiments with any other metal oxides. In analogy with the well-known thermal reduction of ZnO, we conclude that the ZnO itself appears to be the most likely source of oxygen in these experiments.

Molecular hydrogen yields from the radiolysis of water adsorbed to ZnO nano-particles were an order of magnitude greater than G(H₂) from pure water. G(H₂) was observed to decrease as the number of water layers increased, which indicates that some form of energy transfer from the ZnO particle to the adsorbed water layers takes place. The increased H₂ yields, however, are less pronounced compared to other oxides previously studied, suggesting a less-efficient energy transfer mechanism.

The amount of H₂ detected from the radiolysis of aqueous suspensions of ZnO was lower than the value observed for radically scavenged water, but in line with the value observed for pure water. This indicates that ZnO is inert to radiation-produced radicals in aqueous solution.

Acknowledgments

This work was jointly funded by EPSRC and Nuclear Decommissioning Authority. The research described was carried out at the Dalton Cumbrian Facility, The University of Manchester and the authors thank all the staff and students kindly for their time and assistance.

References

- ¹ Rieff. S. C, LaVerne. J. A, *J. Phys. Chem. B*, **2015**, 119, 7358-7365
- ² Rieff. S. C, LaVerne. J. A, *J. Phys. Chem. C*, **2015**, 119, 8821-8828
- ³ Roth. O, Dahlgren. B, LaVerne. J. A, *J. Phys. Chem. C*, **2012**, 116, 17619-17624
- ⁴ Sunder. S, Boyer. G. D, Miller. N. H, *J Nuc. Mat.*, **1990**, 175, 163-169
- ⁵ Skotnicki. K, Bobrowski. K, *J. Rad. Nuc. Chem.*, **2015**, 304, 473-480
- ⁶ Carrasco- Flores. E. A, LaVerne. J. A, *J. Chem. Phys.*, **2007**, 127, 234703
- ⁷ Le Caër. S, *Water*, **2011**, 3, 235-253
- ⁸ Petrik. N. G, Alexandrov. A. B, Vall. A. I; *J. Phys. Chem. B*, **2001**, 105, 5935-5944
- ⁹ Burton. M, *J. Phys. Chem.*, **1947**, 51, 611-625
- ¹⁰ Spinks. J. W. T, Woods. R. J, *An Introduction to Radiation Chemistry*, 3rd Edition, John Wiley & Sons, Inc, New York, **1964**, 39-77
- ¹¹ LaVerne. J. A, Tandon. L, *J. Phys. Chem. B*, **2002**, 106, 380-386
- ¹² Sims. H. E, Webb. K. J, Brown. J, Morris. J, Taylor. J. R, *J. Nuc. Mater.*, 2013, 437, 359-364
- ¹³ Barr. N. F, Allen. A. O, *J. Phys. Chem.*, **1959**, 63, 928-931
- ¹⁴ LaVerne. J. A, *Radiat. Res.*, **2000**, 153, 487
- ¹⁵ Hiroki. A, LaVerne J. A, *J. Phys. Chem. B*, **2005**, 109, 3364-3370
- ¹⁶ Sterniczuk. M, Bartels. D. M, *J. Phys. Chem. A*, **2016**, 120, 200-209
- ¹⁷ Schofield. J, Reiff. S. C, Pimblott. S. M, LaVerne. J. A, *J. Nuc. Mater.*, **2016**, 469, 43-50
- ¹⁸ Puyane. R, *J. Mater. Processing Technology*, **1996**, 56, 863-872
- ¹⁹ Coogan. C. K, Rees. A. L. G, *J. Chem. Phys.*, **1942**, 20, 1650-1651
- ²⁰ Wieberg. E, Holleman. A. F, *Lehrbuch der Anorganischen Chemie*, de Gruyter, Berlin, 101, 1995
- ²¹ Lv. J, Li. X, *Phys. Chem. Chem. Phys.*, **2018**, 20, 11882-11887
- ²² Young. J. F, *J. Appl. Chem.*, **1967**, 17, 241-245
- ²³ Johnston. H. L, Grilly. E. R, *J. Chem. Phys.*, **1946**, 14, 233-238
- ²⁴ Guildner. L. A, *Journal of Research of the National Bureau of Standards*, **1975**, 79A, 407-413
- ²⁵ Pacholski. C, Kornowski. A, Weller. H, *Angew. Chem. Int. Ed*, **2002**, 41, 1189-1191
- ²⁶ Hudgins. D, Sandford. S, Allamandola. L, Tielems. A, *Astrophys. J. Suppl. Ser*, **1993**, 86, 713-870
- ²⁷ Rotureau. P, Renault. J. P, Lebeau. B, Patarin. J, Mialocq. J. C, *ChemPhysChem*, **2005**, 6, 1316-1323
- ²⁸ LaVerne. J. A, Tonnies. S. E, *J. Phys. Chem. B*, **2003**, 107, 7277-7820
- ²⁹ Aleksandrov. A. B, Bychkov. A. Y, Vall. A. I, Petrik. N. G, Sedov. V. M, *Russian J. Phys. Chem.*, **1991**, 65, 1604-1608
- ³⁰ Debanath. M. K, Karmakar. S, *Materials Letters*, **2013**, 111, 116-119
- ³¹ LaVerne. J. A, Tandon. L, *J. Phys. Chem. B*, **2003**, 107, 13623-13628
- ³² Baidak. A, LaVerne. J. A, *J. Nuc. Mat.*, **2010**, 407, 211-219
- ³³ Rieff. S. C, LaVerne. J. A, *Rad. Phys. and Chem.*, **2017**, 131, 46-50

Supplementary Information

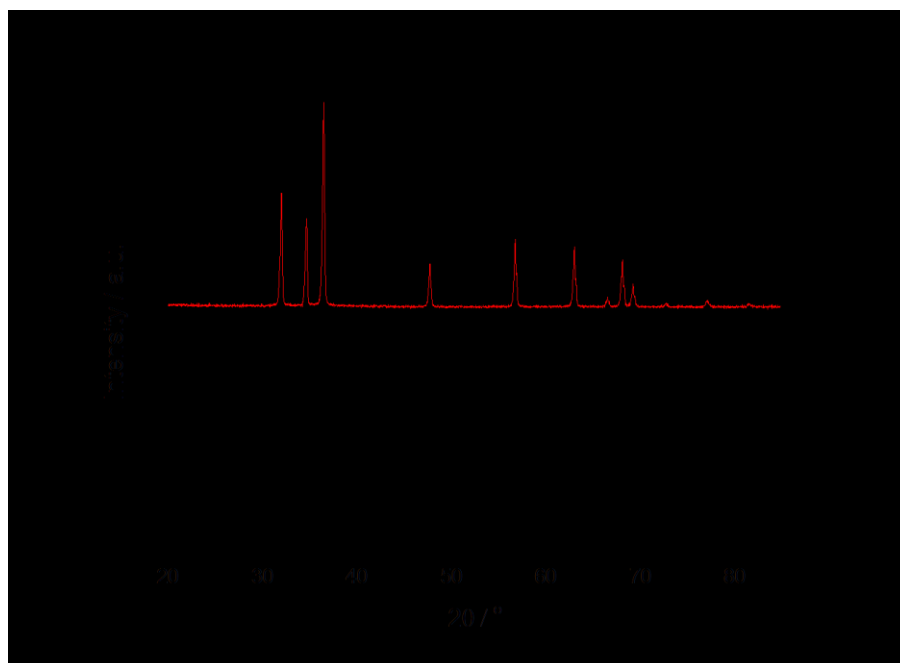


Figure S1- X-ray diffraction patterns of ZnO before irradiation (top, red) and after γ -irradiation to a dose of 36.5 kGy (bottom, black) which was not observed to change the crystal structure. Assignment in agreement with Ref. [25].

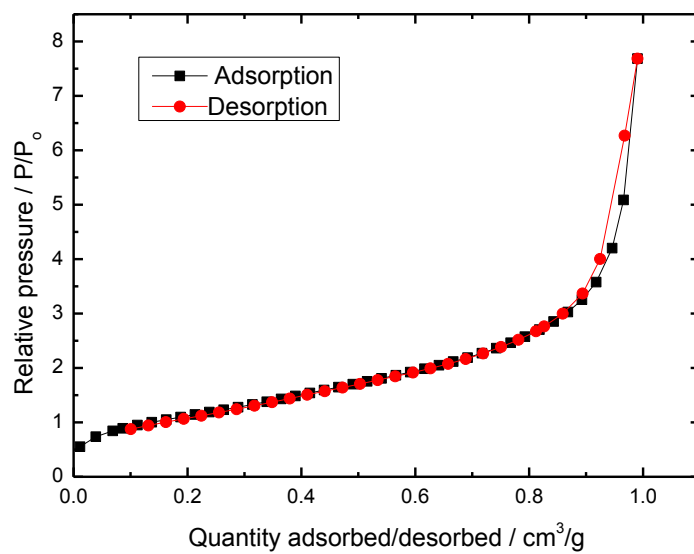


Figure S2– Full adsorption/desorption isotherm (using N₂) used to determine the BET surface area of ZnO nano-particles which was, in this case, $4.121 \pm 0.1 \text{ m}^2/\text{g}$. The shape of the isotherm and lack of hysteresis loop indicates that the particles are highly non-porous.