DOI: 10.1002/cctc.201402361



## Enhanced Au–Pd Activity in the Direct Synthesis of Hydrogen Peroxide using Nanostructured Titanate Nanotube Supports

Laura Torrente-Murciano,<sup>[a]</sup> Qian He,<sup>[c]</sup> Graham J. Hutchings,<sup>[b]</sup> Christopher J. Kiely,<sup>[c]</sup> and David Chadwick<sup>\*[a]</sup>

Nanostructured supports with tubular morphologies can impose one dimensional external constraints to supported metal nanoparticles affording small sizes (<2 nm) with high dispersion. Specifically, the curvature and chemical environment of the external nanotube surface appears to play a key role in determining the morphology and stability of the supported Au–Pd nanoparticles. This strategy is presented as an alternative nanoparticle stabilisation approach rather than encapsulation within porous structures or the use of organic capping agents with associated diffusional limitations. Here, we report the enhancement achieved in the Au–Pd alloy reactivity for the direct synthesis of hydrogen peroxide when supported on titanate nanotubes (Ti-NT) with a productivity above 11600 mol<sub>H<sub>2</sub>O<sub>2</sub>kg<sub>metal</sub><sup>-1</sup>h<sup>-1</sup> afforded by the high metal–support interaction.</sub>

Hydrogen peroxide ( $H_2O_2$ ) has the potential to become a feasible green alternative to the use of stoichiometric oxidants in the chemical industry for a wide range of synthetic reactions such as oxidation,<sup>[1]</sup> epoxidation,<sup>[2]</sup> and hydroxylation.<sup>[3]</sup> Over the past two decades, there has been a major scientific effort to develop a system for the direct synthesis of hydrogen peroxide to overcome the limitations associated with its large scale production via the anthraquinone autoxidation process, specifically, waste water production and safe transport and storage of concentrated  $H_2O_2$  solutions.<sup>[4]</sup> The relatively low concentration of  $H_2O_2$  achieved during the direct synthesis

[a]	Dr. L. Torrente-Murciano, <sup>+</sup> Prof. D. Chadwick Department of Chemical Engineering Imperial College London London, SW7 2AZ (UK) E-mail: d.chadwick@imperial.ac.uk
[b]	Prof. G. J. Hutchings Cardiff Catalysis Institute, School of Chemistry Cardiff University Cardiff, CF10 3TB (UK)
[c]	Dr. Q. He, Prof. C. J. Kiely Department of Materials Science and Engineering Lehigh University Bethlehem, PA18015-3195 (USA)
[+]	Current address: Department of Chemical Engineering University of Bath Bath BA2 7AY (UK)
	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201402361.

process (1–3 wt%), may be advantageous since this concentration is typically that required for oxidation reactions.

The direct synthesis of hydrogen peroxide from H<sub>2</sub> and O<sub>2</sub> using palladium catalysts has been extensively studied by both academic researchers<sup>[5]</sup> and industry.<sup>[6]</sup> However, the process has not yet been commercialised, owing to the overall lack of productivity when using H<sub>2</sub> and O<sub>2</sub> mixtures outside the explosive range. The use of bimetallic alloys has been a focus of research in recent years, leading to a particularly significant enhancement of the activity when gold is added to palladium<sup>[7]</sup> although other bimetallic catalysts such as Pd-Pt<sup>[8]</sup> have also been studied. The effect of the support on the metal activity<sup>[7a,9]</sup> has also been identified as a key factor in determining the catalyst activity and selectivity. These advances have inspired this work exploiting nanostructured supports for Au-Pd alloy catalysts, specifically tubular supports with diameters of 15-30 nm, in which the morphology creates physical one dimensional (1D) external constraints on the metal nanoparticles leading to small sizes (<2 nm) with high dispersion. Herein we report the enhancement achieved in the reactivity of Au-Pd for the direct synthesis of hydrogen peroxide when supported on titanate nanotubes (Ti-NT). The morphology and chemical environment of the external nanotube surface is shown to determine the morphology and stability of the supported Au-Pd nanoparticles.

Au–Pd alloy nanoparticles supported on nanostructured titanate nanotubes exhibit an extraordinary activity towards the direct synthesis of hydrogen peroxide from non-explosive mixtures of molecular hydrogen and oxygen (1:2 volumetric ratio). A productivity of 11670 mol<sub>H2O2</sub> kg<sub>metal</sub><sup>-1</sup> h<sup>-1</sup> (174.9 mol<sub>H2O2</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) is obtained at moderate gas pressures (3 bar P<sub>H2</sub> + P<sub>O2</sub>, 1 bar = 0.1 MPa) with a turnover frequency above 1200 h<sup>-1</sup>. To compare these results with other reported Au–Pd catalytic systems using ceramic oxide support materials such as TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub><sup>[7a,9b,c]</sup> under the same reaction conditions, commercial oxides have been used as supports for gold– palladium nanoparticles whose activity has been tested for the direct synthesis of hydrogen peroxide in the same catalytic reactor system (Table 1).

Pre-reduction of the titanate nanotubes catalysts increases their activity compared to their unreduced counterparts and at the same time, inhibits the leaching of the metals into the acidified solution. By way of contrast, a decrease of the activity by reduction is observed in the cases of Au–Pd nanoparticles supported on titanium dioxide and silica, most likely due to metal agglomeration at the reduction temperature of 200 °C.

Table 1. Direct synthesis of $H_2O_2$ from molecular $O_2$ and $H_2$ using supported Au–Pd catalysts. <sup>[a]</sup>									
Catalyst <sup>[b]</sup>	Pre- reduced <sup>[c]</sup>	Metal size [nm]	H <sub>2</sub> O <sub>2</sub> formation [mmol]	$\begin{array}{l} H_2O_2\\ productivity\\ [mol_{H_2O_2}k{g_{cat}}^{-1}h^{-1}] \end{array}$	$\begin{array}{l} H_2O_2\\ productivity\\ [mol_{H_2O_2}kg_{metal}{}^{-1}h^{-1}] \end{array}$	TOF <sup>(f)</sup> [h <sup>-1</sup> ]	H <sub>2</sub> O <sub>2</sub> decomp <sup>[f]</sup> [%]		
0.4Au –1.1Pd/Ti-NT	No	1.5	0.247	9.9	660	69	n.a		
0.4 Au-1.1Pd/Ti-NT	Yes	1.6 <sup>[d]</sup>	4.372	174.9	11 600	1233	22.5		
1.5Au-1.5Pd/TiO <sub>2</sub>	No	n.a	0.683	27.3	910	127	n.a		
1.5Au-1.5Pd/TiO₂	Yes	6.4 <sup>[e]</sup>	0.323	12.9	430	60	19.7		
1.5Au-1.5Pd/SiO₂	No	n.a	0.588	23.5	784	109	n.a		
1.5Au-1.5Pd/SiO₂	Yes	25.3 <sup>[e]</sup>	0.215	8.6	287	40	2.5		
1.5Au-1.5Pd/Al₂O₃	No	n.a	0.578	23.1	770	107	n.a		
1.5Au-1.5Pd/Al <sub>2</sub> O <sub>3</sub>	Yes	24.4 <sup>[e]</sup>	2.681	107.2	3575	498	6.8		

[a] Typical reaction conditions: time: 40 min, 5 °C, total pressure: 20 bar  $H_2/O_2/Ar$  (5:10:85%), stirring rate: 1000 rpm, catalyst: 75 mg, reaction volume: 75 mL, methanol, 0.04 M HCl. [b] Metal loading expressed as %wt. Calculated by ICP after digesting the catalysts in a HNO<sub>3</sub>:HCl mixture in the AuPd/Ti-NT catalysts. [c] Catalysts were pre-reduced under  $H_2$  flow at 200 °C for 1.5 h. [d] Calculated from analysis of HAADF STEM images. [e] Calculated by analysis of XRD data using the Scherrer equation. [f] Calculated as moles(H<sub>2</sub>O<sub>2</sub>)/moles(metal)·h. [f] Decomposition reaction conditions: time: 90 min, atmospheric pressure, stirring rate: 800 rpm, catalyst: 10 mg, reaction volume: 50 mL, methanol, 0.04 M HCl, [H<sub>2</sub>O<sub>2</sub>)<sub>Initial</sub>: 1.5 M.

During reduction of the metals, a structural rearrangement is likely to take place,<sup>[10]</sup> which is strongly influenced by the support. In the case of titanate nanotubes, the surface curvature (radius of curvature  $\approx 10 \text{ nm}^{[11]}$ ) in combination with a strong metal–support interaction creates physical and chemical constraints respectively that impart a degree of metal stabilisation, affording a high dispersion of small, even sub-nanometre, metal nanoparticles.

Energy dispersive X-ray spectroscopy (see below) confirmed alloy formation in the bimetallic Au–Pd/Ti-NT catalyst, which is known to impart a synergetic effect.<sup>[12]</sup> Alloy formation also takes place in Au–Pd systems supported on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> as shown by a shift of the gold diffraction peaks on the X-Ray diffraction spectra (see Supporting Information, Figure S1). However, in the Au–Pd/Ti-NT case, the XRD spectrum only shows diffraction peaks characteristic of the tri-titanate phase (H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) with 2 $\theta$  values of 9.8, 24.6, 28.7 and 48.5°.<sup>[13]</sup> No diffraction peaks corresponding to the metal were observed indicating extremely small (i.e. sub-3 nm) metal particle sizes.

The titanate nanotube morphology was investigated by conventional bright field TEM imaging, Figure 1A,B. The titanate nanotubes are typically 15–30 nm in diameter, 0.5–1.0  $\mu$ m in length, and have a strong tendency to agglomerate into aligned bundles. Very few metallic nanoparticles could be observed supported on the nanotubes in the TEM imaging mode. High angle annular dark field (HAADF) images taken in an aberration corrected STEM proved to be the most effective way of revealing the size and spatial distribution of the metal particles by virtue of their higher atomic number relative to the titanate support material.

Shown in Figure 1 C,D are typical images of the un-reduced bimetallic Au–Pd/Ti-NT catalysts in which the majority of the metal is present as very small (mean value 1.5 nm) particles (Figure 1 E). However, single atoms decorating the support surface were also seen. Energy dispersive X-ray spectroscopy (STEM-XEDS) confirmed that the supported particles were Au–

Pd alloys, and that the larger particles were usually Au-rich, which implies that the very small particles were Pd-rich.

Pre-reduction under H<sub>2</sub> flow at 200 °C for 1.5 h was required to improve the hydrogen peroxide productivity of the Au-Pd/Ti-NT catalyst (Table 1). It might be expected that the metal nanoparticles would coarsen during such a reduction process. However, a very similar particle size distribution and morphology was observed before (Figure 1C-D,E) and after the H<sub>2</sub> reduction treatment (Figure 2A-D,E). Interestingly, it is noted that many of the larger metal nanoparticles, which represent relatively



**Figure 1.** BF TEM images showing the morphology of the titanate nanotubes at A) 0.2  $\mu$ m and B) 20 nm; STEM-HAADF images of the un-reduced bimetallic AuPd/Ti-NT catalyst at C) 20 nm and B) 5 nm; E) Particle size distribution of the un-reduced AuPd/Ti-NT catalysts.

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

## CHEMCATCHEM COMMUNICATIONS



**Figure 2.** STEM-HAADF images of the pre-reduced AuPd/Ti-NT catalyst at A) 10 nm, B) 5 nm, C) 1 nm, D) 2 nm; E) Particle size distribution of the pre-reduced AuPd/Ti-NT catalyst.

a minor fraction of the total population, are often elongated along the length of the nanotube. Additional representative STEM-HAADF images of such elongated particles are shown in the Supporting Information, Figure S2. These stretched particles predominate when the nanoparticle diameter exceeds  $\approx$  2 nm and they tend to have a characteristic length-to-width aspect ratio somewhere in the range of 1.5:1 to 2.5:1. This shape modification probably occurs to minimise the overall internal strain energy of the particles as they try to lattice match onto the curved support surface. Less strain would be induced in the larger crystalline metal particle if it were to elongate along the axial direction as opposed to extending around the highly curved circumferential direction. The 'before' and 'after use' particle size distributions suggest that the curved nanotube surface imparts a high degree of structural and thermal stability to the sub-2 nm metal nanoparticles due to the metal-support interaction.

A high metal dispersion (48%) and an active metal surface area of  $3.4 \text{ m}^2\text{g}^{-1}$  in the AuPd/Ti-NT catalyst were quantified by carbon monoxide pulse chemisorption. The estimated active particle diameter considering a hemispherical shape is 2.4 nm,



**Figure 3.** Effect of pressure on the formation of  $H_2O_2$  using Au–Pd/Ti-NT as catalyst. Reaction conditions:  $H_2/O_2/Ar$  (5:10:85%), 0.04  $\mu$  HCl, methanol, 5 °C. Dashed lines show the data fitting to a consecutive reaction for 20 and 7 bar; the dashed line for 1 bar is a simulation using parameters from 20 bar

which is in reasonable agreement with our STEM characterisation.

The variation in hydrogen peroxide concentration with reaction time during direct synthesis over Au-Pd/Ti-NT catalyst is shown in Figure 3. An increase in hydrogen peroxide production is observed as the reaction pressure increases as expected, owing to the increased gas solubility in the liquid.<sup>[14]</sup> At all three reaction pressures, the hydrogen peroxide concentration increases with reaction time reaching a maximum after about 40 min as a consequence of the decreasing hydrogen partial pressure and decomposition of the product hydrogen peroxide. The extent of the H<sub>2</sub>O<sub>2</sub> decomposition over the catalyst was assessed separately using a  $1.5\,\,\text{m}$   $\,\text{H}_2\text{O}_2$  concentration under atmospheric pressure reaction conditions and are summarised in Table 1. The decomposition of hydrogen peroxide to water and oxygen was found to present a molar ratio of 2:1 which is consistent with the overall reaction  $2H_2O_2 \rightarrow 2H_2O +$  $O_2^{[15]}$  The first order rate constant for  $H_2O_2$  decomposition over Au-Pd/Ti-NT was determined to be 0.0031 min<sup>-1</sup> under the conditions used (see the Supporting Information, Figure S3). The concentration profiles in Figure 3 can be fitted to consecutive pseudo first-order reactions corresponding to synthesis and decomposition of hydrogen peroxide  $(H_2 + O_2 \rightarrow H_2O_2 \rightarrow$  $H_2O + \frac{1}{2}O_2$ ). At 20 and 7 bar the pseudo first-order rate constants were 0.049 and 0.046  $min^{-1}$  for synthesis and 0.0030 and 0.0031 min<sup>-1</sup> for decomposition respectively (see Supporting Information, Figure S4). The rate constants for decomposition are in good agreement with the independently determined value. Measurements of the residual hydrogen concentration after 90 min at 20 bar were consistent with these kinetics indicating no significant direct combustion of hydrogen. The ratio of synthesis/decomposition rate constant over Au-Pd/Ti-NT is about 16. This H<sub>2</sub>O<sub>2</sub> decomposition is possibly associated with residual traces of NaOH remaining on the titanate support after its hydrothermal synthesis. The high activity of the Au-Pd/Ti-NT catalyst for in situ hydrogen peroxide synthesis could be exploited in a tandem system (e.g. in oxidation reactions) to enhance further the hydrogen utilisation.

In summary, we have shown that extremely small bi-metallic gold-palladium clusters (<2 nm) are stabilised by titanate nanotubes and show extraordinary catalytic properties for the direct synthesis of hydrogen peroxide. Its activity is ascribed to the high metal dispersion combined with strong support interaction.

## **Experimental Section**

Titanate nanotubes (Ti-NT) were synthesised by a hydrothermal method.<sup>[16]</sup> Au–Pd/Ti-NT catalysts were prepared by adsorption;<sup>[17]</sup> Au-Pd supported on conventional oxide supports (TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) were prepared by incipient wetness impregnation. HAuCl<sub>4</sub> and PdCl<sub>2</sub> were used as metal precursors. Full details are given in the Supporting Information. Pre-reduction was performed in a flow of H<sub>2</sub> at 200 °C for 1.5 h. Hydrogen peroxide synthesis reactions was carried out in a 250 mL Parr stainless steel autoclave reactor using a glass liner under different pressures (below 20 bar). The reaction temperature was controlled at 5°C by an external cooler/ heater and a thermopar inside the reaction mixture. A four propeller gas entrainment stirrer was used for agitation at a speed of 1000 rpm. The solvent (methanol with 0.04 м HCl) was purged three times with the feed gas  $H_2/O_2/Ar$  (5:10:85%) before being filled at the desired pressure. Synthesis of hydrogen peroxide was followed by titration of liquid aliquots with cerium sulphate at regular intervals. After reaction, the gas phase was analysed by gas chromatography to determine hydrogen selectivity.

Decomposition reactions were carried out at atmospheric pressure and the order of reactions were determined by measuring the accumulation of oxygen gas inside the reactor with a Dwyer 1223 M200-D u-tube manometer. Hydrogen peroxide concentration was determined at the beginning and end to confirm that the mass balance was satisfied.

Atomic-resolution, high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) was carried out using a 200 kV JEOL 2200FS TEM/STEM equipped with CEOS spherical aberration corrector. All STEM-HAADF images were light low-pass filtered using a  $3 \times 3$  kernel to reduce high-frequency noise.

**Keywords:** gold • hydrogen peroxide • nanostructured catalysts • nanotubes • palladium

- a) Z. Q. Lei, R. R. Wang, *Catal. Commun.* 2008, *9*, 740; b) K. Jeyakumar,
   D. K. Chand, *Tetrahedron Lett.* 2006, *47*, 4573.
- [2] a) G. Blanco-Brieva, M. C. Capel-Sanchez, M. P. de Frutos, A. Padilla-Polo, J. M. Campos-Martin, J. L. G. Fierro, *Ind. Eng. Chem. Res.* 2008, 47, 8011;
  b) F. G. Gelalcha, B. Bitterlich, G. Anilkumar, M. K. Tse, M. Beller, *Angew. Chem. Int. Ed.* 2007, 46, 7293; *Angew. Chem.* 2007, 119, 7431.
- [3] a) P. Battioni, J. P. Renaud, J. F. Bartoli, D. Mansuy, J. Chem. Soc. Chem. Commun. 1986, 341; b) J. A. Martens, P. Buskens, P. A. Jacobs, A. Vanderpol, J. H. C. Vanhooff, C. Ferrini, H. W. Kouwenhoven, P. J. Kooyman, H. Vanbekkum, Appl. Catal. A 1993, 99, 71.
- [4] J. M. Campos-Martin, G. Blanco-Brieva, J. L. G. Fierro, Angew. Chem. Int. Ed. 2006, 45, 6962; Angew. Chem. 2006, 118, 7116.
- [5] a) M. S. Yalfani, S. Contreras, F. Medina, J. Sueiras, *Chem. Commun.* 2008, 3885; b) B. Z. Hu, Q. H. Zhang, Y. Wang, *Chem. Lett.* 2009, *38*, 256.
- [6] a) L. W. Gosser, J. A. T. Schwartz, J. T. Schwartz, (Du Pont De Nemours & Co), EP342047A2; b) L. W. Gosser, (Du Pont De Nemours & Co), US4832938A; c) J. Van Weynbergh, J. Schoebrechts, J. Colery, (Interox Int. Solvay Interox), WO9215520A1; d) G. Paparatto, G. DeAlberti, R. D'Aloisio, R. Daloisio, G. Dealberti, (ENI SPA), WO200292502A1.
- [7] a) J. K. Edwards, A. Thomas, A. F. Carley, A. A. Herzing, C. J. Kiely, G. J. Hutchings, *Green Chem.* 2008, *10*, 388; b) J. K. Edwards, A. Thomas, B. E. Solsona, P. Landon, A. F. Carley, G. J. Hutchings, *Catal. Today* 2007, *122*, 397; c) T. García, R. Murillo, S. Agouram, A. Dejoz, M. J. Lazaro, L. Torrente-Murciano, B. Solsona, *Chem. Commun.* 2012, *48*, 5316.
- [8] Q. S. Liu, J. C. Bauer, R. E. Schaak, J. H. Lunsford, Appl. Catal. A 2008, 339, 130.
- [9] a) A. Abad, P. Concepcion, A. Corma, H. Garcia, Angew. Chem. Int. Ed. 2005, 44, 4066; Angew. Chem. 2005, 117, 4134; b) A. G. Gaikwad, S. D. Sansare, V. R. Choudhary, J. Mol. Catal. A 2002, 181, 143; c) T. Ishihara, Y. Hata, Y. Nomura, K. Kaneko, H. Matsumoto, Chem. Lett. 2007, 36, 878.
- [10] S. Melada, R. Rioda, F. Menegazzo, F. Pinna, G. Strukul, J. Catal. 2006, 239, 422.
- [11] L. Torrente-Murciano, A. A. Lapkin, D. Chadwick, J. Mater. Chem. 2010, 20, 6484.
- [12] a) C. Della Pina, E. Falletta, L. Prati, M. Rossi, *Chem. Soc. Rev.* 2008, *37*, 2077; b) N. Dimitratos, F. Porta, L. Prati, A. Villa, *Catal. Lett.* 2005, *99*, 181.
- [13] Q. Chen, G. H. Du, S. Zhang, L. M. Peng, Acta Crystallogr. Sect. B 2002, 58, 587.
- [14] P. Landon, P. J. Collier, A. F. Carley, D. Chadwick, A. J. Papworth, A. Burrows, C. J. Kiely, G. J. Hutchings, Phys. Chem. Chem. Phys. 2003, 5, 1917.
- [15] A. Hiroki, J. A. LaVerne, J. Phys. Chem. B 2005, 109, 3364.
- [16] L. Torrente-Murciano, A. Lapkin, D. J. Nielsen, I. Fallis, K. J. Cavell, Green Chem. 2010, 12, 866.
- [17] L. Torrente-Murciano, A. A. Lapkin, D. V. Bavykin, F. C. Walsh, K. Wilson, J. Catal. 2007, 245, 272.

Received: May 29, 2014 Published online on July 23, 2014