Inorganic Chemistry

ARTICLE

pubs.acs.org/IC

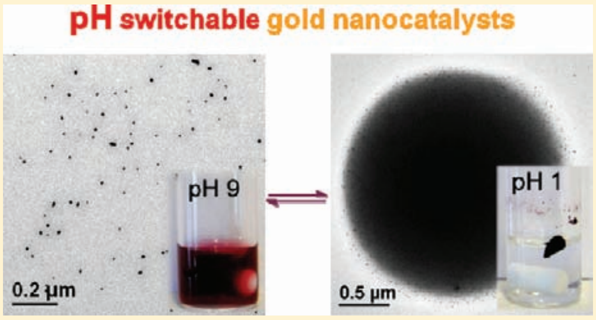
pH-Sensitive Gold Nanoparticle Catalysts for the Aerobic Oxidation of Alcohols

Yuan Yuan, Ning Yan, and Paul J. Dyson*

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Supporting Information

ABSTRACT: Gold nanoparticles (NPs) stabilized by carboxylate modified polyvinylpyrrolidone have been prepared and fully characterized. The gold NPs efficiently catalyze the aerobic oxidation of benzyl alcohol in water at ambient temperature and are easily separated from the reaction mixture by lowering the pH of the solution, causing the NPs to precipitate. The mechanism of the precipitation process has been studied. Due to the efficiency of this process, the NPs may be reused as catalysts by readjusting their pH.



INTRODUCTION

Gold is chemically inert and catalytically inactive in the bulky state but becomes highly catalytic for many reactions when formulated into nanoparticles (NPs) with diameters < 10 nm.[1] Since Haruta et al.'s discovery of CO oxidation, catalyzed by supported Au NPs,[2] the catalytic properties of Au NPs have been extensively explored.[3] In the domain of colloid chemistry (in which NPs are homogenously dispersed in solvents), catalytically active Au NPs have been successfully prepared in the presence of various stabilizers, including poly(N-vinyl-2-pyrrolidone) (PVP),[4] dendrimers,[5] amphiphilic copolymers,[6] and polyelectrolytes.[7] These "soluble" NP systems allow reactions to be carried out in a pseudohomogenous manner, generally leading to higher activities and selectivities, and the application of milder reaction conditions compared to heterogeneous systems.[8] One of the limiting factors that hinders the practical use of soluble Au NP catalysts, however, is the difficulty in recycling and reusing them.[9] While, PVP-stabilized Au NPs are highly active catalysts for aerobic alcohol oxidation, for example, recycling these NPs is problematic.[4] Indeed, only a few examples describing the recovery of Au NP catalysts from water have been reported,[10] and consequently the development of new Au NP systems that can be used in a facile fashion is desirable.

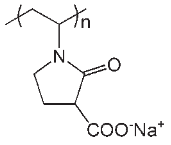
The main approaches used to recycle "soluble" NP catalysts are based on the use of biphasic reaction conditions,[11] the application of membrane separation methods and ultra filtration,[12] and magnetic separation.[13] In addition to these more traditional approaches, a protocol based on "smart" NPs has been proposed,[14] in which the NPs are coated with a stimuli-sensitive polymer that undergoes physical changes as environmental parameters, such as pH[15] or temperature, are modified.[16] Au NPs that are pH-sensitive have recently attracted attention;[17] however, their catalytic activity and recyclability have been scarcely explored. Indeed, the catalytic activity of Au NPs is highly sensitive to their size and the surface modifiers used.[4e] Moreover, while the mechanism of the pH-switch comprises a simple protonation/deprotontion process, as far as we are aware, a detailed picture of the aggregation process has yet to be reported.

Herein, we describe Au NPs stabilized by sodium poly(1-vinylpirrolidin-2-one-3-carboxylate) (polymer **1** in Figure 1). These NPs form pseudohomogenous aqueous solutions at pH > 2.5 and spontaneously precipitate at pH < 2.4. Moreover, the Au NPs are active, stable catalysts for the aerobic oxidation of alcohols and operate under ambient conditions. By switching the pH, the NPs could be easily separated from the reaction mixture, enabling facile recycling with only a minor loss of the catalyst (0.0002% per cycle) and aggregation (from 6.7 to 7.9 nm) of the NPs.

RESULTS AND DISCUSSION

Au NPs coated with stabilizer **1** (Figure 1), denoted as **1**-Au NPs, were prepared from an aqueous solution of $HAuCl_4$ and the stabilizer by $NaBH_4$ reduction (see Experimental Section for details). TEM of the **1**-Au NPs shows that they are spherical with a diameter of 6.7 ± 1.8 nm (Figure 2). The high-resolution TEM image (Figure 2c) reveals that the Au NPs have well-defined crystalline planes; the marked interplanar d spacings are 0.235 and 0.203 nm, which correspond to the d_{111} (0.2355 nm) and the d_{200} (0.2039 nm) planes for face-centered cubic (fcc) gold. The powder XRD pattern of the **1**-Au NPs, shown in Figure 3, contains information regarding both the stabilizer and the Au NP. The three broad diffraction peaks positioned at a Bragg angle (2θ) between 10 and 30° correspond to the stabilizer and

Received: July 27, 2011
Published: October 10, 2011



1

Figure 1. Sodium poly(1-vinylpirrolidin-2-one-3-carboxylate), **1**.

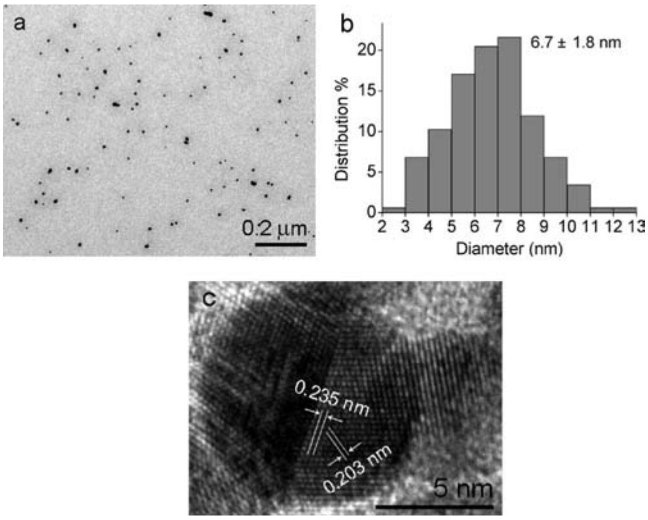


Figure 2. (a) Representative TEM image, (b) size distribution, and (c) HRTEM image of the **1**-Au NPs at pH 9.2.

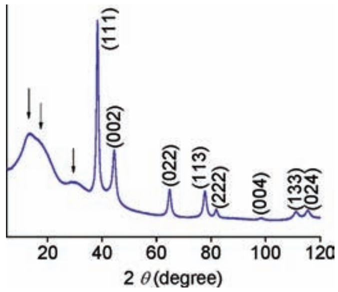


Figure 3. X-ray diffraction pattern of a **1**-Au NP. The arrows indicate the diffraction pattern due to the polymer.

indicate that **1** is highly disordered. All of the other peaks appear at higher angles that are sharper and can be attributed to the diffraction from the different gold lattice planes. Following a Rietveld refinement,[18] the Au (111) peak gives a full-width at half-maximum (fwhm) of 1.10° at a 2θ value of 38.32°, and from this, the average crystallite size of the Au NPs was calculated to be 8.3 nm using the Scherrer equation.[19] Although this value is slightly larger than the average size estimated from the TEM images, the two values match satisfactorily—TEM provides a number-average distribution which is more sensitive to small NPs.[20] Finally, the UV/vis spectrum of the **1**-Au NP solution exhibited a strong absorption at 520 nm which was attributed to the surface plasmon resonance characteristic of Au NPs (Figure 4), further confirming the formation of Au NPs.[21]

The **1**-Au NPs are pH-sensitive, precipitating spontaneously from solution at pH < 2.4, with the solution remaining transparent and homogeneous at pH > 2.5. The surface plasmon bands of the **1**-Au NPs did not change when the pH changed from 9.6 to 2.5, as shown in Figure 4, indicating that the NPs remain dispersed in the solution phase. The onset of precipitation commences at ca. pH 2.4 and is complete (based on UV/vis spectroscopy—see Figure 4) at pH 2.0, resulting in a colorless solution and a dark purple solid. The precipitate may be redissolved (quantitatively—see below) by raising the pH of the solution. Following redissolution, the plasmon band maximum is observed at 520 nm, the value observed prior to precipitation, suggesting that the size and shape of the Au NPs remain unaltered during pH switching. TEM analysis of the Au NPs after redissolution revealed a slight increase in NP size, essentially within the error of TEM analysis (see Figure S1 in the Supporting Information).

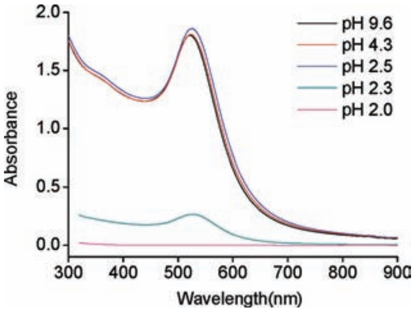


Figure 4. UV—vis spectra of the **1**-Au NP solution as a function of pH.

The response of the **1**-Au NPs to pH was characterized by TEM at pH values of 2.4, 2.0, and 1.5 (Figure 5). Since rapid precipitation of the NPs occurs, especially at pH values ≤ 2.0, the samples for TEM analysis were prepared immediately after the desired pH was reached. Compared to the **1**-Au NPs obtained from solution at high pH, which are homogenously dispersed on the copper grid (Figure 2a), the **1**-Au NPs self-assemble into spheres with diameters of several hundred nanometers at pH 2.4 (Figure 5a, d), although significant numbers of free Au NPs are present. At pH 2.0, **1**-Au NPs further aggregate, with only a few Au NPs observed outside the sphere (Figure 5b,e). At pH 1.5, the sphere structure is much denser, and free Au NPs outside the spheres are not observed (Figure 5c,f). These TEM images provide insight into the dynamic changes of the **1**-Au NPs during the precipitation process, and importantly, the Au NPs appear to remain separated from each other within the spherical aggregates at low pH, indicating that the individual NPs are stable at the low pH values.

According to Derjaguin—Landau—Verwey—Overbeek (DLVO) theory,[22] NPs are stabilized by a combination of van der Waals interactions and double-layer forces. In the system described herein, van der Waals interactions presumably originate from the polymer chain of **1** with the carboxylate group providing electrostatic stabilization. Chloride ions originating from the chloroauric acid NP precursor may also play a role in the overall stabilization mechanism, although control experiments in which TBA^+Cl^- was added to the Au NP solution did not change the pH-sensitive nature of the Au NPs. The pH-induced aggregation/redispersion process originates from the protonation/deprotonation of carboxyl groups on **1**, which modify the double layer. At higher pH, a majority of carboxyl groups are deprotonated, giving an ionic stabilizer, which generates a strong negative electrostatic repulsion between the NPs. At low pH, the carboxyl groups are protonated, which in turn decreases the negative charges on Au NPs, and as a result the attractive forces dominate and aggregation

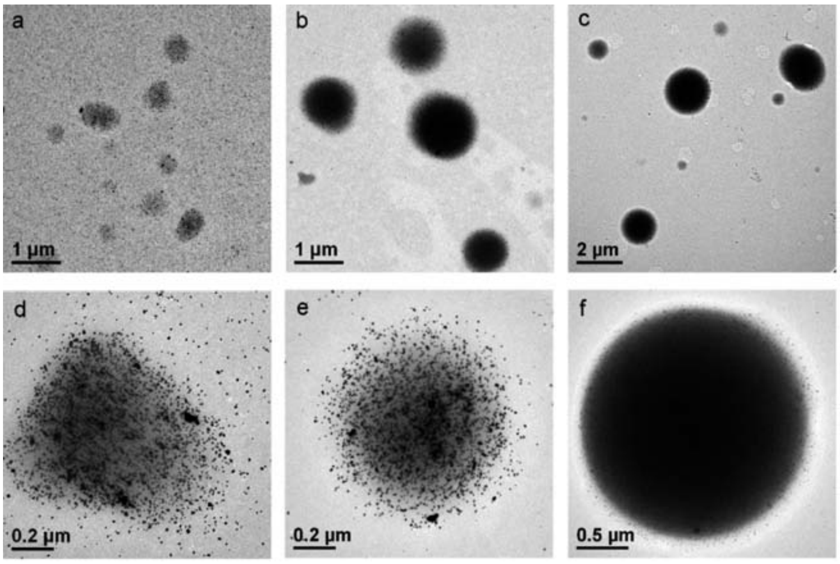


Figure 5. TEM images of the **1**-Au NPs at pH 2.4 (a and d), 2.0 (b and e), and 1.5 (c and f), showing the stepwise aggregation process as a function of the pH.

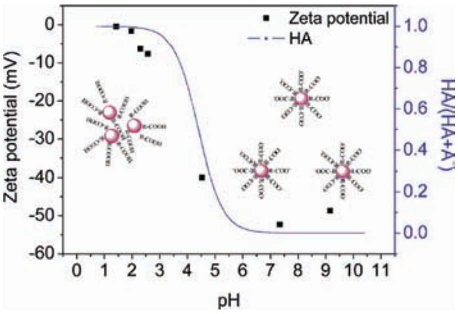


Figure 6. Variation of ζ potential of the **1**-Au NP solution (■) and the % formation of the monoprotic acid of **1** (HA) and its conjugate base (A^-; —) as a function of pH.

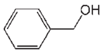
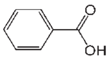
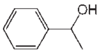
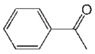
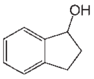
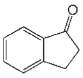
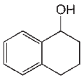
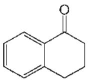
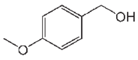
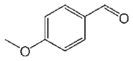
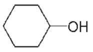
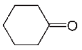
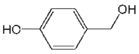
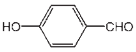
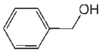
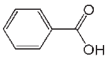
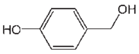
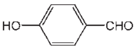
takes place, as shown by the ζ potentials (mV) of **1**-Au NP solutions at different pH values (Figure 6). The ζ value represents the charge on the NPs, either positive or negative, with the surface charge density indicated by the absolute value of the ζ potential. The **1**-Au NPs are negatively charged in the pH range 1.4−9.2, with a dramatic change in charge density between pH 2 and 4. The pK_a of **1** was determined as 4.4, and based on this value, the percentage of the protonated form of **1** (HA) versus pH was also plotted in Figure 6, which shows that the ζ potential of **1**-Au NPs corresponds closely to the protonation states of **1**. At pH > 4.5, the ζ potential is > −40 mV. Thus, the NP surface is highly negatively charged, and the electrostatic repulsion is sufficient to prevent attraction between the NPs. As the pH decreases, the carboxyl groups become increasingly protonated, which in turn compresses the electrical double layer, resulting in a lowered ζ potential and reduced NP stability.[23] At pH < 2.6, when a majority of carboxyl groups are protonated, the ζ potential is very low. Under these conditions, the dispersion is no longer stable, and Au NPs "salt out" of the solution.

The **1**-Au NPs were evaluated as catalysts for the oxidation of alcohols using air as the oxidant; primary and secondary alcohols were oxidized to their corresponding carboxylic acids and ketones, respectively (Table 1). For activated alcohols, the reactions take place under ambient conditions (Table 1, entries 1−5), whereas nonactivated alcohols require slightly harsher conditions (Table 1, entries 6 and 7). The use of pure O_2 only slightly increases the reaction rate, suggesting the uptake of O_2 into water is not rate-determining. Control experiments showed that neither $HAuCl_4$ nor **1** catalyze the oxidation of benzyl alcohol oxidation, indicating that the Au NPs are the active catalytic species.

Au NP catalysts exhibit strong, size-dependent activity; as the size of Au NPs increases, a dramatic decrease in catalytic activity is observed.[4c,24] The results in this paper, however, indicate that Au NPs with a relatively large particle size may be highly active. The turnover frequency (TOF) of benzyl alcohol was calculated to be 21 h^{-1} on the basis of the total number of Au atoms or 105 h^{-1} on the basis of the surface Au atoms,[25] which is higher or at least comparable to the performance of other polymer-protected gold NPs under similar conditions (a comparison is given in Table S1 in the Supporting Information). We speculate that the carboxylate group on the stabilizer transfers sufficient electron density to the Au NP surface, facilitating O_2 activation, the key step in alcohol oxidation. Both IR spectroscopy and gas-phase studies on Au clusters show that Au_n^- systems exhibit higher reactivity toward oxygen than cationic clusters—rationalized in terms of partial electron transfer from Au_n^- to the LUMO (π^*) of oxygen.[26] Indeed, Au NPs with a smaller size (5.4 nm) were obtained by performing the synthesis at 0 °C (see Figure S2 in the Supporting Information for the TEM image), but the catalytic activity did not increase. We also evaluated the reaction mechanism by adding CCl_4, a radical scavenger (Table 1, entries 9−10), and a dramatic decrease in activity was observed. The detrimental effect of CCl_4 to the reaction highlights the important role of radicals for alcohol oxidation in this system, although the mechanism of Au-catalyzed oxidation reactions is not consistent in literature.[27]

It is noteworthy that the **1**-Au NPs appear to be very stable in these reactions, and no precipitation was observed. Moreover, since the pH-induced precipitation−redispersion process is highly

Table 1. Aerobic Oxidation of Alcohols Catalyzed by the 1-Au NPs[a]

Entry	Substrate	Product	Time [h]	Temp.[°C]	Conversion [%]	Selectivity [%]
1[b]			4	22	83	81
			22	22	>99	63
2			22	22	36	97
			22	50	96	99[c]
3			22	22	>99	>99
4			22	22	61	>99
5			22	22	>99	71
6			22	50	40	87[c]
7	n-$C_6H_{13}OH$	n-$C_5H_{11}COOH$	22	50	>99	99
8			4	22	36	87
9[d]			4	22	2	-
10[d]			4	22	4	88

[a] All oxidations were performed as follows: alcohol (0.2 mmol), the **1**-Au NP solution (2.0 mL, 1.0 mM), K_2CO_3 (0.4 mmol) under air. The conversion and selectivity were estimated from GC analysis. [b] The other product is mainly benzyl benzoate (20−30%). [c] Reaction conditions: alcohol (0.4 mmol), **1**-Au NP solution (4.0 mL, 1.0 mM), K_2CO_3 (0.8 mmol) under an atmospheric pressure of O_2. [d] CCl_4 (0.1 mL) was added.

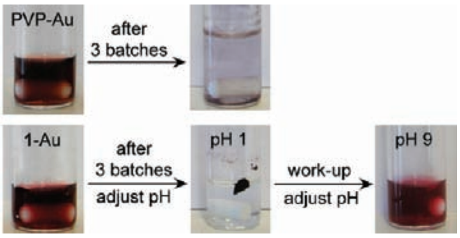


Figure 7. Images for the recycling of the PVP-Au and **1**-Au NPs.

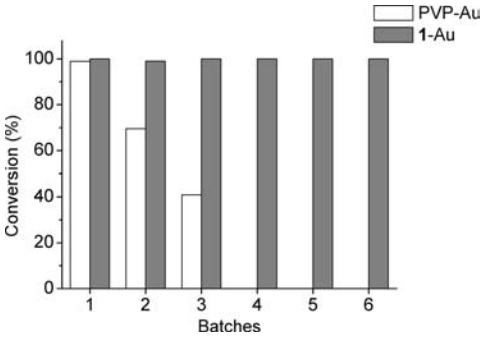


Figure 8. Recycling of PVP-Au and **1**-Au NPs in the oxidation of benzyl alcohol.

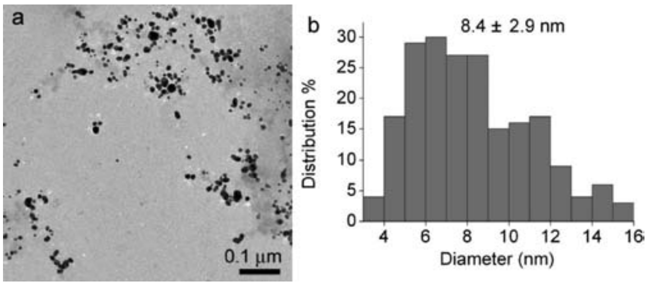


Figure 9. TEM image (a) and size distribution (b) of **1**-Au NPs after six batches.

reversible, the **1**-Au NPs could be recycled and reused by adjusting the pH to 1, removing the entire solution phase, and then redispersing the NPs in water at pH 9. The activity of the recycled NPs was equivalent to that observed in the original batch. This recycling protocol is extremely facile to implement, and images for the workup process for the third catalytic batch for the oxidation of benzyl alcohol are shown in Figure 7. The conversion of benzyl alcohol to benzoic acid showed no decrease in activity over six batches (Figure 8), whereas the PVP−Au NP control rapidly deactivated, in agreement with other studies.[28] After the first oxidation reaction, the size of the **1**-Au NPs increased slightly to ca. 7.4 nm (see Figure S4 in the Supporting Information for TEM images), and Figure 9 shows the TEM image of the **1**-Au NPs after six batches, in which the size of the **1**-Au NPs has further increased to 8.4 nm (from an average of $Au_{\sim 9300}$ to $Au_{\sim 18300}$ after six cycles, estimated using a literature method).[29]

ICP-MS was used to determine the extent of leaching of gold into the product phase, revealing a gold content of only 38 ng mL^{-1}, corresponding to a molar concentration of 2 × 10^{-6} mM, an amount that is below the detection limit of inductively coupled plasma optical emission spectrometry (ICP-OES).[30] On the basis of the original concentration of the catalytic solution (1 mM), the leaching level is 0.0002% per cycle, indicting why reuse of the system is so efficient.

EXPERIMENTAL SECTION

Materials and Methods. THF was dried with a solvent drying system and was stored with 4 Å molecular sieves. Diisopropylamine was refluxed with Na wire and distilled prior to use. N-vinyl-2-pyrrolidone (NVP) was distilled under reduced pressure prior to use. Gold chloride trihydrate was purchased from Aldrich with a gold purity of 99.99%. Other chemicals were obtained commercially and used without further purification. The average molecular weight of PVP was 50 kDa (K-30). Polymer **1** was prepared using a literature route[31] and was freeze-dried on a Christ Alpha 1-2 LD freeze-dryer (Germany).

pK_a Measurements. The acid dissociation constant (K_a) of **1** was determined by back-titration[32] since the acidic form of **1** is sparingly soluble in water. Compound **1** (154 mg, 0.87 mmol based on repeating unit) was dissolved in deionized water (1.2 mL) at 20 °C. HCl (2 M, 25 μL) was added dropwise, and the pH value of the solution was recorded with a pH meter. The pK_a was obtained by applying the equation pK_a = pH + log[HA]/[A^-]. The pK_a was found to be 4.4 ± 0.1, an average of 10 values.

Synthesis of Polymer-Protected Au NPs. The polymer-protected Au NPs were prepared by $NaBH_4$ reduction.[33] An aqueous solution of $HAuCl_4$ (10 mM, 1.0 mL) was mixed with the solution of **1** or PVP (100 mM based on pyrolidone monomer, 2.0 mL) and water (6 mL). The mixture was adjusted to pH 9−10 with 1 M NaOH and stirred for 1 h. $NaBH_4$ (0.1 M aqueous solution, 0.3 mL) was rapidly added in one portion with a stirring rate of 1000 rpm, affording a deep red solution. The mixture was stirred for another 1 h and diluted to 10 mL with water.

Characterization of 1-Au NPs. The morphology and core size of **1**-Au NPs was established by transmission electron microscopy (TEM), on a JEOL JEM-2010 microscope operating at 200 keV. One drop of **1**-Au NP solution at different pH values was placed on a copper grid coated with carbon film. The grids were dried in a desiccator for 24 h at room temperature before analysis. The size of Au NPs was estimated from the average diameter of 180 particles. The composition and phase of the NPs was determined by powder X-ray diffraction (XRD) analysis. The data were measured in reflection mode on a Panalytical X-ray Powder Diffraction System (MPD) using Cu Kα radiation and a PIX cell detector. The data were collected in the 2θ range of 5−120° (step size 0.01, 1 s per step, 20 scans). UV/vis absorption spectra were recorded on a Lambda 850 UV/vis spectrometer (Perkin-Elmer) at 25 °C.

Measurement of ζ Potentials. ζ potentials of the **1**-Au NPs at different pH values were measured on a Malvern Zetasizer nano ZS equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the ζ potential using the Smoluchowski equation.[34] The samples were equilibrated at 25 °C for 3 min, and an average of 15 measurements was taken to calculate the potential. The concentration of the Au NPs used for the ζ potential (and UV−vis spectroscopy—see above) measurements was 0.5 mM (based on Au atoms) with a polymer (repeating unit) to gold ratio of 20:1. The solutions were adjusted to the desired pH with either 1 M HCl or 1 M NaOH (monitored with a pH meter), and after 24 h, the solution (or supernatant in cases where a precipitate had formed) of each sample was analyzed.

Procedure for Alcohol Oxidation. In a typical experiment, the **1**-Au NP solution (2.0 mL, 1.0 mM), alcohol (0.2 mmol), and K_2CO_3 (0.4 mmol) were stirred in the air at the desired temperature. After the appropriate time, the reaction was quenched by the addition of 1 M HCl (added until the solution reached pH 1), causing the Au NP catalyst to precipitate. The product was then extracted with ethyl acetate (2 × 2 mL). The combined organic layers were analyzed on a Varian Chrompack CP-3380 gas chromatogram (GC) equipped with an OV-101 capillary column (30 m × 0.25 mm, using nitrogen as carrier gas). After extraction of the product, the water phase was collected and diluted 1000 times for analysis by inductively coupled plasma mass spectrometry (ICP-MS—see below). The solid was separated for recycling experiments and mixed with fresh water (2 mL), and the pH was adjusted to 9 by the addition of 1 M NaOH, resulting in complete dispersion of the **1**-Au NPs. The alcohol substrate and K_2CO_3 were added and the reaction started. Since the PVP-Au NPs are not pH-sensitive, recycling was achieved by adjusting the pH to 9 and adding new substrate and K_2CO_3, following the product extraction process. An Agilent 7500ce ICP-MS, interfaced to a CETAC CEI-100 microconcentric nebulizer, was used to determine the gold content in the aqueous phase. Instrument control as well as data analysis was carried out using the ChemStation B.03.03 software. The nebulizer was operated in self-aspiration mode with the sheath liquid (50 mM formic acid, 20 ppb Ge) closing the electrical circuit. Analyses were only started when a sufficiently stable signal (RSD 72Ge < 5%) was obtained. An ICP-MS tuning solution containing lithium, yttrium, cerium, thallium, and cobalt in 2% HNO_3 (each 10 mg L^{-1}, Agilent Technologies) was used for calibration.

CONCLUSIONS

Gold NPs stabilized by carboxylate-modified PVP display excellent activity and stability in the aerobic oxidation of various alcohols under mild conditions. Moreover, the carboxylate groups give rise to a pH responsive precipitation−redispersion switch, visualized by TEM, that allows facile recycling of the catalytic system. The excellent activity of the NP catalyst observed in recycling experiments may be attributed to the high stability of the **1**-Au NPs, due to the stabilizer, combined with an extremely low loss of the catalyst during recycling steps.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Listings of change in size of the Au NPs during the precipitation−redispersion, synthesis of **1**-Au NPs with a smaller size, XPS analysis of **1**-Au NPs, ICP-AES analysis of the palladium concentration in $HAuCl_4$, size distribution after the oxidation reaction of benzyl alcohol, and a comparison of the catalytic activity of **1**-Au NPs with examples from the literature for the oxidation of benzyl alcohol under similar conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +41 21 693 98 54. Fax: +41 21 693 98 85. E-mail: paul.dyson@epfl.ch.

ACKNOWLEDGMENT

This work was supported by the Sino-Swiss Science and Technology Corporation Programme (No. 2010DFA42110). N.Y. thanks the Marie-Curie Fellowship for financial support (Number: 252125-TCPBRCBDP). We thank the Interdisciplinary Centre for Electron Microscopy (CIME) at EPFL for access and assistance with TEM. Dr. M. Groessl and C. Clavel are thanked for ICP-MS measurements.

■ REFERENCES

(1) (a) Pina, C. D.; Falletta, E.; Prati, L.; Rossi, M. *Chem. Soc. Rev.* **2008**, *37*, 2077. (b) Corma, A.; Garcia, H. *Chem. Soc. Rev.* **2008**, *37*, 2096.

(2) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, 405.

(3) For recent reviews, see: (a) Chen, M.; Goodman, D. W. *Acc. Chem. Res.* **2006**, *39*, 739. (b) Shan, J.; Tenhu, H. *Chem. Commun.* **2007**, *44*, 4580. (c) Ishida, T.; Haruta, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7154. (d) Grabow, L. C.; Mavrikakis, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7390. (e) Gautier, C.; Burgi, T. *ChemPhysChem* **2009**, *10*, 483. (f) Gong, J.; Mullins, C. B. *Acc. Chem. Res.* **2009**, *42*, 1063.

(4) (a) Tsunoyama, H.; Sakurai, H.; Ichikuni, N.; Negishi, Y.; Tsukuda, T. *Langmuir* **2004**, *20*, 11293. (b) Tsunoyama, H.; Sakurai, H.; Negishi, Y.; Tsukuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 9374. (c) Tsunoyama, H.; Sakurai, H.; Tsukuda, T. *Chem. Phys. Lett.* **2006**, *429*, 528. (d) Tsunoyama, H.; Tsukuda, T.; Sakurai, H. *Chem. Lett.* **2007**, *36*, 212. (e) Tsunoyama, H.; Ichikuni, N.; Sakurai, H.; Tsukuda, T. *J. Am. Chem. Soc.* **2009**, *131*, 7086.

(5) (a) Wilson, O. M.; Scott, R. W. J.; Garcia-Martinez, J. C.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 1015. (b) Scott, R. W. J.; Sivadinarayana, C.; Wilson, O. M.; Yan, Z.; Goodman, D. W.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 1380. (c) Garcia-Martinez, J. C.; Lezutekong, R.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 5097. (d) Ye, H. C.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 4930.

(6) Wang, X.; Kawanami, H.; Islam, N. M.; Chattergee, M.; Yokoyama, T.; Ikushima, Y. *Chem. Commun.* **2008**, 4442.

(7) Schrinner, M.; Proch, S.; Mei, Y.; Kempe, R.; Miyajima, N.; Ballauff, M. *Adv. Mater.* **2008**, *20*, 1928.

(8) Yan, N.; Xiao, X.-C.; Kou, Y. *Coord. Chem. Rev.* **2010**, *254*, 1179.

(9) (a) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757. (b) Astruc, D.; Lu, F.; Ruiz, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852.

(10) (a) Kanaoka, S.; Yagi, N.; Fukuyama, Y.; Aoshima, S.; Tsunoyama, H.; Tsukuda, T.; Sakurai, H. *J. Am. Chem. Soc.* **2007**, *129*, 12060. (b) Sistach, S.; Rahme, K.; Pérignon, N.; Marty, J.; Viguerie, N. L.; Gauffre, F.; Mingotaud, C. *Chem. Mater.* **2008**, *20*, 1221. (c) Li, S.; Wu, Y.; Wang, J.; Zhang, Q.; Kou, Y.; Zhang, S. *J. Mater. Chem.* **2010**, *20*, 4379.

(11) For examples, see: (a) Zhao, D.; Wu, M.; Kou, Y.; Min, E. *Catal. Today* **2002**, *74*, 157. (b) Dyson, P. J.; Geldbach, T.; Moro, F.; Taeschler, C.; Zhao, D. *ACS Symp. Ser.* **2005**, *902*, 322. (c) Scott, R. W.; Wilson, O. M.; Crooks, R. M. *J. Phys. Chem. B* **2005**, *109*, 692. (d) Migowski, P.; Dupont, J. *Chem.—Eur. J.* **2006**, *13*, 32. (e) Feng, X. Y.; Zhang, J. L.; Cheng, S. Q.; Zhang, C. X.; Li, W.; Han, B. X. *Green Chem.* **2008**, *10*, 578. (f) Dupont, J.; Scholten, J. D. *Chem. Soc. Rev.* **2010**, *39*, 1780.

(12) (a) Vankelecom, I. F. J.; Moermans, B.; Verschueren, G.; Jacobs, P. A. *J. Membr. Sci.* **1999**, *158*, 289. (b) Sablong, R.; Schlotterbeck, U.; Vogt, D.; Mecking, S. *Adv. Synth. Catal.* **2003**, *345*, 333. (c) Mertens, P. G. N.; Bulut, M.; Gevers, L. E. M.; Vankelecom, I. F. J.; Jacobs, P. A.; De Vos, D. E. *Catal. Lett.* **2005**, *102*, 57. (d) Mertens, P. G. N.; Cuypers, F.; Vandezande, P.; Ye, X.; Verpoort, F.; Vankelecom, I. F. J.; De Vos, D. E. *Appl. Catal. A Gen.* **2007**, *325*, 130. (e) Wang, X.; Kawanami, H.; Islam, N. M.; Chattergee, M. *Chem. Commun.* **2008**, 4442.

(13) Kohler, N.; Fryxell, G. E.; Zhang, M. *J. Am. Chem. Soc.* **2004**, *126*, 7206. (b) Li, G.; Fan, J.; Jiang, R.; Gao, Y. *Chem. Mater.* **2004**, *16*, 1835. (c) Shokouhimehr, M.; Piao, Y.; Kim, J.; Jang, Y.; Hyeon, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 7039. (d) Shi, F. M.; Tse, K.; Pohl, M.-M.; Brckner, A.; Zhang, S.; Beller, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8866. (e) Yan, J.-M.; Zhang, X.-B.; Han, S.; Shioyama, H.; Xu, Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 2287. (f) Shylesh, S.; Schweizer, J.; Demeshko, S.; Schunemann, V.; Ernst, S.; Thiel, W. R. *Adv. Synth. Catal.* **2009**, *351*, 1789. (g) Shi, F.; Tse, M. K.; Zhou, S.; Pohl, M.-M.; Radnik, J.; Hubner, S.; Jähnisch, K.; Brückner, A.; Beller, M. *J. Am. Chem. Soc.* **2009**, *131*, 1775. (h) Fan, X. B.; Yan, N.; Tao, Z.; Evans, D.; Xiao, C.; Kou, Y. *ChemSusChem* **2009**, *2*, 941.

(14) (a) Lu, Y.; Mei, Y.; Drechsler, M.; Ballauff, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 813. (b) Ikegami, S.; Hamamoto, H. *Chem. Rev.* **2009**, *109*, 583. (c) Wang, Y.; Yan, R.; Zhang, J.; Zhang, W. *J. Mol. Catal. A: Chem.* **2010**, *317*, 81.

(15) (a) Bronstein, L. M.; Vamvakaki, M.; Kostylev, M.; Katsamanis, V.; Stein, B.; Anastasiadis, S. H. *Langmuir* **2005**, *21*, 9747. (b) Palioura, D.; Armes, S. P.; Anastasiadis, S. H.; Vamvakaki, M. *Langmuir* **2007**, *23*, 5761. (c) Li, D. X.; He, Q.; Cui, Y.; Li, J. B. *Chem. Mater.* **2007**, *19*, 412. (d) Kozlovskaya, V.; Kharlampieva, E.; Khanal, B. P.; Manna, P.; Zubarev, E. R.; Tsukruk, V. V. *Chem. Mater.* **2008**, *20*, 7474. (e) Preston, T. C.; Nuruzzaman, M.; Jones, N. D.; Mittler, S. *J. Phys. Chem. C* **2009**, *113*, 14236.

(16) (a) Bergbreiter, D. E.; Case, B. L.; Liu, Y. S.; Caraway, J. W. *Macromolecules* **1998**, *31*, 6053. (b) Chen, C. W.; Arai, K.; Yamamoto, K.; Serizawa, T.; Akashi, M. *Macromol. Chem. Phys.* **2000**, *201*, 2811. (c) Hamamoto, H.; Suzuki, Y.; Yamada, Y. M. A.; Tabata, H.; Takahashi, H.; Ikegami, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 4536. (d) Wang, Y.; Wei, G.; Zhang, W.; Jiang, X.; Zheng, P.; Shi, L.; Dong, A. *J. Mol. Catal. A: Chem.* **2007**, *266*, 233. (e) Wang, Y.; Wei, G.; Wen, F.; Zhang, X.; Zhang, W.; Shi, L. *J. Mol. Catal. A: Chem.* **2008**, *280*, 1. (f) Lu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815.

(17) (a) Nuopponen, M.; Tenhu, H. *Langmuir* **2007**, *23*, 5352. (b) Li, D.; He, Q.; Yang, Y.; Mohwald, H.; Li, J. *Macromolecules* **2008**, *41*, 7254. (c) Guan, J.; Li, J.; Guo, Y.; Yang, W.-S. *Langmuir* **2009**, *25*, 2679. (d) Lazim, A. M.; Eastoe, J.; Bradley, M.; Trickett, K.; Mohameda, A.; Rogersb, S. E. *Soft Matter.* **2010**, *6*, 2050. (e) Tan, J.-J.; Liu, R.-G.; Wang, W.; Liu, W.-Y.; Tian, Y.; Wu, M.; Huang, Y. *Langmuir* **2010**, *26*, 2093. (f) Li, L.-Y.; He, W.-D.; Li, W.-T.; Zhang, K.-R.; Pan, T.-T.; Ding, Z.-L.; Zhang, B.-Y. *J. Polym. Sci. Chem.* **2010**, *48*, 5018.

(18) Rietveld, H. M. *J. App. Crystallogr.* **1969**, *2*, 65.

(19) Jenkins, R.; Snyder, R. *Introduction to X-Ray Powder Diffractometry*; John Wiley & Sons: New York, 1996.

(20) Dieckmann, Y.; Cölfen, H.; Hofmann, H.; Petri-Fink, A. *Anal. Chem.* **2009**, *81*, 3889.

(21) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; John Wiley: New York, 1983.

(22) Evans, D. F.; Wennerström, H. *The Colloidal Domain*, 2nd ed.; Wiley-VCH: New York, 1999.

(23) Finke, R. G. *Metal Nanoparticles: Synthesis, Characterization and Applications*; Feldheim, D. L., Foss, C. A. Jr., Eds.; Marcel Dekker: New York, 2002.

(24) Yoon, B.; Häkkinen, H.; Landman, U. *J. Phys. Chem. A* **2003**, *107*, 4066.

(25) Hvolbæk, B.; Janssens, T. V. W.; Clausen, B. S.; Falsig, H.; Christensen, C. H.; Nørskov, J. K. *Nanotoday* **2007**, *2*, 14.

(26) Sun, Q.; Jena, P.; Kim, Y. D.; Fischer, M.; Ganteför, G. *J. Chem. Phys.* **2004**, *120*, 6510.

(27) (a) LIgnier, P.; Morfin, F.; Piccolo, L.; Rousset, J.-L.; Caps, V. *Catal. Today* **2007**, *122*, 284. (b) Fristrup, P.; Johansen, L. B.; Christensen, C. H. *Chem. Commun.* **2008**, 2750. (c) Nunes, G. S.; Alexiou, A. D. P.; Toma, H. E. *J. Catal.* **2008**, *260*, 188. (d) Conte, M.; Miyamura, H.; Kobayashi, S.; Chechik, V. *J. Am. Chem. Soc.* **2009**, *131*, 7189.

(28) Tsunoyama, H.; Ichikuni, N.; Sakurai, H.; Tsukuda, T. *J. Am. Chem. Soc.* **2009**, *131*, 7086.

(29) Liu, X.; Atwater, M.; Wang, J.; Huo, Q. *Colloid Surf. B, Biointerfaces* **2007**, *58*, 3.

(30) Meyers, R. A. *Encyclopedia of Analytical Chemistry: Applications, Theory, and Instrumentation*; John Wiley & Sons, Inc.: New York, 2000.

(31) (a) Bencini, M.; Ranucci, E.; Ferruti, P.; Oldani, C.; Licandro, E.; Maiorana, S. *Macromolecules* **2005**, *38*, 8211. (b) Yan, N.; Yuan, Y.; Dyson, P. J. *Chem. Commun.* **2011**, *47*, 2529.

(32) Albert, A.; Seargent, E. P. *The Determination of Ionization Constants - A Laboratory Manual*; Chapman and Hall: New York, 1984.

(33) Tsunoyama, H.; Sakurai, H.; Ichikuni, N.; Negishi, Y.; Tsukuda, T. *Langmuir* **2004**, *20*, 11293.

(34) Hunter, R. J. *Zeta Potential in Colloid Science*; Academic Press: New York, 1981.