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Controlled deposition of size-selected MnO nanoparticle thin films for water splitting applications: reduction of onset potential with particle size

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Abstract

Emulating water oxidation catalyzed by the oxomanganese clusters in the photosynthetic apparatus of plants has been a long-standing scientific challenge. The use of manganese oxide films has been explored, but while they may be catalytically active on the surface, their poor conductivity hinders their overall performance. We have approached this problem by using manganese oxide nanoparticles with sizes of 4, 6 and 8 nm, produced in a sputter-gas-aggregation source and soft-landed onto conducting electrodes. The mass loading of these catalytic particles was kept constant and corresponded to 45%–80% of a monolayer coverage. Measurements of the water oxidation threshold revealed that the onset potential decreases significantly with decreasing particle size. The final stoichiometry of the catalytically active nanoparticles, after exposure to air, was identified as predominantly MnO. The ability of such a sub-monolayer film to lower the reaction threshold implies that the key role is played by intrinsic size effects, i.e., by changes in the electronic properties and surface fields of the nanoparticles with decreasing size. We anticipate that this work will serve to bridge the knowledge gap between bulk thick film electrocatalysts and natural photosynthetic molecular-cluster complexes.

Keywords: water splitting, water oxidation, nanocluster thin films, size-selective deposition, nanoparticle catalysts, gas aggregation source, manganese nanoparticles

(Some figures may appear in colour only in the online journal)

1. Introduction

Emulating photosynthetic water oxidation in higher plants with inorganic metal oxides has been a long-standing challenge in electrochemistry (McEvoy and Brudvig 2006, Nocera 2012). The process has special appeal because of its relevance to solar-to-fuel light harvesting, in which a photovoltage is used to oxidize water and to drive uphill reduction reactions, thereby storing the light energy in chemical bonds. Plants achieve water oxidation using the photoexcitation collected by chlorophylls and funneled into a cluster composed of manganese, oxygen, and calcium (Mn₄CaO₅) known as the oxygen evolving complex (OEC). The mechanistic details of water oxidation by OEC have been studied for

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decades (Ferreira et al 2004, Nelson and Ben-Shem 2004, Yano et al 2006, Kärkäs et al 2014) and still remain at the forefront of research (Khan et al 2015, Barber 2017, Vinyard and Brudvig 2017). Inspired by the natural OEC complex, it seems reasonable to study the water oxidation problem in an artificial material using manganese oxide minerals as electrocatalysts or photocatalysts. Several forms of manganese oxides have been studied for this purpose (Gorlin and Jaramillo 2010, Najafpour et al 2010, Takashima et al 2012, Zaharieva et al 2012), however not as extensively as other first row transition metal oxide films (Harriman et al 1988, Artero et al 2011, Sivula et al 2011, Singh and Spiccia 2013). Many forms of MnO_x minerals are predominantly poor conductors and are also studied in the context of materials for capacitors (Wei et al 2011, Li et al 2012). Using them in bulk form as thick electrocatalytic films on an electrode demands that the material function as a catalyst on the surface and as a conductor within the bulk of the film at the same time. This dual requirement is very different from the natural photosynthesis, in which the OEC is a nanocluster catalyst and is not required to conduct charge over large distances. For this reason, it is productive to resort to studying MnO_x nanoparticles, so that the catalytic properties are decoupled from transport properties as much as possible.

Manganese oxide nanoparticles produced by solutionprocessed methods have been used for water oxidation (Robinson et al 2013, Guo et al 2014, Ramírez et al 2014, Wiechen and Spiccia 2014, Kuo et al 2015, Li et al 2016). However, there are challenges associated with these methods: the associated organic ligands can pose problems, and the particle sizes and the total amount of catalyst loading on the electrodes may not be precisely controlled. Furthermore, they are often restricted to producing nanoparticles larger than 10 nm. To synthesize bare nanoparticles without using any solvents, ligands or surfactants, gas-phase production techniques have been developed (Grammatikopoulos et al 2016). Nanocatalyst particles for water splitting applications have been produced by using metal vapor condensation sources based on direct-current (DC), see, for example (Srivastava et al 2014, Stranak et al 2015, Paoli et al 2016, Chen et al 2017, Fan et al 2017, Lin et al 2017, McInnes et al 2017, Srivastava et al 2017), reactive DC (Patel et al 2016), and radio-frequency (El Koura et al 2016, Kim et al 2016) magnetron sputtering, as well as by using other gas-phase sources such as ion sputtering (Masudy-Panah et al 2016, Sreedhara et al 2017) and laser vaporization (Kwon et al 2013). To the best of our knowledge, though, these techniques have not been employed to prepare bare MnO_x nanoparticle films for water oxidation catalysis. (Water deprotonation by small manganese oxide clusters in a molecular beam was studied by Lang et al 2016.)

In this work, we report the production of electrocatalytic films by low-energy deposition of manganese oxide nanoparticles with sizes smaller than 10 nm on a conducting substrate under well-defined flux conditions. The films were used for water oxidation in a conventional three-electrode cell. We show evidence that the size of nanoparticles is correlated with the overpotential for water oxidation, with clear improvement in catalytic activity when the sizes are made smaller.

Two aspects of our approach make it possible to reveal the effect of size on catalytic activity. The first is fine control over particle size, which is achieved by using a deposition system that combines a nanoparticle source and a mass filter. The second aspect is careful determination of the total amount of catalyst material deposited, or catalyst loading, which is important for comparison of different samples. As described below, catalyst loading in our work has picogram resolution in the total quantity of mass deposited over an area of $\sim 1 \text{ cm}^2$. Such precision in the control of catalyst loading exceeds most conventional approaches based on measuring the thickness of spin-cast films. Using these capabilities, we studied the catalytic activity of nanoparticles with diameters of 4 nm, 6 nm, and 8 nm. These particles are larger than the natural OEC which has dimensions of about $0.5 \text{ nm} \times 0.25 \text{ nm} \times 0.25 \text{ nm}$ (Yano *et al* 2006), and therefore they can serve to bridge the gap between bulk film electrocatalysts and the natural molecular-scale OEC-type systems.

2. Experiment and characterization

2.1. Production and deposition of nanoparticles

Size-selected nanoparticle deposition is performed in the system shown in figure 1. The source produces nanoparticle ions by magnetron sputtering of atoms from a metal target followed by their condensation within a flowing cold inert gas (Huttel 2017). The Nanogen-50 (Mantis Deposition, Ltd) is used in the present setup. It generates metal vapor by DC sputtering of 2 inch diameter metal targets, here 99.95% Mn (ACI Alloys). The magnetron block is equipped with the manufacturer's 'magnet set A' whose benefit lies in producing almost exclusively ionized particles (of which over 80% are anions, see (Mantis Deposition 2017)). This makes it possible to filter and manipulate the entire beam by electric fields and to avoid the deposition of randomly sized neutral species. Argon gas (99.999% purity) is introduced into the source region behind the magnetron head, and the magnetron itself is mounted on a linear translator. The interplay between the source parameters has been discussed in detail by us previously (Khojasteh and Kresin 2016, 2017). In the present case, the flow rate of Ar was 190 sccm, the distance between the magnetron and the beam exit aperture was 9 cm, and the discharge power was 10 W. The sputtered metal atoms enter the condensation zone where they undergo collisions with the cold inert gas (the source jacket is filled with liquid nitrogen) and nanoparticle growth takes place as the mixture moves towards the 5 mm diameter exit aperture. The resulting directed beam passes through a 6 mm skimmer followed by a quadrupole mass filter. The standard mass range of the Mantis MesoQ unit is from ~ 300 amu to $\sim 10^6$ amu, but its performance can be extended somewhat to either side of this range.

The size-selected nanoparticle ions then find themselves in the main deposition chamber (base pressure 10^{-8} Torr).



Figure 1. Schematic of the nanoparticle deposition apparatus, with a magnetron sputtering/vapor condensation source, a quadrupole mass filter, and a deposition stage. Inset: overall size range of Mn nanoparticle ions in the beam, vertical lines mark the sizes selected for deposition in this work.

After collimation by a 1 cm \times 1 cm mask, the beam lands on room-temperature glass slides covered with a fluorine-doped tin oxide (FTO) conducting film. Prior to loading into the substrate holder, the slides are sonicated for five minutes in acetone and methanol, washed with deionized water, and dried with nitrogen gas. The conducting substrates are connected to ground potential, and the impinging nanoparticle ions become neutralized. The beam velocities are in the range of 200 m s⁻¹ (Ayesh *et al* 2007, Ganeva *et al* 2013, Khojasteh and Kresin 2017) which corresponds to less than 0.1 eV kinetic energy per Mn atom. Being significantly below the atomic binding energy, this is generally regarded as the 'softlanding' regime which avoids significant fragmentation and deformation of the nanoparticle (Popok *et al* 2011).

The described setup allows for the deposition of pure, size-selected nanoparticles with a size resolution of $\pm 2\%$ (Baker *et al* 1997). This type of size control is difficult to achieve by solution-processed metal oxide nanoparticle synthesis.

For the electrochemical measurements, care was taken to produce films with the same total amount of deposited metal: $1.7 \ \mu g$ of 4, 6, and 8 nm diameter nanoparticles over the 1 cm² FTO slide sample area. The deposition rate, which can be converted into the mass loading, was measured using both a quartz crystal film thickness monitor and a Keithley 6487 picoammeter. Both tools yielded consistent results. The substrate ion current ranged from 0.065 nA for the 8 nm diameter particles to 0.1 nA for the 6 nm and 4 nm ones. The corresponding deposition times, adjusted to ensure equal mass loading, were 176 min, 55 min, and 36 min for the 4 nm, 6 nm, and 8 nm particle samples, respectively. Knowing the cross-sectional area of one nanoparticle (assumed to be round, as supported by the atomic force microscope (AFM) images in figure 2) and the total number that are deposited, we can estimate the covered surface area. It is found to correspond to the sub-monolayer regime: approximately 80%, 60% and 45% coverage by the 4 nm, 6 nm, and 8 nm particles, respectively.

The origin of this scaling is as follows. Since the mass of a single nanoparticle of diameter d is proportional to its volume, the total number of nanoparticles required for a fixed mass loading is proportional to $1/d^3$. On the other hand the surface projection, or shadow, of each such nanoparticle covers an effective surface area proportional to d^2 . Hence if the diameter of the deposited nanoparticles is varied while keeping their total mass constant, the surface area covered by the film will vary as 1/d. The percentages listed above for the actual samples differ only slightly (~10%) from this scaling due to rounding-off variations in the experimental deposition times.

2.2. AFM and XPS characterization

To verify the nanoparticle sizes, we prepared samples of size selected soft-landed Mn particles on Si/SiO₂ substrates and imaged them using an AFM (Veeco Innova operated in tapping mode using silicon probes with aluminum reflex coating, Tap 150Al-G, BudgetSensors). The images in figure 2 show nearly spherical shaped particles, indicating that they do not shatter or deform to a significant degree. Histograms of height profiles clearly confirm the prevalence of selected nanoparticle diameters.



Figure 2. AFM tapping-mode images and histograms of height distributions of size-selected Mn nanoparticles deposited on Si/SiO_2 substrates with the mass filter set to a diameter of (a) 4, (b) 6, (c) 8 nm. AFM tip convolution makes the images appear much wider than actual nanoparticle size, however profile height measurements confirm the good size selectivity of the deposition setup. (The insets show the profiles of sample particles which are marked in the image panels.)

When removed from the vacuum chamber, the Mn nanoparticles oxidize. To ascertain their composition, an x-ray photoelectron spectroscopy (XPS) measurement was performed on 6 nm particles deposited on highly oriented pyrolytic graphite (HOPG) in a 19 nm (i.e., ≈ 3 monolayer) thick film. HOPG was chosen for this measurement to avoid any substrate contamination of the XPS lines of interest. The measurement was done in a Kratos Axis Ultra spectrometer at room temperature. An Al anode operating at 60 W generated an x-ray beam that was focused at different spots on the HOPG surface with multiple measurements at each spot. The spectra were referenced to a C1s binding energy of 284.8 eV

in all cases. To quantify the elemental concentrations, the peak areas were determined after background subtraction. The spectra of adventitious adsorbates were estimated by performing XPS measurements on an HOPG surface without Mn nanoparticles. The XPS data were fitted using Casa XPS software.

In the XPS spectra of manganese oxide, the Mn 3s and 2p regions enable straightforward identification of the oxidation state (Di Castro and Polzonetti 1989). The splitting ΔE of the Mn 3s line shown in figure 3(a) and the satellite feature in the Mn 2p_{3/2} region highlighted in figure 3(b) are unequivocal signatures of the MnO stoichiometry, therefore



Figure 3. XPS spectra of (a) 3s and (b) 2p regions of nanoparticles deposited on HOPG. The peak positions and the 2p satellite feature identify the material as MnO.

excluding other types of manganese oxide such as Mn_2O_3 or MnO_2 .

2.3. Ultraviolet-visible (UV-vis) spectrum

It is well known that the band gap in semiconductor nanocrystals is increased compared to the bulk value as a result of size quantization, see, e.g., (Kittel 2005). It is therefore to be expected that our MnO nanoparticles also exhibit an increased bandgap. Unfortunately, the minute optical density of their submonolayer films precludes a straightforward analysis using UV–vis spectrophotometry, especially considering that the FTO slides have an absorption edge at essentially the same wavelength (Guan *et al* 2012) as the MnO bandgap of 3.6 eV or 344 nm (Madelung *et al* 2000). Therefore in order to derive an estimate of the gap, we obtained a diffuse reflectance spectrum (DRS) of the same thick 6 nm sample on



Figure 4. Bandgap of the 6 nm diameter MnO nanoparticles estimated from extrapolations of the edge of the Kubelka–Munk function obtained from diffuse reflectance data (see text for details). Both fits indicate a bandgap larger than that of the bulk material, indicated by the arrow.

HOPG as was employed for the XPS measurement described above. The measurement was performed using a PerkinElmer Lambda 950 UV/vis spectrophotometer.

It has been reported in the literature, see, e.g., (López and Gómez 2012) that energy gaps of nanoparticle films can be estimated using the Kubelka–Munk function $F(h\nu)$. Here ν is the light frequency and F is obtained from the measured reflectance $R(h\nu)$ as (Hecht 1976) $F = (1 - R^2)/2R$. It is approximately proportional to the extinction coefficient, and thereby to the nanoparticle absorption coefficient $\alpha(h\nu)$. Furthermore, for semiconductors the optical bandgap can be determined using the Tauc extrapolation of the rising edge of the plot of $(\alpha h\nu)^{1/n}$ versus $h\nu$, where the value of *n* depends on the nature of the transition. For bulk semiconductors with a direct bandgap $n = \frac{1}{2}$, while it was recently argued (Feng *et al* 2015) that n = 1 is a more satisfactory value for semiconductor nanocrystals. Figure 4 shows fits corresponding to both exponents. Despite the approximate nature of the DRS extrapolation, the data support the conclusion that the investigated nanoparticles possess a larger bandgap than bulk MnO.

2.4. Electrochemical data

A Gamry Reference 3000 potentiostat and a three-electrode cell were used with an Ag/AgCl reference electrode and a graphite rod counter electrode. The electrolyte solution was 0.1 M KOH. The cell was purged with nitrogen gas prior to each scan and then was closed to the ambient air. Linear sweep voltammetry experiments were carried out at 10 mV s^{-1} scan rate, between 0 and 2 V. The potentials shown in figure 5 are referenced to the normal hydrogen electrode by adding +197 mV to the applied potentials.

The electrochemical stability of the nanoparticle-coated anodes was tested also. As illustrated in figure 6, even the



Figure 5. (a) The electrochemical water oxidation current versus potential (normal hydrogen electrode) for three electrodes covered with 8, 6, and 4 nm nanoparticles of MnO at equal total amount of material. The data shows enhanced activity (lower onset potential) with decreasing particle size. (b) Tafel plot representation of the data. The slopes in the region of the current onset are 175, 200, and 250 mV/decade for the 4, 6, and 8 nm nanoparticle films, respectively.

submonolayer film of the smallest, 4 nm, nanoparticles exhibited no degradation over the scale of at least hours. The other samples behaved analogously.

3. Results and discussion

The MnO-covered FTO electrodes were used as the anode for water oxidation in a three-electrode cell as described above. Figure 5(a) shows the current density as a function of applied potential for the three different MnO nanoparticle sizes. The onset potential, defined as the voltage corresponding to a current density of 1 mA cm^{-2} , is 1.2 V, 0.9 V, and 0.8 V for the 8 nm, 6 nm, and 4 nm nanoparticles, respectively. The respective currents due to water oxidation at 2.0 V are 6, 9



Figure 6. Water oxidation current of the electrode containing 4 nm nanoparticles, measured near the reaction threshold over a one-hour period. Films of the larger nanoparticles behaved analogously.

and 11 mA. Since the mass loading of nanoparticles for all three scenarios were identical, we attribute the enhancement of catalytic activity to the decrease in nanoparticle size. This is the main finding of our work.

The influence of particle size and composition on catalytic activity is well known (Heiz and Landman 2007, Najafpour et al 2015, Tyo and Vajda 2015, Vajda and White 2015, Wang and Astruc 2017). For example Jin et al (2015) synthesized MnO nanocrystals ranging in size from 10 nm to 80 nm, and reported that the smallest particles showed the lowest onset potential for water oxidation. In a further study the same authors (Jin et al 2017) investigated water oxidation by 300 nm thick films of 10 nm MnO nanoparticles. They proposed that the electrokinetic steps in the nanocatalysts were distinct from their bulk counterparts. Slopes fitted to the Tafel plot representation of our data, figure 5(b), are somewhat larger than the values of \sim 70–120 mV/dec reported by Jin *et al* (2015) for their Mn_xO_y nanoparticles, however the latter were fitted to a steeper part of the current-voltage curve. In point of fact, the nonlinear shape of the plot underscores that the electrochemical reaction rate in the present case is not controlled by a single-electron charge transfer process (Kear and Walsh 2005).

In light of the above studies, our results follow the general trend that smaller particles are better catalysts than larger particles and bulk. However, the previous studies all concentrated on nanoparticles of 10 nm size or larger, and often did not maintain a constant catalyst mass when comparing different particle sizes. In the present work, in contrast, we have focused on a systematic comparison of substantially smaller particles at constant mass loading. In addition, as mentioned above, the nanoparticles in this work formed submonolayer films on the substrate, hence concerns about porosity, diffusion, and electrolyte transport limitations are not relevant, unlike in cases when thick films of nanoparticles are studied. Therefore, our observations reveal inherent differences in the catalytic properties of MnO nanoparticles.

A variety of nanometer size effects have been found in electrocatalytic materials which can be divided into two types (Li and Frenkel 2017). First are the 'geometric size effects' which derive from the increased surface-to-volume ratio. The smaller nanoparticles have larger surface-to-volume ratios and therefore higher densities of catalytically active sites. Second are the size effects that perturb the intrinsic electronic and lattice structure of the particles. A prime example is the change in the band gap of semiconductor nanocrystals with size, as addressed in the preceding section. Another illustrative example is that Co(II) oxide nanoparticles smaller than 8 nm, when dropped into water, spontaneously evolve hydrogen, while larger particles do not (Navrotsky *et al* 2010).

Having a larger number of active surface sites can multiply the count of charge transfer reactions proportionally, and with them the electrode current. However, the key observation that the smaller nanoparticles initiate catalysis at a significantly lower onset potential signifies that an inherent change takes place in the charge transfer energetics itself. This in turn implies that size effects in the electronic structure, as indeed commonly observed in nanoparticles, are likely to be responsible for the observed onset potential variation.

At its core, the catalytic reaction is related to the fact that the reactant-surface interaction opens up additional quantummechanical transition channels which vastly enhance the reactant-product Franck-Condon factor (Kresin and Lester 1992). Therefore an increase in surface electric fields characteristic of nanocatalysts (Zhu et al 2017) may underlie the observed lowering of the onset potential. Indeed, analogous to the discussion of the diffusion voltage in semiconductor junctions (Ibach and Lüth 2009) a dipole layer forming at the surface-electrolyte interface will give rise to a potential difference across the junction whose magnitude grows with the energy bandgap of the material. Consequently, the fact that the bandgap rises with decreasing nanoparticle size is accompanied by a strengthening of the surface dipole field which enhances the nanocatalyst's efficacy. A direct investigation of such surface fields is difficult by electrochemical methods alone and lies beyond the scope of this study, but a future careful characterization of the electric fields at nanocatalyst surfaces by a combination of theoretical and spectroscopic methods would be highly informative.

4. Conclusions

Sub-monolayer films of size-selected manganese nanoparticles, ranging from 4 to 8 nm in diameter, were produced on FTO substrates by low energy beam deposition. After they oxidized in air, the films' electrochemical catalytic activities for the water splitting reaction were investigated. It was found that the onset potential decreases with decreasing particle size. To the best of our knowledge, this is the first systematic study of the size effect in water oxidation for pure (ligand-and surfactant-free) sub-10 nm MnO nanocatalysts.

The ability of individual size-selected Mn-based nanoparticles to lower the water oxidation threshold illustrates the potency of nanocatalysts in improving the efficiency of important chemical reactions, highlights their interesting placement between bulk film electrocatalysts and the natural photosynthetic complexes, and raises interesting questions about the mechanism of their catalytic action and productive ways of optimizing it.

Since a reduction in nanoparticle size directly affects the reaction energetics, it may be concluded that the effect derives from intrinsic electronic properties of the particles: a change in the band gap and the appearance of strong electric fields at the nanoparticle surface. It may be possible to investigate the electronic energy level changes by means of optical and tunneling spectroscopy, while the presence of surface fields can be studied by nonlinear spectroscopic techniques.

In addition, it can be beneficial to take advantage of the ability of aggregation sources to regulate the nanoparticle composition and structure. For example, inspired by the photosynthetic OEC complex, in future work it will be interesting to produce mixed Mn/Ca nanoparticle catalysts with different stoichiometries. Furthermore, it has been demonstrated that by varying the source nucleation and growth parameters it is possible to alter the morphology of the generated nanoparticles (Johnson *et al* 2015, Zhao *et al* 2016, Krishnan *et al* 2017) which offers an additional path to tuning the functionality of deposited nanocatalyst films.

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References

- Artero V, Chavarot-Kerlidou M and Fontecave M 2011 Splitting water with cobalt Angew Chem., Int. Ed. 50 7238–66
- Ayesh A I, Lassesson A, Brown S A, Dunbar A D F, Kaufmann M, Partridge J G, Reichel R and Lith J V 2007 Experimental and simulational study of the operation for a high transmission mass filter *Rev. Sci. Instrum.* **78** 053906
- Baker S H, Thornton S C, Keen A M, Preston T I, Norris C, Edmonds K W and Binns C 1997 The construction of a gas aggregation source for the preparation of mass-selected ultrasmall metal particles *Rev. Sci. Instrum.* 68 1853–7

- Barber J 2017 A mechanism for water splitting and oxygen production in photosynthesis *Nat. Plants* **3** 17041
- Chen G, Zhou W, Guan D, Sunarso J, Zhu Y, Hu X, Zhang W and Shao Z 2017 Two orders of magnitude enhancement in oxygen evolution reactivity on amorphous $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\sigma}$ nanofilms with tunable oxidation *Sci. Adv.* **3** e1603206
- Di Castro V and Polzonetti G 1989 XPS study of MnO oxidation J. Electron Spectrosc. Relat. Phenom. 48 117–23
- El Koura Z, Cazzanelli M, Bazzanella N, Patel N, Fernandes R, Arnaoutakis G E, Gakamsky A, Dick A, Quaranta A and Miotello A 2016 synthesis and characterization of Cu and N codoped RF-sputtered TiO₂ films: photoluminescence dynamics of charge carriers relevant for water splitting *J. Phys. Chem.* C 120 12042–50
- Fan R, Mao J, Yin Z, Jie J, Dong W, Fang L, Zheng F and Shen M 2017 Efficient and stable silicon photocathodes coated with vertically standing nano-MOS₂ films for solar hydrogen production ACS Appl. Mater. Interfaces 9 6123–9
- Feng Y, Lin S, Huang S, Shrestha S and Conibeer G 2015 Can Tauc plot extrapolation be used for direct-band-gap semiconductor nanocrystals? J. Appl. Phys. 117 125701
- Ferreira K N, Iverson T M, Maghlaoui K, Barber J and Iwata S 2004 Architecture of the photosynthetic oxygen-evolving center *Science* 303 1831–8
- Ganeva M, Pipa A V, Smirnov B M, Kashtanov P V and Hippler R 2013 Velocity distribution of mass selected nano-size clusters *Plasma Sources Sci. Technol.* 22 045011
- Gorlin Y and Jaramillo T F 2010 A bifunctional nonprecious metal catalyst for oxygen reduction and water oxidation *J. Am. Chem. Soc.* **132** 13612–4
- Grammatikopoulos P, Steinhauer S, Vernieres J, Singh V and Sowwan M 2016 Nanoparticle design by gas-phase synthesis *Adv. Phys.* X **1** 81–100
- Guan J, Zhang J, Yu T, Xue G, Yu X, Tang Z, Wei Y, Yang J, Li Z and Zou Z 2012 Interfacial modification of photoelectrode in ZnO-based dye-sensitized solar cells and its efficiency improvement mechanism RSC Adv. 2 7708–13
- Guo C X, Chen S and Lu X 2014 Ethylenediamine-mediated synthesis of Mn_3O_4 nano-octahedrons and their performance as electrocatalysts for the oxygen evolution reaction *Nanoscale* **6** 10896–901
- Harriman A, Pickering I J, Thomas J M and Christensen P A 1988
 Metal oxides as heterogeneous catalysts for oxygen evolution under photo chemical conditions *J. Chem. Soc. Faraday Trans.* I 84 2795–806
- Hecht H G 1976 The interpretation of diffuse reflectance spectra J. Res. Natl Bur. Stand. A 80A 567–83
- Heiz U and Landman U (ed) 2007 Nanocatalysis (Berlin: Springer)
- Huttel Y (ed) 2017 Gas-Phase Synthesis of Nanoparticles
- (Weinheim: Wiley-VCH) Ibach H and Lüth H 2009 *Solid-State Physics* (Berlin: Springer) section 12.6
- Jin K *et al* 2015 Partially oxidized sub-10 nm MnO nanocrystals with high activity for water oxidation catalysis *Sci. Rep.* **5** 10279
- Jin K et al 2017 Mechanistic investigation of water oxidation catalyzed by uniform, assembled MnO nanoparticles J. Am. Chem. Soc. 139 2277–85
- Johnson G E, Colby R and Laskin J 2015 Soft landing of bare nanoparticles with controlled size, composition, and morphology *Nanoscale* 7 3491–503
- Kärkäs M D, Verho O, Johnston E V and Åkermark B 2014 Artificial photosynthesis: molecular systems for catalytic water oxidation *Chem. Rev.* **114** 11863–2001
- Kear G and Walsh F C 2005 The characteristics of a true Tafel slope Corros. Mater. 30 S1–4
- Kim J H, Kaneko H, Minegishi T, Kubota J, Domen K and Lee J S 2016 Overall photoelectrochemical water splitting using tandem cell under simulated sunlight *ChemSusChem* 9 61–6

Kittel C 2005 Introduction to Solid State Physics (Hoboken: Wiley)

- Khan S, Yang K R, Ertem M Z, Batista V S and Brudvig G W 2015 Mechanism of manganese-catalyzed oxygen evolution from experimental and theoretical analyses of ¹⁸O kinetic isotope effects ACS Catal. 5 7104–13
- Khojasteh M and Kresin V V 2016 Formation of manganese nanoclusters in a sputtering/aggregation source and the roles of individual operating parameters *Proc. SPIE* 10174 1017407
- Khojasteh M and Kresin V V 2017 Influence of source parameters on the growth of metal nanoparticles by sputter-gasaggregation Appl. Nanosci. 7 875–83
- Kresin V Z and Lester W A Jr 1992 Quantum-mechanical model of heterogeneous catalysis *Chem. Phys. Lett.* 197 1–6
- Krishnan G, de Graaf S, ter Brink G H, Persson P O Å, Kooi B J and Palasantzas G 2017 Strategies to initiate and control the nucleation behavior of bimetallic nanoparticles *Nanoscale* 9 8149–56
- Kuo C-H *et al* 2015 Facet-dependent catalytic activity of MnO electrocatalysts for oxygen reduction and oxygen evolution reactions *Chem. Commun.* **51** 5951–4
- Kwon G et al 2013 Size-dependent subnanometer Pd cluster (Pd₄, Pd₆, and Pd₁₇) water oxidation electrocatalysis ACS Nano 7 5808–17
- Lang S M, Bernhardt T M, Kiawi D M, Bakker J M, Barnett N R and Landman U 2016 Cluster size and composition dependent water deprotonation by free manganese oxide clusters *Phys. Chem. Chem. Phys.* 18 15727–37
- Li Y and Frenkel A I 2017 Metal nanocatalysts XAFS Techniques for Catalysts, Nanomaterials, and Surfaces ed Y Iwasawa et al (Cham: Springer) ch 19, pp 273–98
- Li X, Hao X, Abudula A and Guan G 2016 Nanostructured catalysts for electrochemical water splitting: current state and prospects *J. Mater. Chem.* A **4** 11973–2000
- Li Q, Wang Z-L, Li G-R, Guo R, Ding L-X and Tong Y-X 2012 Design and synthesis of MnO₂/Mn/MnO₂ sandwichstructured nanotube arrays with high supercapacitive performance for electrochemical energy storage *Nano Lett.* **12** 3803–7
- Lin J, Zhang X, Zhou L, Li S and Qin G 2017 Pt-doped α -Fe₂O₃ photoanodes prepared by a magnetron sputtering method for photoelectrochemical water splitting *Mater. Res. Bull.* **91** 214–9
- López R and Gómez R 2012 Band-gap energy estimation from diffuse reflectance measurements on sol–gel and commercial TiO₂: a comparative study *J. Sol-Gel Sci. Technol.* **61** 1–7
- Madelung O, Rössler U and Schulz M (ed) 2000 MnO: band structure, energy gap *Landolt-Börnstein—Group III Condensed Matter 41D (Non-Tetrahedrally Bonded Binary Compounds II)* (Berlin: Springer)
- Mantis Deposition Ltd Application Note App-001 (Oxfordshire, UK)
- Masudy-Panah S, Moakhar R S, Chua C S, Tan H R, Wong T I, Chi D and Dalapati G K 2016 Nanocrystal engineering of sputter-grown CuO photocathode for visible-light-driven electrochemical water splitting ACS Appl. Mater. Interfaces 8 1206–13
- McEvoy J P and Brudvig G W 2006 Water-splitting chemistry of photosystem II *Chem. Rev.* **106** 4455–83
- McInnes A, Plant S R, Ornelas I M, Palmer R E and Wijayantha K G U 2017 Enhanced photoelectrochemical water splitting using oxidized mass-selected Ti nanoclusters on metal oxide photoelectrodes *Sustain. Energy Fuels* **1** 336–44
- Najafpour M M, Ehrenberg T, Wiechen M and Kurz P 2010 Calcium manganese(III) oxides (CaMn₂O₄ · x H₂O) as biomimetic oxygen-evolving catalysts *Angew Chem.*, *Int. Ed.* **49** 2233–7
- Najafpour M M, Zarei Ghobadi M, Haghighi B, Tomo T, Shen J and Allakhverdiev S I 2015 Comparison of nano-sized Mn oxides with the Mn cluster of photosystem II as catalysts for water oxidation *Biochim. Biophys. Acta Bioenergy* 1847 294–306

Navrotsky A, Ma C, Lilova K and Birkner N 2010 Nanophase transition metal oxides show large thermodynamically driven shifts in oxidation-reduction equilibria *Science* **330** 199–201

- Nelson N and Ben-Shem A 2004 The complex architecture of oxygenic photosynthesis Nat. Rev. Mol. Cell Biol. 5 971–82
- Nocera D G 2012 The artificial leaf *Acc. Chem. Res.* **45** 767–76 Paoli E A, Masini F, Frydendal R, Deiana D, Malacrida P,

Hansen T W, Chorkendorff I and Stephens I E L 2016 Finetuning the activity of oxygen evolution catalysts: the effect of oxidation pre-treatment on size-selected Ru nanoparticles *Catal .Today* **262** 57–64

Patel M, Kim H-S, Patel D B and Kim J 2016 CuO photocathodeembedded semitransparent photoelectrochemical cell J. Mater. Res. 31 3205–13

Popok V N, Barke I, Campbell E E B and Meiwes-Broer K-H 2011 Cluster-surface interaction: from soft landing to implantation *Surf. Sci. Rep.* **66** 347–77

Ramírez A, Hillebrand P, Stellmach D, May M M, Bogdanoff P and Fiechter S 2014 Evaluation of MnO_x, Mn₂O₃, and Mn₃O₄ electrodeposited films for the oxygen evolution reaction of water J. Phys. Chem. C **118** 14073–81

Robinson D M, Go Y B, Mui M, Gardner G, Zhang Z, Mastrogiovanni D, Garfunkel E, Li J, Greenblatt M and Dismuke G C 2013 Photochemical water oxidation by crystalline polymorphs of manganese oxides: structural requirements for catalysis J. Am. Chem. Soc. 135 3494–501

Singh A and Spiccia L 2013 Water oxidation catalysts based on abundant 1st row transition metals *Coord. Chem. Rev.* 257 2607–22

Sivula K, Le Formal F and Grätzel M 2011 Solar water splitting: progress using hematite (α-Fe₂O₃) photoelectrodes *ChemSusChem* **4** 432–49

Sreedhar A, Sreekanth T V M, Kwon J H, Yi J, Sohn Y and Gwag J S 2017 Ag nanoparticles decorated ion-beam-assisted TiO₂ thin films for tuning the water splitting activity from UV to visible light harvesting *Ceram. Int.* **43** 12814–21

Srivastava S, Thomas J P, Rahman M A, Abd-Ellah M, Mohapatra M, Pradhan D, Heinig N F and Leung K T 2014 Size-selected TiO₂ nanocluster catalysts for efficient photoelectrochemical water splitting ACS Nano 8 11891–8 Srivastava S, Thomas J P, Heinig N, Abd-Ellah M, Rahman M A and Leung K T 2017 Photoelectrochemical water splitting on ultrasmall defect-rich TaO_x nanoclusters enhanced by size-selected Pt nanocluster promoters *Nanoscale* 9 14395–404

Stranak V, Drache S, Wulff H, Hubicka Z, Tichy M, Kruth A, Helm C A and Hippler R 2015 Oxidation behavior of Cu nanoparticles embedded into semiconductive TiO₂ matrix *Thin Solid Films* 589 864–71

Takashima T, Hashimoto K and Nakamura R 2012 Mechanisms of pH-dependent activity for water oxidation to molecular oxygen by MnO₂ electrocatalysts *J. Am. Chem. Soc.* **134** 1519–27

Tyo E C and Vajda S 2015 Catalysis by clusters with precise numbers of atoms *Nat. Nanotechnol.* **10** 577–88

- Vajda S and White M G 2015 Catalysis applications of size selected cluster deposition ACS Catal. 5 7152–76
- Vinyard D J and Brudvig G W 2017 Progress toward a molecular mechanism of water oxidation in photosystem II Annu. Rev. Phys. Chem. 68 101–16
- Wang D and Astruc D 2017 The recent development of efficient earth-abundant transition-metal nanocatalysts *Chem. Soc. Rev.* 46 816–54
- Wei W, Cui X, Chen W and Ivey D G 2011 Manganese oxide-based materials as electrochemical supercapacitor electrodes *Chem. Soc. Rev.* 40 1697–721
- Wiechen M and Spiccia L 2014 Manganese oxides as efficient water oxidation catalysts *ChemCatChem* 6 439–41
- Yano J *et al* 2006 Where water is oxidized to dioxygen: structure of the photosynthetic Mn₄Ca cluster *Science* **314** 821–5
- Zaharieva I, Chernev P, Risch M, Klingan K, Kohlhoff M, Fischer A and Dau H 2012 Electrosynthesis, functional, and structural characterization of a water-oxidizing manganese oxide *Energy Environ. Sci.* **5** 7081–9
- Zhao J *et al* 2016 Formation mechanism of Fe nanocubes by magnetron sputtering inert gas condensation *ACS Nano* **10** 4684–94
- Zhu J, Pang S, Dittrich T, Gao Y, Nie W, Cui J, Chen R, An H, Fan F and Li C 2017 Visualizing the nano cocatalyst aligned electric fields on single photocatalyst particles *Nano Lett.* 17 6735–41