Environmentally benign aqueous oxidative catalysis using AuPd/TiO_2 colloidal nanoparticle system stabilized in absence of organic ligands†

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The use of nanoparticles (NPs) for efficient, environmentally benign catalysis is receiving increasing attention, with gold and palladium NPs being an important area of research. Herein we present a simple, reliable and cost-effective preparation of a catalytically active gold-palladium NP system that is stabilized by an aqueous titania dispersion (AuPd/TiO_2) in the absence of organic ligands. The major advantages of this system are that it is catalytically active in the as-prepared colloidal state, eliminating the need for drying and sintering before use and is colloidally stable in oxidative conditions. The AuPd/TiO_2 system exhibits efficient oxidative catalysis in both the presence of hydrogen peroxide and atmospheric oxygen, even at ambient temperatures for our model aqueous phase reaction of 1-phenylethanol oxidation. The preparation and characterization of the AuPd/TiO_2 system is described with respect to the effects of colloidal stability, particle size and morphology on aqueous oxidative catalysis. The major finding is that NPs with a gold core and thin palladium shell (70 mol% gold, 30 mol% palladium, $Au_{70}Pd_{30}/TiO_2$) provides the most catalytically active system. The ability of the catalyst to use atmospheric oxygen at ambient temperatures in aqueous media highlights the strong potential of the developed catalytic system for green oxidative processes. The presented approach provides a new platform of all-inorganic colloidal nanoparticle systems for future development of industrially viable, environmentally friendly catalysts.

Introduction

Oxidative catalysis is an area of research that is actively explored in a quest for environmentally friendly and energy-efficient processes.[1,2] Most oxidation reactions are highly exothermic, yet they have high activation energies and therefore often require elevated temperatures for efficient conversion. Furthermore, the majority of stoichiometric oxidizing agents are toxic due to heavy metals and are problematic environmentally. Considering these challenges, low-temperature catalytic oxidation processes are especially attractive.

Gold is a unique metal,[3] though due to perceived inertness its great potential in catalysis was not appreciated until the 1980s,[4,5] when it was found that gold is an excellent catalyst for both oxidation of carbon monoxide[6] and vapour phase chlorination of acetylene with HCl.[7] One prominent aspect of catalysis with gold is that the smallest nanoparticles (clusters) are most active.[8,9] Gold nanoparticles (AuNPs) used in catalysis are mostly supported on inorganic oxides, which are important for both stabilizing the small clusters and assisting in the oxidative processes.[10–14] Titania has gained recognition as one of the primary support materials since the pioneering studies on gold clusters.[6] Titania is also actively employed in photocatalysis, and gold-doped titania systems are widely investigated in this regard.[15]

While catalysts based on AuNPs have already been successfully implemented in commercial technologies, research of mixed metal systems based on gold has recently shown considerable promise.[16] Palladium was found especially effective to enhance catalysis with AuNPs.[17] In a prominent series of reports, Hutchings and coworkers have demonstrated remarkable utility of a gold-palladium system[18–20] (with 10 to 50% Pd) which, among other applications, can be used for direct synthesis of H_2O_2 from H_2 and O_2.[21,22] One limitation of current metal nanoparticle-based catalysts is the need for drying, sintering and subsequent redispersion of a catalyst. A colloidally-stable active catalyst with a simple and efficient preparation is advantageous for designing a catalytic platform for benign oxidation at near ambient conditions.

A conventional way to prepare supported gold catalysts is the reduction of metal salts on crystalline surfaces or different forms of nanocrystalline materials.[23] High-temperature processing is often employed to completely reduce the metals and/or remove organic ligands and stabilizers.[24] As a consequence, the resulting catalysts are heterogeneous. However, homogeneity as well as uniform active surface area are important factors in catalysis.[25] Thus, development of highly dispersed catalysts with the largest active surface area and stability is an ongoing area of research.

Another aspect of supported gold catalysts is that crystallinity of the nanoparticle support may not be essential, given that amorphous materials were recently shown to function effectively

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† Electronic supplementary information (ESI) available: Specific catalytic activity details and additional SEM, TEM and EDX information are available; Tables S1, S2 and Figures S1 to S8. See DOI: 10.1039/c0gc00084a

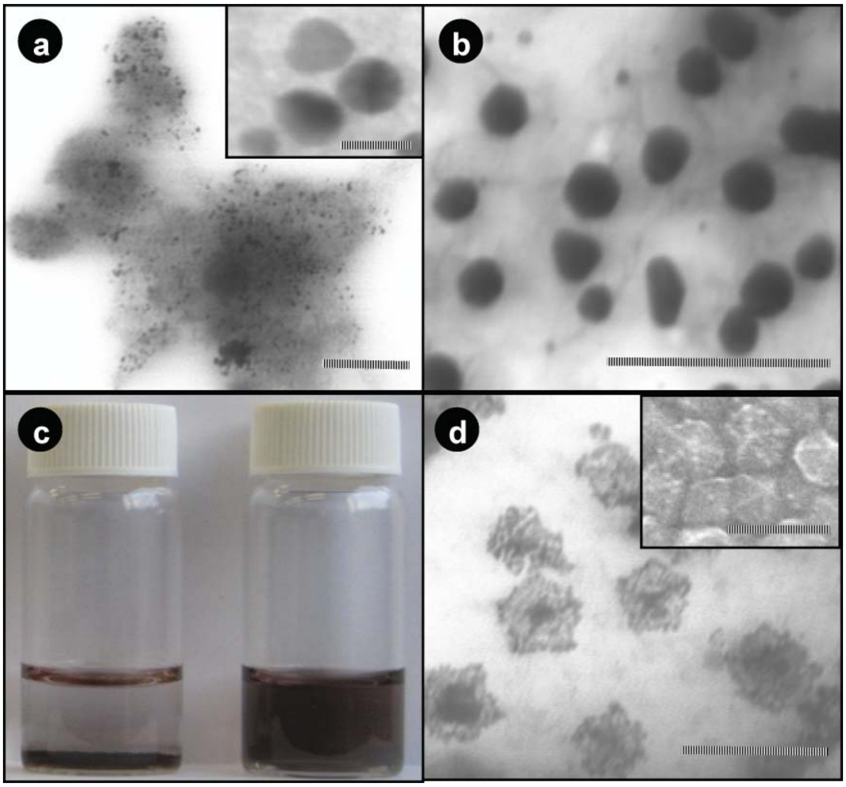

Fig. 1 (a) Transmission electron microscopy (TEM) image of $Au_{70}Pd_{30}/TiO_2$. Scale bar is 100 nm. Inset: TEM image of $Au_{70}Pd_{30}/TiO_2$. Scale bar is 10 nm. (b) Au/TiO_2 produced by $NaBH_4$ addition subsequent to $HAuCl_4$, which resulted in larger AuNPs in contrast with the addition of $NaBH_4$ before $HAuCl_4$ that produced smaller, more catalytically active AuNPs. The average AuNP size is 22.5 ± 2.7 nm. Scale bar is 100 nm. (c) Photograph of the $Au_{70}Pd_{30}/TiO_2$ dispersion before (left) and after (right) H_2O_2 addition. Note that the flocculating heterogeneous dispersion becomes more homogenous after H_2O_2 is added. Unlike the sample without H_2O_2, the sample with H_2O_2 will not settle over time. (d) TEM of gold-palladium decahedral cages. Inset: scanning electron microscopy (SEM) image of silver decahedra coated with gold-palladium before H_2O_2 etching of silver. Scale bar is 100 nm for both images.

for small gold clusters.[26] The reactivity of the support in the vicinity of an active metal center is crucial,[27] and modification of the support can have beneficial effects, as was convincingly demonstrated in reports on acid treatment of titania.[15] Not using thermal treatment of catalysts opens a range of opportunities in using colloidal dispersions with tailored chemical environments as the support for catalytically-active metal nanoparticles.

Herein we report preparation of gold and gold-palladium nanoparticles supported on aqueous dispersions of titania ($AuPd/TiO_2$) by ambient hydrolysis of titania precursors and controlled metal reduction. These nanoparticles display remarkable colloidal stability in the absence of organic ligands, and do not require high-temperature annealing for highly effective catalysis in alcohol oxidation in aqueous systems at near-ambient temperatures. We optimized the system using H_2O_2 as the oxidant, and then extended it to the green readily available oxidant, atmospheric O_2. This catalytic system has several attractive features, including: 1) the use of water instead of organic solvents, 2) the potential to use atmospheric oxygen as the oxidant at near ambient temperatures, and 3) reduced energy consumption by eliminating the need for high temperature annealing of the catalyst and use of near ambient temperatures for oxidation.

Results and discussion

The inorganically-stabilized $AuPd/TiO_2$ system was prepared in accordance with the following key points: the titania precursor was prehydrolyzed in deionized water and formed colloidally stable slightly opalescent dispersions. Titanium diisopropoxide bis(acetylacetonate) has been selected since it has two different functional groups. The isopropoxide hydrolyzes faster, providing reactivity and dispersability in water. The acetyl acetonate reacts more slowly thus stabilizing and preventing aggregation of the dispersions.[28] Sodium borohydride was added to the titania dispersion, immediately followed by gold and palladium salts. This order of reagent addition produced the best results in terms of catalytic activity. Adding a reducing agent prior to the metal salts provided an excess of the reducing agent at all the stages of reduction and afforded the smallest metal NPs (Fig. 1a *vs.* Fig. 1b). Using a less reactive reducing agent, such as the commonly employed hydrazine, yields appreciably larger particles (Fig. S1†). Adding palladium last and thus forming palladium clusters on top of gold was found to be most efficient for high catalytic activity, compared to premixing gold and palladium solutions before reduction or reducing palladium first (Table S1†). Notably, the catalyst was found to be very tolerant to high level of chloride ions.

The AuPd/TiO_2 system was characterized using transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) analysis (Fig. 2), X-ray diffraction (XRD) (Fig. S2†) and UV-vis spectroscopy (Fig. 3, Fig. S3†). The TEM images show a well-dispersed framework of titania supporting AuPdNPs (Fig. 1a), with an average diameter of 6.6 ± 1.2 nm. Metal NPs displayed minimal irreversible aggregation upon preparation and during many tens of hours of oxidative catalysis at as high as 90 °C (we have measured for one of the catalyst batches 7.5 ± 1.5 nm and 7.7 ± 1.4 nm before and after catalysis, respectively, see Fig. S4†).

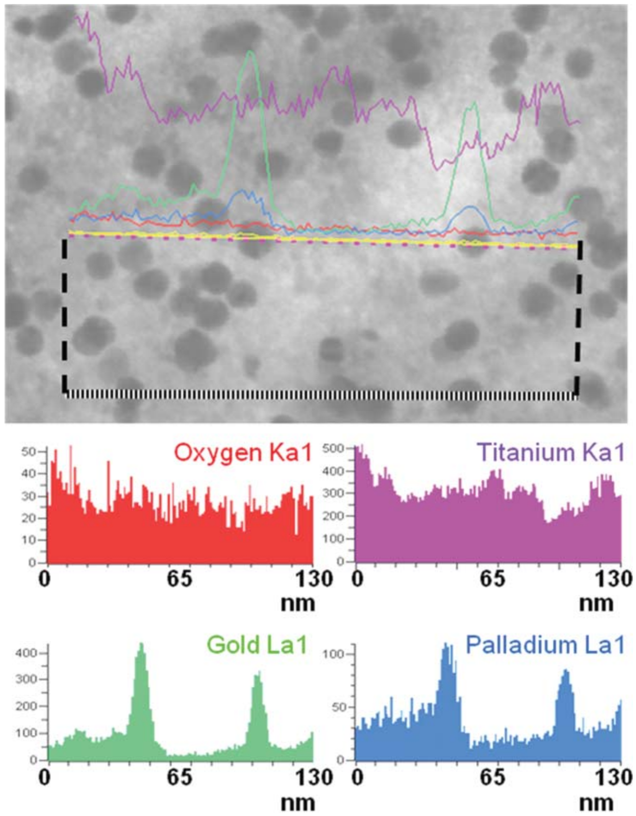

Fig. 2 Energy-dispersive X-ray (EDX) spectra of $Au_{70}Pd_{30}/TiO_2$, treated with H_2O_2. There was very little carbon detected (yellow line), indicating that H_2O_2 removed the organic residue from the surface of the titania, which allows for a homogenous dispersion in water. Scale bar is 130 nm.

XRD clearly revealed the presence of crystalline gold and no evidence of crystalline palladium. Furthermore, no noticeable changes in gold peak positions indicated that there was no alloying occurring (Fig. S2b†). For XRD samples obtained using low-pressure evaporation at ambient conditions, titania was found to be nearly amorphous, as expected for the precursor hydrolysis without subsequent annealing. At the same time, the evidence of anatase in the form of broad peaks was present for all samples. In addition, the presence of nanocrystalline anatase could be observed for several samples studied after catalysis at 90 °C (Fig. S2b†), as well as for the samples dried by water evaporation through boiling (Fig. S2a†). This observation is consistent with the literature findings on anatase preparation *via* titanium diisopropoxide bis(acetylacetonate) hydrolysis in water in acidic conditions without hydrothermal treatment.[27] EDX line scans (Fig. 2) clearly showed presence of both gold and palladium in NPs, while titanium and oxygen were homogeneously distributed (see Fig. S5† for EDX maps). No carbon was evident in the AuPd/TiO_2 samples exposed to peroxide, indicating complete hydrolysis and clearly supporting all-inorganic stabilization. This evidence corroborates the role of hydrogen peroxide in removing residual organic ligands and improving stabilization of AuPd/TiO_2 systems with lower titania-to-gold ratios.

Of principal importance to efficient aqueous catalysis was the remarkable colloidal stability and resistance to coagulation of both Au/TiO_2 and AuPd/TiO_2 in absence of any additional stabilizing ligands in a relatively wide range of titania-to-metal ratios from *ca.* 5 to >20. Addition of hydrogen peroxide (in excess relative to titania) makes these samples more homogenous and non-flocculating (Fig. 1c). The effect of the peroxide is observed by decreased light scattering which can be qualitatively documented by UV-vis spectroscopy, where the lower levels of scattering are clearly evident (Fig. 3a). At the same time, we found that a partially flocculating AuPd/TiO_2 system is advantageous for reversible catalyst separation and actively employed it for oxidative catalysis with hydrogen peroxide. Colloidal and, as a consequence, catalytic stability of the system was provided by steric stabilization of metal NPs by titania and charge-stabilization of titania in the presence of borates.

To test the catalytic properties of Au/TiO_2 and AuPd/TiO_2, the oxidation of 1-phenylethanol to acetophenone was chosen as a proof-of-concept process, given its common use for catalyst testing.[29] Hydrogen peroxide was used as the main aqueous oxidizer[14] to find the optimal parameters for the AuPd/TiO_2 system. Subsequently, use of atmospheric oxygen from air was explored due to the attractiveness for an environmentally-friendly cost-effective aqueous oxidation, taking into consideration the relatively high cost and limited production capacity of hydrogen peroxide. In a typical experiment, 1-phenylethanol was added to the as prepared colloidal nanoparticle dispersion, followed by hydrogen peroxide or alternatively left to stir under atmospheric oxygen in the case of O_2 oxidation experiments. After a predetermined amount of time, the catalytic activity was evaluated by extraction of the reaction mixture with diethyl ether and analysis by gas chromatography.

Palladium has been found to have a very strong effect on the catalytic activity. Presence of 20 to 40 mol% Pd in the system enhances catalytic activity relative to pure gold *ca.* 7 times, while pure Pd/TiO_2 is appreciably less active compared to pure Au/TiO_2 (Fig. 4a, Table S2†). The best catalysts were obtained when palladium was reduced after gold, producing a thin palladium shell that is not detectable by XRD but clearly evident in EDX. These findings are consistent with the literature reports on effectiveness of gold-palladium supported nanoparticles.[16,18] It is noteworthy that the highest activity in oxidative catalysis, starting with 30 mol% palladium, also coincides with the extinction of the plasmon resonance by the gold (Fig. 3b) previously reported in literature.[30] NPs with higher than 30% palladium content did not show characteristic peaks at ~530 nm in UV-vis spectra. This observation can be attributed to optimal palladium coverage on the gold surface to suppress plasmonic resonances and to reach the optimal

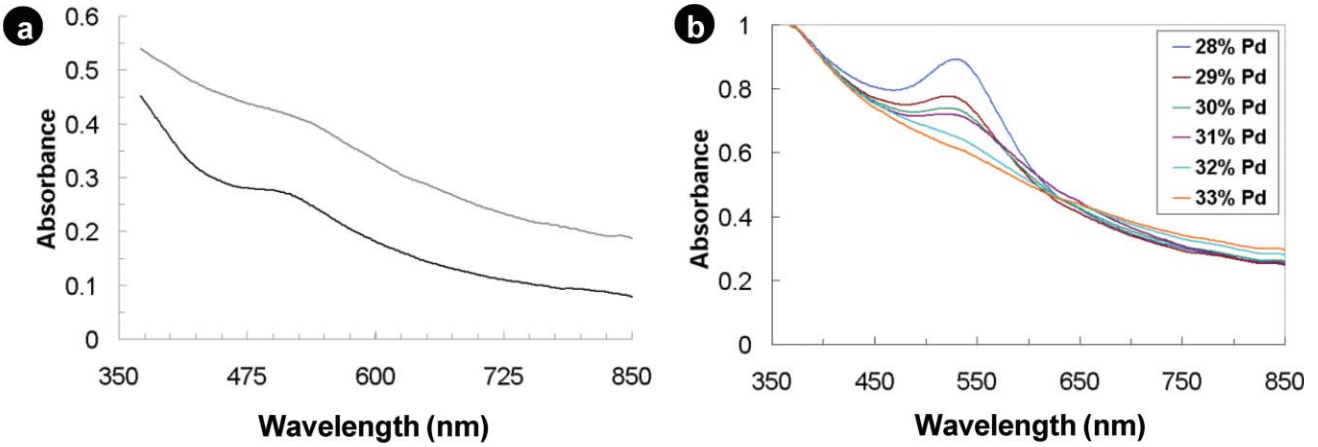

Fig. 3 (a) UV-vis spectra of $Au_{70}Pd_{30}/TiO_2$ before (grey line) and after (black line) addition of H_2O_2. (b) Normalized UV-vis spectra of 28% to 33% Pd content in $AuPd/TiO_2$. The complete loss of the gold plasmon can be observed for AuPdNPs with Pd content over 31%.

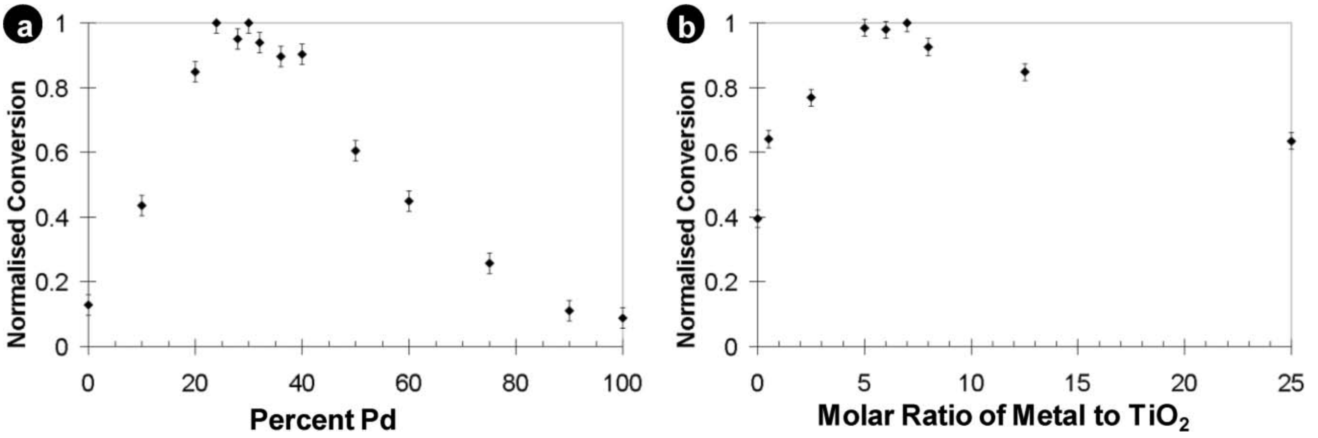

Fig. 4 (a) Plot illustrating the catalytic ability of Au_xPd_y/TiO_2 with different amounts of Pd. All reactions were carried out at 50 °C for 30 min, employing H_2O_2 as the oxidant. A normalised conversion of 1 is equivalent to 29.8% conversion to acetophenone. (b) Plot illustrating the catalytic ability of different ratios between TiO_2 and $Au_{70}Pd_{30}$. All reactions were carried out at 50 °C for 30 min using H_2O_2 as the oxidant. A normalised conversion of 1 is equivalent to 25.3% conversion to acetophenone.

palladium distribution for enhancing catalytic activity of the system. Incidentally, the most reactive small gold clusters also do not display plasmonic resonances.[3] Lastly, replacement of palladium with platinum in otherwise similar conditions did not afford active catalysts (Table S1†).

Colloidal stability is crucial for catalytic performance, which is evident in the effect of titania-to-metal ratio (Fig. 4b). In this graph, catalytic activity was normalized per amount of metal, so the effect of the support should not be a factor, given the stoichiometric excess of titania in the system. As a demonstration of the importance of colloidal stability and the role of titania, AuPdNPs reduced by borohydride in a control run in absence of titania precipitated irreversibly when exposed to peroxide at elevated temperatures, halting the catalytic activity. Furthermore, the catalytic ability of as prepared $AuPd/TiO_2$ has been found to be far superior to that of sintered or even gently dried samples, which were subsequently redispersed, by *ca.* five-fold difference in the conversion rate of 1-phenylethanol (Table S1†), a significant drop in catalytic activity.

Small AuPdNP size and the open surface of homogeneously dispersed titania support were also important for catalytic performance. In several experiments, we have prepared AuPd shells on silver decahedral nanoparticles[31] using galvanic replacement.[32] Two different types of shells were made: galvanic replacement first, then addition of titania dispersions; and adding titania dispersions to decahedra first and then performing replacement. The latter system produced significantly rougher shells with significant amount of AuPd grains less than 5 nm in diameter (Fig. 1d), which were expected to be more effective in catalysis. While gold nanocages have been shown to be catalytically active,[33] quite surprisingly both types of shells displayed very low catalytic activity despite the fact that all quantities of palladium, gold and titania were identical to the active $AuPd/TiO_2$ system, and silver was removed by peroxide. A possible reason for such low catalytic activity is that the continuity of the shell led to the effective absence of smaller metal clusters necessary for oxidative catalysis.[8] We are currently studying this system, further exploring reduction conditions.

An optimized $AuPd/TiO_2$ system (7 : 1 titania ratio, 30 mol% Pd referred as $Au_{70}Pd_{30}/TiO_2$) was tested at different conditions using 1×10^{-6} moles of metal catalyst and 1×10^{-3} moles of 1-phenylethanol. A 6 : 1 molar ratio of hydrogen peroxide to 1-phenylethanol was used since at this ratio a plateau is approached in the dependence of conversion on peroxide concentration (Fig. S6†). For this system, the results for the conversion of 1-phenylethanol to acetophenone are presented in Fig. 5 for three different temperatures. The observed linearity is indicative of a first-order reaction relative to 1-phenylethanol. There is an appreciable conversion rate observed at 25 °C (in contrast, there is negligible conversion in absence of catalysts). At 75 °C the reaction is the most efficient, however there is a plateau in conversion reached after an hour, which can be attributed to peroxide decomposition in presence of catalyst at these high temperatures. We have run the reaction at as high as 90 °C (Table S1†) reaching complete conversion. There, the reaction should be run efficiently by using constant peroxide addition, which has yet to be explored. The first-order rate combined with other evidence likely suggests the formation of a peroxide complex with AuPdNPs as a first stage and its subsequent rate-determining reaction with 1-phenylethanol. It is proposed that the reaction mechanism involves formation of a Ti–O–O–H intermediate.[27] We were not able to reliably detect peaks at 330 nm in UV-vis spectra (Fig. S3†) attributed to Ti–O–O–H[27] to conclusively confirm the presence of this species in our $Au_{70}Pd_{30}/TiO_2$ system. Overall, these observations are consistent with hydrogen abstraction by a peroxide complex of the catalyst with stabilization of the transition state by an aromatic system. For instance, oxidation of benzyl alcohol, 2-butanol, 1-octanol, and 2-octanol with hydrogen peroxide was found to be appreciably slower than our model substrate 1-phenylethanol (Table 1), and conversion rates were not sufficient to be reliably tested using atmospheric oxygen.

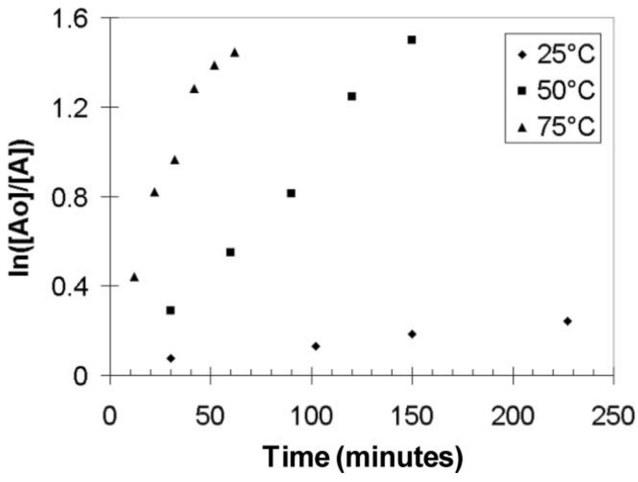

Fig. 5 Kinetic plots for the conversion of 1-phenylethanol to acetophenone using $Au_{70}Pd_{30}/TiO_2$ and H_2O_2 at different temperatures. Loss of first-order linearity for the 75 °C sample is attributed to the decomposition of H_2O_2 at higher temperatures.

It has been reported that the addition of base increases the rate of alcohol oxidation with an AuPd catalyst.[34] For our $AuPd/TiO_2$ system, addition of one equivalent of base (potassium hydroxide) provided a threefold increase in the rate of 1-phenylethanol oxidation. At the same time, $AuPd/TiO_2$ underwent aggregation in the process and the catalyst could not be recycled successfully. To further address the issue of colloidal stability of $AuPd/TiO_2$ with pH, we realized that borates (product of the borohydride reaction) play a significant role in stabilizing the dispersions. Borates are present in a ratio of 4 : 1 with metal and play an advantageous role in providing counterions for colloidal stabilization at this level. We have explored the influence of borate concentration on catalytic activity (Fig. S7†) and found that the amount used in our preparation is indeed in the optimal range. More borohydride/borates are deleterious for stability increasing ionic strength; using less borohydride affords larger, less catalytically active metal NPs upon reduction.

The $Au_{70}Pd_{30}/TiO_2$ system remained quite stable in catalysis conditions and could be reused multiple times for both H_2O_2 and O_2 oxidation, as shown in Fig. 6a and Fig. 6b respectively. The slow decay of catalytic performance is likely due to the process of diethyl ether extraction used for analysis. In the case of Fig. 6a, dilution from addition of H_2O_2 to the aqueous phase, which is decomposed to water and oxygen upon cleaning of the catalyst for subsequent catalytic cycles, also plays a role in the constant decrease in catalytic activity. This decrease in activity may not be a factor in large-scale preparations since products can be separated by low-pressure distillation or other methods. The claim that the NPs are not degrading is supported by Fig. S4† where TEM images before and after catalysis indicate that the $Au_{70}Pd_{30}$NPs remain the same size. In addition, there is no evidence of increase in intensity of the gold plasmon after the catalyst has been used multiple times, indicating that loss of the surface palladium on the AuPdNPs and potential alloying is not taking place. With hydrogen peroxide, the second cycle features a noticeably higher rate of conversion compared to the first cycle. This observation can be rationalized that upon H_2O_2 addition the heterogeneous colloidal dispersion becomes homogenous due to complete cleavage and oxidation of residual organic ligands (Fig. 1c), which aids efficient catalysis. For the most efficient second cycle, the turnover number can be estimated as 468 molecules of 1-phenylethanol per atom of metal per hour. Fig. S8† illustrates the catalytic efficiency *versus* the amount of $Au_{70}Pd_{30}$ in the system. When using O_2 as the oxidant, some fluctuation in conversion is evident, and is attributed to lower conversion rates as well as inconsistent atmospheric O_2 concentration in the sealed reaction vessels.

Oxidation of secondary alcohols usually proceeds without by-products. Nevertheless, it is worthy to note that at higher concentrations of palladium (>40 mol%) with higher temperatures, the reduction of 1-phenylethanol to ethylbenzene was observed (Table S2†) and confirmed using ^{1}H NMR spectroscopy. For $Au_{70}Pd_{30}/TiO_2$ this side reaction was not a factor.

Oxidative catalysis was performed in an aqueous environment, where both 1-phenylethanol and acetophenone were sparingly soluble. Since acetophenone is the least soluble in water, we tested whether it presents a potential problem for its release from the catalytic surface of a nebulous titania network. We added different amounts of *t*-butanol to the system to increase solubility of organic molecules and did not find any conversion improvements (Table S1†). These experiments indicated that the product solubility is not an issue in the studied system.

After studying the catalytic performance of the $Au_{70}Pd_{30}/TiO_2$ system with peroxide oxidation of alcohols, we have further explored an effect of support modification. Addition of 5 mol%

Table 1 Data for oxidation of substrates other than 1-phenylethanol

Catalyst composition	Substrate	Oxidant	$T/°C$	Time/h	% Conversion	Comments
$Au_{70}Pd_{30}$	2-butanol	H_2O_2	50	22	0.7	
$Au_{70}Pd_{30}$	1-octanol	H_2O_2	50	22	0	
$Au_{70}Pd_{30}$	2-octanol	H_2O_2	50	112.5	15.2	
$Au_{70}Pd_{30}$	benzyl alcohol	H_2O_2	50	0.5	3.3	1.3% benzoic acid also observed

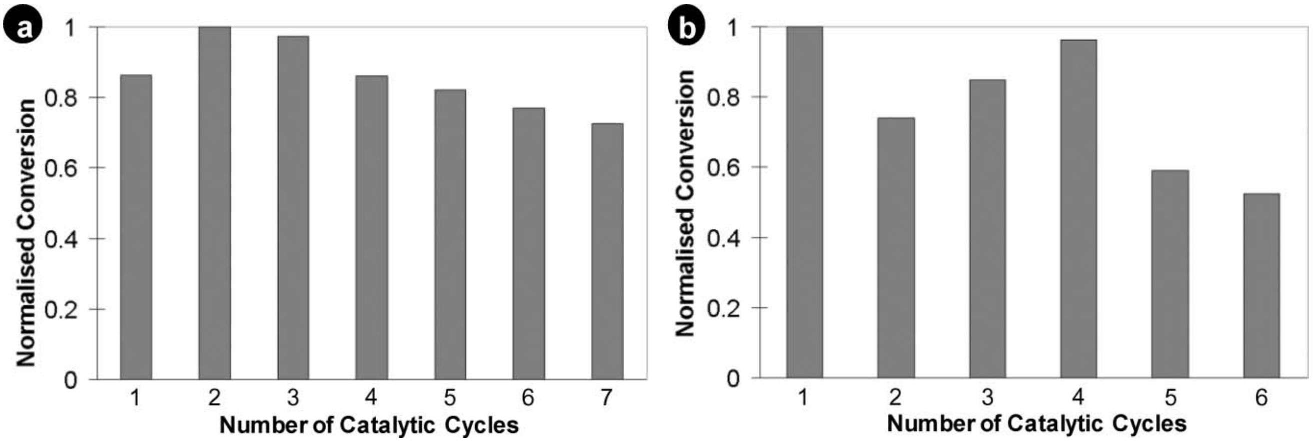

Fig. 6 (a) Recycling of $Au_{70}Pd_{30}/TiO_2$ catalyst using H_2O_2. The highest conversion occurs in the second cycle, after the system has been initially exposed to H_2O_2 in the first cycle. The turnover number for the second cycle is 468 molecules of 1-phenylethanol per atom of metal (Au and Pd) per hour. Extrapolation indicates that conversion will drop to zero after 19 cycles. (b) Recycling of $Au_{70}Pd_{30}/TiO_2$ catalyst using atmospheric O_2.

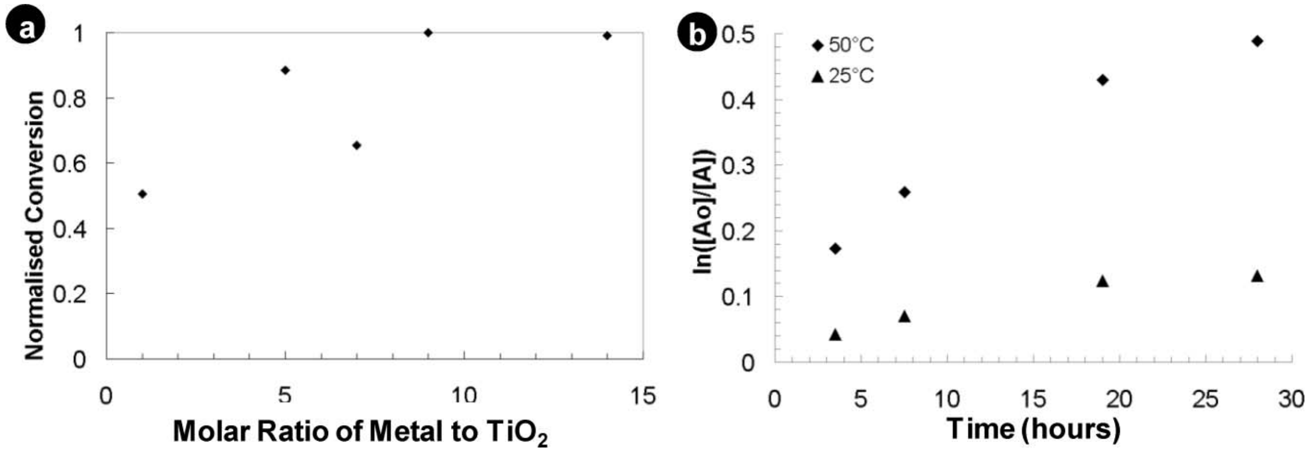

Fig. 7 (a) Plot illustrating the catalytic effectiveness of systems with different ratios between TiO_2 and $Au_{70}Pd_{30}$. All reactions were carried out at 50 °C for 20 h using air as the oxidant. A normalized conversion of 1 is equivalent to 63.1% conversion to acetophenone. (b) First-order kinetic plot for the conversion of 1-phenylethanol to acetophenone using $Au_{70}Pd_{30}/TiO_2$ with air as the oxidant.

of ceria was found only to decrease the catalytic activity slightly, as did doping with iron oxyhydroxide (Table S1†). Using colloidally stable β-FeOOH spindles as an oxide support for AuPdNPs also did not produce a catalytically active system (Table S1†).

Photocatalytic activity of the system was tested, given the applications of titania in this area. It was found that intense light exposure (400 W metal halide lamp, 5 cm distance, see ESI†) with $AuPd/TiO_2$ for the conversion of 1-phenylethanol to acetophenone in the presence of hydrogen peroxide was not effective in enhancing catalysis (Table S1†). It seems that light absorption by the metals compromises an active transition state, such as a complex with peroxide.

Finally, we explored direct use of air for catalytic oxidation of 1-phenyethanol in aqueous media using $Au_{70}Pd_{30}/TiO_2$ due to its importance as an environmentally friendly process. We used a larger titania content (titania-to-metal ratio of 9 : 1) to assure homogeneity and colloidal stability of the $Au_{70}Pd_{30}/TiO_2$ system in absence of peroxide (Fig. 7a). We were able to achieve conversions as high as 63% for 20 h of reaction at 50 °C with a 1 : 1000 metal-to-substrate ratio (Fig. 7b, Table 2). The value of the turnover number was 32 molecules of 1-phenylethanol per atom of metal per hour, which is reasonable for the proof-of-concept of catalytic oxidation in water with air at low temperatures. At first glance, our turnover number appears much lower than that of Hutchings *et al.*,[16] however our

Table 2 Data for oxidation of 1-phenylethanol to acetophenone using atmospheric oxygen

Catalyst composition	Substrate	Oxidant	$T/°C$	Time/h	% Conversion	Comments
$Au_{70}Pd_{30}$	1-phenylethanol	air	25	28	12.3	7 : 1 TiO_2 to $Au_{70}Pd_{30}$
$Au_{70}Pd_{30}$	1-phenylethanol	air	50	20	41.4	7 : 1 TiO_2 to $Au_{70}Pd_{30}$
$Au_{70}Pd_{30}$	1-phenylethanol	air	50	20	63.1	9 : 1 TiO_2 to $Au_{70}Pd_{30}$

system functions at a lower temperature (25–50 °C *vs.* 160 °C), lower catalyst loading (0.1% *vs.* 5%) and 5 times lower oxygen partial pressure (0.2 atm *vs.* 1 atm). With this considered, and the fact that our catalyst exhibits its highest catalytic activity in the colloidal state with no need for drying and sintering, the true value of our system in green oxidative catalysis can be realized.

Experimental

Materials

Titanium diisopropoxide bis(acetylacetonate) 75 wt% in isopropanol, sodium borohydride (99%), chloroauric acid (99.9+%), palladium(II) chloride (99.9+%), 1-phenylethanol (98%), hydrogen peroxide 30 wt% (99.999%) were supplied by Sigma-Aldrich and used as received. Sodium chloride (99.0%) was supplied by VWR and used as received. High purity deionized water (>18.3 MΩ cm) was produced by Millipore A10 Milli-Q.

Catalyst preparation

Aqueous dispersions of titania were synthesized by adding titanium diisopropoxide bis(acetylacetonate) 75 wt% in isopropanol to high purity deionized water and sonicating the reaction mixture (VWR Ultrasonic Cleaner, Model 75T) until a uniform stable dispersion was produced. This was typically performed in large batches producing the desired concentration of titania to be used as a support for the AuPdNPs. A typical titania batch was made by adding 135 µL of titanium diisopropoxide bis(acetylacetonate) to 252 mL of high purity deionized water, and sonicating for approximately 10 min. This titania dispersion was used for several months.

AuPd/TiO_2 was typically synthesized in 20-mL borosilicate scintillation vials (VWR) by adding 6 mL of titania dispersion (as prepared above) to which 40 µL of 100 mM freshly prepared sodium borohydride aqueous solution were introduced under rapid stirring. Next, 140 µL of 5 mM $HAuCl_4$ aqueous solution were added, immediately followed by 60 µL of 5 mM Na_2PdCl_4 aqueous solution. The Na_2PdCl_4 solution was produced by adding palladium(II) chloride and sodium chloride to high purity deionized water in a 1 : 3 mole ratio.

Silver decahedra were prepared following an established procedure.[31] With a concentration of 2.56×10^{-4} M silver, decahedra with a size of 58.5 ± 2.9 nm were obtained. The gold-palladium shell was then added to the surface of the silver decahedra *via* galvanic replacement by addition of 140 µL $HAuCl_4$ (5 mM) and lastly 60 µL Na_2PdCl_4 (5 mM) to 11.7 mL solution of silver decahedra. The silver can be etched away to yield a hollow gold-palladium shell by addition of 3 mL 30 wt% hydrogen peroxide.

Analysis of catalytic activity

To test the catalytic ability of AuPd–TiO_2, 1 mmol of 1-phenylethanol (121 µL) was added to the aqueous catalyst dispersion followed by 6 mmol of hydrogen peroxide (574 µL of 30 wt%). The system then was heated at a specific temperature for a given amount of time; most comparisons were done at 50 °C for 30 min. Once the reaction time elapsed, the remaining 1-phenylethanol and resulting acetophenone were extracted from the aqueous solution by adding 4 mL of diethyl ether to the vial, with shaking and sonication. Once the organic and aqueous layers had fully separated, the organic layer was removed and analyzed.

The primary sample analysis was performed by gas chromatography using a Perkin Elmer Clarus 500 Gas Chromatograph with helium as the carrier gas at 16 psi. The column employed was 30 m, 0.25 mm internal diameter, with a 0.25 µm film thickness of 5% diphenyl, 95% dimethyl polysiloxane. Detection was done using a flame ionization detector. The injector temperature was 200 °C, and 1 µL samples were injected using a 10 µL syringe.

Characterization

Electron microscopy (TEM and SEM) was performed using a Hitachi S-5200 with a typical operating voltage of 30.0 kV. The NPs were deposited on a carbon-coated Formvar grid (EMS Corp.). The average sizes and standard deviations of the NPs were determined from TEM images by averaging the diameters of at least 100 NPs. Energy dispersive X-ray (EDX) mapping was done using an EDX system for elemental analysis (Inca, Oxford Instruments). UV-vis spectra were acquired using either an Ocean Optics QE65000 fibre-optic UV-vis spectrometer or a Cary 50 Bio UV-vis spectrometer. VWR 1410 vacuum oven and Vacuubrand PC2001 Vario chemical resistant vacuum pump were used to dry samples at low pressure. A Lindberg Tube Furnace TF55035A-1 was used for sintering. To obtain X-ray diffraction patterns (XRD), samples were run on an automated Siemens/Bruker D5000 diffractometer. The system was equipped with a high power line focus Cu-K_α source operating at 50 kV and 35 mA. A solid-state Si/Li Kevex detector was used for removal of K_β lines. The diffraction patterns were collected using Bragg-Brentano reflection geometry with fixed slits. A step scan mode was used for data acquisition with step size of 0.02° 2-θ and counting time of 2.5 s per step. The preliminary qualitative phase analysis was performed by Search/Match™ routine incorporated in Bruker AXS data processing software Eva™ v. 8.0. The Rietveld refinement was carried out with Bruker AXS general profile fitting software Topas™ v. 2.1.

Conclusion

Overall, we have demonstrated that AuPdNPs can be effectively supported by aqueous titania dispersions in absence of any organic stabilizing ligands with excellent colloidal stability. Without the need for sintering, $Au_{70}Pd_{30}/TiO_2$ is catalytically active in aqueous oxidation of 1-phenylethanol by hydrogen peroxide with good conversions at 75 °C and appreciable activity at 25 °C. Importantly, the use of air as an oxidant with this system was demonstrated at as low as 50 °C, which opens new possibilities for environmentally benign oxidative catalysis. The low toxicity of titania and gold, combined with the all aqueous ambient synthesis makes the reported system a promising catalyst for green chemistry applications.

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