



Editor's Choice paper

Chitosan-stabilized gold, gold–palladium, and gold–platinum nanoclusters as efficient catalysts for aerobic oxidation of alcohols

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ABSTRACT

Chitosan was used as a stabilizer for the synthesis of Au, AuPd and AuPt nanoclusters (NCs). The produced NCs had a narrow particle size distribution with sizes less than 2.3 nm in diameter and were characterized by various techniques such as UV–Visible spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy and scanning electron microscope energy dispersive spectroscopy (STEM-EDS). These metal NCs exhibited high catalytic activity toward the aerobic oxidation of various alcohols under ambient conditions comparable with the reported Au:PVP catalyst. Au NCs protected by chitosan could easily be recovered for repeated use.

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1. Introduction

Polymer-stabilized gold nanoclusters (NCs) have recently received a tremendous amount of attention due to their high performance catalytic activity toward organic transformations, including aerobic oxidation, as well as their potential to control chemical reactions by the design of their various protective hydrophilic functional polymers [1]. Polyvinyl-2-pyrrolidone (PVP) enhances the catalytic activity of gold for aerobic alcohol oxidation better than other protective polymers, such as polyvinyl alcohol or polyallylamine, owing to the electron donating effect of the polymer matrices to the gold clusters [2,3]. Thermosensitive star-shaped polymer matrices realize high reusability in the direct aerobic oxidation of alcohols to acids under basic aqueous conditions [4]. These studies prompted us to develop other hydrophilic polymers, in particular, biopolymer-stabilized gold NCs and to investigate their catalytic activity.

Chitosan (β -1,4-linked poly D-glucosamine), derived from the deacetylation of chitin, is the second most abundant biopolymer in nature after cellulose [5]. The presence of primary amine, hydroxyl and ester groups makes the polymer an excellent support for metal NCs [6]. However, most chitosan-stabilized metal NCs have been

applied to biosensors [7] and other therapeutic materials [8] and catalytic applications are scarce [9].

Herein, we report a new preparative method of chitosan-stabilized gold (Au:Chit), gold–palladium (AuPd:Chit) and gold–platinum (AuPt:Chit) NCs. These NCs showed high catalytic activity toward the aerobic oxidation of various alcohols into corresponding carbonyl compounds and acids.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were used as received without further purification. Hydrogen tetrachloroaurate tetrahydrate (HAuCl₄·4H₂O, Tanaka Kikinzoku), chloroplatinic acid (H₂PtCl₆, Wako), palladium chloride (PdCl₂, Wako), sodium tetraborohydride (NaBH₄, Wako), acetic acid (Wako), *p*-hydroxy benzyl alcohol, benzylalcohol, *p*-methoxy benzylalcohol, *p*-nitrobenzylalcohol, 1-hydroxy indane, ascorbic acid and potassium hydroxide (KOH) were obtained from Wako pure chemical industries. Ethyl acetate and hexane were purchased from Wako. Chitosan, poly (D-glucosamine), with a medium molecular weight of 75–85% deacetylated was from Sigma–Aldrich. Milli-Q grade water was used in all experiments.

2.1.1. Preparation of Metal:Chit

Chitosan (0.15 g) was dissolved into 50 mL of 0.18% aqueous acetic acid solution. To the solution was added 0.5 mM of HAuCl₄

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and the mixture was stirred for 30 min at room temperature under 1600 rpm. Aqueous solution of 0.1 M NaBH₄ (2.5 mL) was rapidly added at 6 °C under vigorous stirring. The color of the reaction mixture immediately turned from pale yellow to dark red in color, indicating the formation of smaller Au NCs. The hydrosol of Au:Chit was stored in refrigerator. The preparation of AuPd:Chit and AuPt:Chit was based on the co-complexation of mixing of the corresponding two metal ions. Chitosan (0.15 g) was dissolved into 50 mL 0.18% of aqueous acetic acid and followed by addition of 0.4 mM HAuCl₄ and 0.1 mM PdCl₂ aqueous solutions or 0.1 mM of H₂PtCl₆ aqueous solutions. The molar ratio of metal ions are used in these reaction is 4:1 (Au/Pd or Pt). Other procedures are followed as same as Au:Chit for the preparation of bimetallic AuPd:Chit and AuPt:Chit.

2.1.2. Characterization studies

UV–vis spectra were measured by JASCO V-670 spectrophotometer at 24 °C. FTIR spectra of the chitosan and Au:Chit were measured using a JASCO FTIR spectrometer with model of FTIR 4100 series. X-ray diffraction pattern of Au:Chit as in flake form, placed on microscope glass slide was recorded using Rigaku Ultima III, RINT-2000/PC (Cu K α radiation under operation at 40 kV and 40 mA), in thin film mode. XPS measurement of Au:Chit was carried out using a Vacuum Generators ESCALAB 220iXL electron spectrometer. The base pressure in the analyzer was ca. 2×10^{-8} Torr. X-rays from the Mg K α line at 1253.6 eV (15 kV, 20 mA) were used for excitation. Photoelectrons were corrected in the constant analyzer energy mode with pass energy of 50 eV. The overall resolution was 1 eV for the XPS measurements. The core level binding energies (BE) were calibrated using graphitic carbon tap with the adventitious carbon binding energy of 286.2 eV. Inductively coupled plasmon-Atomic emission spectrometry (ICP-AES (LEEMAN LABS INC, *Profile plus*)) was adopted to measure the Au, Pd and Pt contents in chitosan. The Au:Chit, AuPd:Chit and AuPt:Chit were added into aqua regia, respectively, and were allowed to react for 3 h in order to dissolve the Au, Pd and Pt completely. The resulting samples were analyzed by ICP-AES. The high-resolution TEM images of chitosan stabilized metal NCs were recorded with a JEOL JEM-3100FE at an accelerating voltage of 300 kV. Typical magnification of the images was 100,000–120,000 \times . The composition of individual bimetallic NCs were evaluated using 0.25 nm EDS (energy-dispersive spectrometry) probe in JEOL 3100FE TEM, operating in the STEM mode. NMR spectra (400 MHz for ¹H) were recorded using JEOL JMN LAMBDA 400 spectrometer with CDCl₃ as solvent at 23 °C and (CH₃)₄Si as internal standard.

2.1.3. General procedure for aerobic alcohol oxidation

In a test tube ($\phi = 30$ mm), benzyl alcohol (0.25 mmol), K₂CO₃ (103.7 mg, 0.75 mmol), and water (5 mL) were placed. The aqueous solution of Metal (Au, AuPd, or AuPt):Chit (0.005 mmol, 10 mL, 2 atom%) was added and the reaction mixture was stirred vigorously (1300 rpm) under air at a given temperature. If needed, the catalysts were separated by centrifugation (KUBOTA 5200) at 4000 rpm. The reaction mixture was quenched with 10 mL of 0.1 M HCl and then extracted with ethyl acetate (3 \times 10 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated in vacuo. The crude product was purified either by column chromatography or by preparative thin layer chromatography (50% ethyl acetate in hexane) to provide pure product(s) as listed. The products were confirmed by ¹H NMR spectra.

2.1.4. Procedure for the reuse of Au:Chit catalyst

After completion of the reaction, the catalysts were separated by centrifugation (KUBOTA 5200) at 4000 rpm, and then washed with water several times (preferably more than 4 times). Thus-recovered

gelatinous Au:Chit were transferred to the reaction test tube to run for the next cycle.

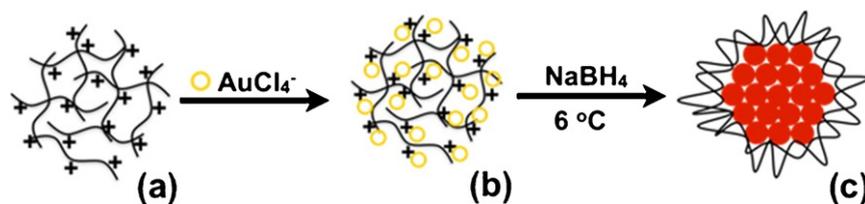
3. Results and discussion

For catalytic applications, it is very important to control the size of the gold cluster during preparation because smaller clusters exhibit superior catalytic activity for aerobic oxidations [1a,10]. Previous methods, such as a one-pot synthesis of chitosan with metal salts at higher temperature, produced larger particle sizes and a broad size distribution [11]. Generally, the higher temperature treatment with weak stabilizing agents such as citric acid, chitosan, PVP and starch produces the larger size gold NCs [7c,12]. Our preparative scheme for the synthesis of Au:Chit involves two steps, the formation of ion pairs by AuCl₄⁻ with an aqueous acetic acid solution of chitosan, followed by rapid reduction with NaBH₄ at 6 °C (Scheme 1). Strong electrostatic interactions between the polycations of chitosan with AuCl₄⁻ might be the decisive factor for controlling the size of gold NCs [13]. Furthermore, the reducing agent NaBH₄ also played an important role in the formation of smaller gold NCs than weak reducing agents (Fig. S1). This could be due to the instantaneously, formation of large number of nuclei, whose growth can be further retarded with chitosan polymer by anchoring them.

It is noteworthy to mention that Au:Chit, a 1:34 molar ratio of gold and chitosan (monomer unit) is required as an optimized condition. The amount of Au loading on chitosan was measured to be 33 mg of Au per gram of chitosan on ICP analysis. At higher pH, Au:Chit precipitates and the resulting filtrate showed neither unreduced metal ions nor unbound metal NCs were present, which was confirmed from the ICP analysis. This observation indicated that Au NCs were efficiently entrapped on chitosan matrix. At high molar ratio of Au:Chit (1:44), the reaction mixture was highly viscous, which causes formation of bigger size gold clusters. Under the condition of lower molar ratio of Au:Chit (1:22), the nanoclusters were not well stable than 1:34 molar ratio of Au:Chit. Since a 1:100 molar ratio is necessary for the preparation of Au:PVP, the present procedure allows significant reduction of the required monomer unit per gold atom. In addition, the thus-prepared Au:Chit does not require any special purification techniques and can be used as prepared. Au:Chit is storable either as a solution or in solid form in the refrigerator for months without any noticeable aggregation.

Fig. 1a shows the transmission electron microscopic analysis of Au:Chit. The clusters are narrow in size distribution and the average diameters are determined to be 2.3 ± 0.2 nm from the histogram plot of Fig. 1b. The X-ray diffraction studies (Fig. 1c) reveal a broad (1 1 1) peak associated with a small face-centered cubic crystal. The average crystallite sizes are also estimated to be 2.4 nm from the diffraction peak of the Au (1 1 1) plane (Fig. S2), which is consistent with diameters estimated from the TEM histogram plot. The UV–vis spectrum (Fig. 1d) of Au:Chit exhibits a broad band at ~ 500 nm, which is blue shifted significantly from the well known surface plasmon resonance (SPR) band of the Au clusters (cf. Au:PVP at 520 nm) [1a,2,14]. The blue shift of the SPR band might be attributed to the chemical interaction between the gold core and stabilizing molecule of chitosan [15].

The interaction between gold core and chitosan was also depicted by XPS analysis (Fig. 2). The smaller BE in Au 4f_{7/2} (82.9 eV) is ascribed that core Au has negative charge in state due to the interaction of chitosan with surface of the Au clusters [2]. The higher BEs of both N1s (399.5 eV) and O1s (532.7) in Au:Chit than those of N1s (398.1 eV) and O1s (531.7 eV) in chitosan (Fig. S3) are observed. Miyama and coworkers reported that core level N1s (400.5 eV) spectrum of amine group of chitosan coordinated with gold exhibits higher BEs than free chitosan molecules [16]. Kumar et al., also



Scheme 1. The schematic representation of formation of Au:Chit. (a) Polycationic form of chitosan, (b) formation of ion pairs with AuCl_4^- and (c) Au:Chit formation.

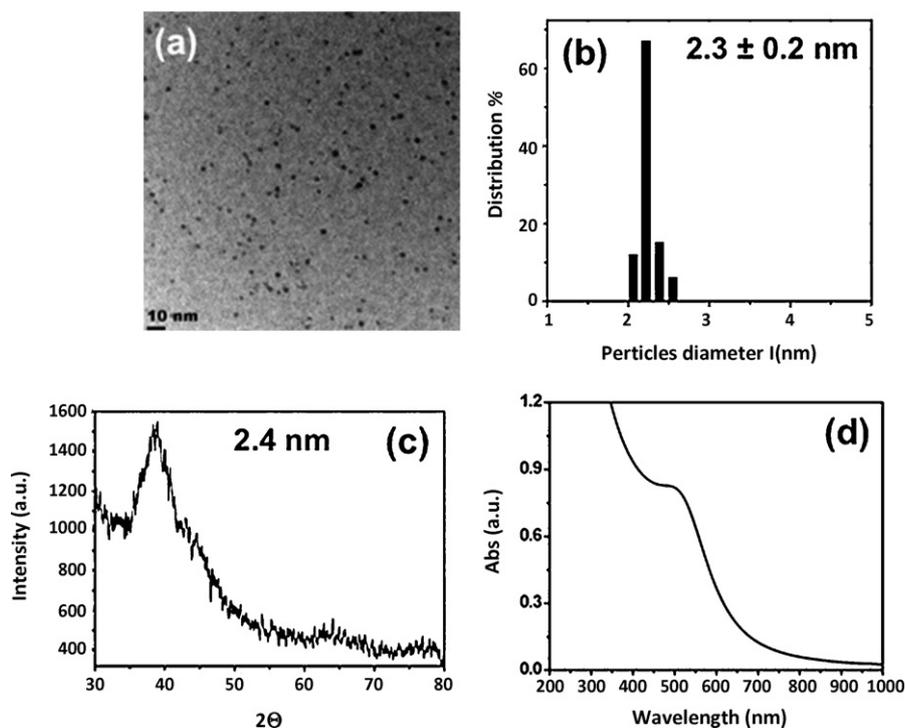


Fig. 1. (a) TEM image of chitosan-stabilized Au NCs. (b) Particle size histogram plot obtained from (a). (c) X-ray diffraction pattern of Au:Chit. (d) UV-vis spectrum of Au:Chit.

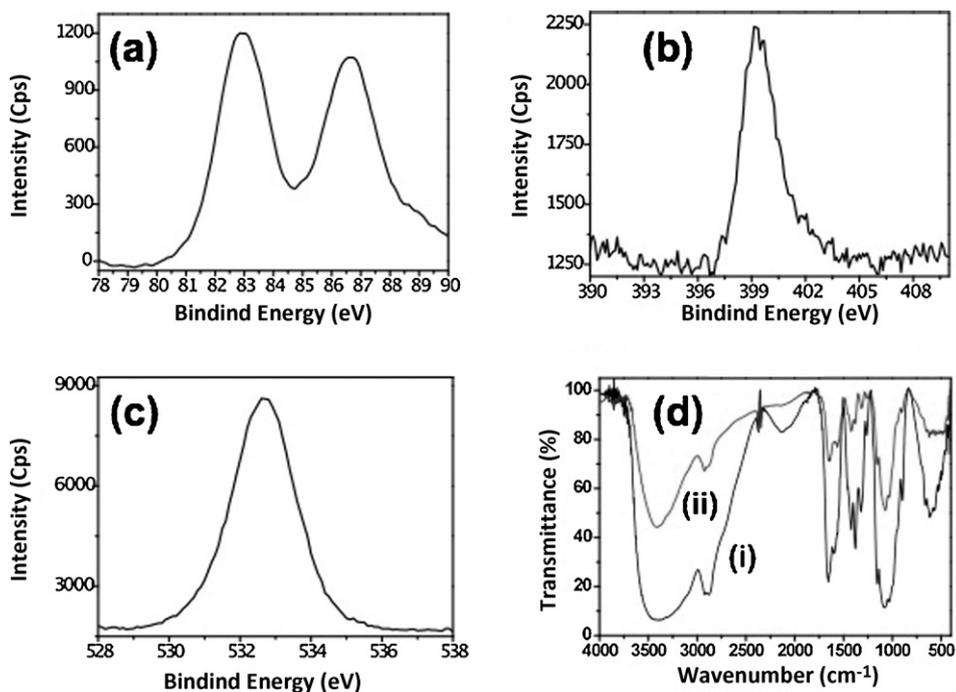
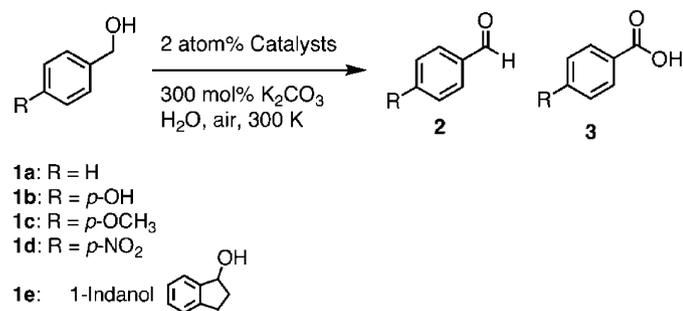


Fig. 2. (a) XPS spectra of core Au 4f, (b) N1s and (c) O1s. (d) FTIR spectra of pure chitosan (i) and Au:Chit (ii).

Table 1
Aerobic oxidation of aromatic primary alcohols and comparative studies with Au:Chit and Au:PVP catalysts.



Entry	Substrate	Catalysts	Time (h)	Yield (%)	
				2	3
1	1a	Au:Chit	8	0	96
2	1a	Au:PVP	6	0	85
3	1b	Au:Chit	8	98	0
4	1b	Au:PVP	8	91	0
5	1c	Au:Chit	8	71	25
6	1c	Au:PVP	3	0	91
7	1d	Au:Chit	30	0	98
8	1d	Au:PVP	24	0	99
9	1e	Au:Chit	1.5	96	0
10	1e	Au:PVP	0.5	99	0

claimed that N1s spectrum of primary amine bound gold particles shifted to higher BEs than that of unbound primary amine due to strong electrostatic interaction between amine and gold clusters [17]. Therefore, it can be concluded that the interaction between chitosan and Au NCs exists through the multidendate coordination of amine and hydroxyl group. These observations were further supported from the FTIR analysis of chitosan and Au:Chit as shown in Fig. 2d. Significant differences are observed in the 1800–1300 cm⁻¹ region of the spectra between chitosan and Au:Chit. The intense band of bending vibration of –NH is observed at 1595 cm⁻¹ in chitosan and at 1560 cm⁻¹ in Au:Chit. This lower frequency shift might be due to the interaction with gold clusters [9a,18]. The shifting of the –OH bending vibration from 1426 and 1313 cm⁻¹ (I) to 1416 and 1305 cm⁻¹ (II) may also account for the interaction of gold clusters with –OH group of chitosan. Furthermore, Au:Chit exhibits more intense set of bands in the region of 650–500 cm⁻¹ compared to chitosan and it has been proposed that these new bands are ascribed to the stretching vibration of Au–N and Au–O bonds [9a,19].

The catalytic activity of Au:Chit for the aerobic oxidation of alcohols was then tested and compared with that of previously reported Au:PVP (mean size 1.3 nm) as shown in Table 1.

The reactions were carried out in water in the presence of 2 atom% of Au:Chit and 300 mol% of K₂CO₃ at 300 K under aerobic conditions. Under basic conditions Au:Chit immediately precipitates out, functioning as a heterogeneous catalyst. This is in sharp contrast with Au:PVP, which behaves as a *quasi*-homogeneous catalyst. The oxidation of benzyl alcohol (Entry 1: **1a**) was tested, giving the corresponding acid (**3a**) in 96% yield after 8 h (Entry 1). In the case of Au:PVP, the reaction was completed within 6 h although the yield was somewhat lower (85%) (Entry 2). *p*-Hydroxybenzyl alcohol (**1b**) is oxidized into *p*-hydroxy benzaldehyde under the same conditions as in the case of Au:PVP (Entry 4). Indeed, the aldehyde **2b** was selectively obtained in 98% yield in the reaction catalyzed by Au:Chit (Entry 3). The electronic effect was monitored by the reactions of *p*-methoxybenzyl alcohol (**1c**) and *p*-nitrobenzyl alcohol (**1d**). The former reaction gave the aldehyde **2c** in 71% yield and the acid **3c** in 25% yield after 8 h (Entry 5). In contrast, the Au:PVP reaction affords **3c** in 91% yield (Entry 6). In the latter case, the

reaction rate was slow, with completion in 30 h, giving the acid **3d** in 98% yield (Entry 7). The reaction of 1-indanol (**1e**) afforded the corresponding ketone (**2e**) in 96% yield after 1.5 h (Entry 9) and in quantitative yield for 30 min by Au:PVP (Entry 10), respectively. Thus, Au:Chit has comparable catalytic activity to Au:PVP toward the oxidation of various aromatic primary/secondary alcohols [20]. Such similar catalytic activity of Au:Chit and Au:PVP is unexpected because of the following two reasons. First, Au:PVP NCs are smaller in diameter (1.3 nm) than Au:Chit (2.3–2.4 nm). The catalytic activity of Au:PVP depends highly on its cluster size and the activity drastically decreases above 2 nm [10]. The activity of Au:Chit is significantly higher than that of Au:PVP of comparable mean size. Second, in basic media Au:PVP and Au:Chit behave as *quasi*-homogeneous and heterogeneous catalysts, respectively, and even though the former is believed to be more active, the Au:Chit catalyst works as efficiently as Au:PVP. This unexpectedly high catalytic activity of Au:Chit might arise from the matrix dependence interaction between chitosan and Au NCs as depicted by XPS and FTIR analyses. The detailed mechanistic studies for the aerobic oxidation of alcohol catalyzed by *quasi-homogeneous* Au nanocatalysts have been described well in elsewhere [2]. In addition, the use of excess capping agents or protective agents of the polymers may completely cover the active sites of the cluster surface, which act as poison to the catalysts [21]. In comparison to Au:Chit (1:34 molar ratio), more PVP (1:100 molar ratio) is used to stabilize the Au NCs for the preparation of Au:PVP. Since Au:Chit works as a heterogeneous catalyst, it is expected to be easily recoverable and reusable by simple filtration or centrifugation.

We found that the catalyst could easily be recovered by simple centrifugation after the reaction and no special treatment was required to reuse the catalyst in the oxidation reaction. The reusability of Au:Chit was tested by the oxidation of **1b** under the same reaction conditions as listed in Entry 3 of Table 1, and the yield of **2b** in three cycles were 95, 93, and 97%, respectively. The size of the Au in Au:Chit remained the same even after the third cycle, which was confirmed by TEM analysis of recovered Au:Chit (Fig. 3). Histogram plot of recovered Au:Chit (Fig. 3c) indicates that Au clusters are uniform in size and particles are not aggregated during the catalytic reactions. The X-ray diffraction pattern of recovered Au:Chit (Fig. 3d) shows the crystallite size is 2.4 nm as fresh Au:Chit. The leaching of Au was also checked by inductively coupled Plasmon (ICP) analysis of the filtrate, which showed that no Au was present (detection limit: 0.02 ppm).

As demonstrated above, chitosan possesses great potential as an excellent matrix for metal cluster catalysts. These results further motivated us to apply chitosan matrices to stabilize bimetallic cluster systems because the doping of other metals into gold NCs may enhance the catalytic activity and selectivity of monometallic Au nanocatalysts [22]. AuPd:Chit and AuPt:Chit bimetallic clusters were efficiently prepared based on the procedure as shown in Scheme 1 by co-complexation via mixing of the corresponding two metal ions (HAuCl₄/PdCl₂ or HAuCl₄/H₂PtCl₆). The average diameters of AuPd:Chit and AuPt:Chit were determined to be 2.4 ± 0.5 nm and 2.4 ± 0.4 nm, respectively, from HRTEM analysis by measuring more than 350 particles (Fig. 4a and b).

The distribution of each bimetallic NCs were analyzed by 0.25 nm scanning transmission electron microscope-energy dispersive spectroscopy (STEM-EDS) shown in Supporting information (Figs. S4 and S5). These spectra indicate that each bimetallic NCs were made by composition of two metal and the ratio of the metals (4:1 of Au and Pd or Pt) were almost consistent with the initial concentration of metals used during the preparation of bimetallic NCs. The amount of metal loading in AuPd:Chit and AuPt:Chit was found to be 26 mg (Au) and 3.5 mg (Pd), 26 mg (Au) and 6.5 mg (Pt) per gram of chitosan, respectively, on ICP elemental analysis. As same

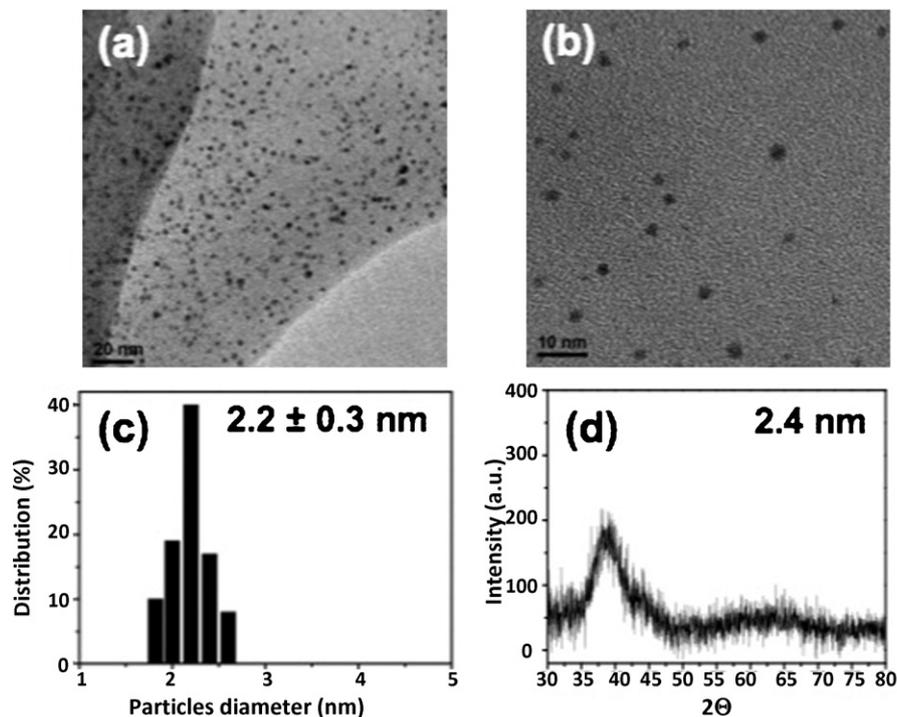


Fig. 3. (a) TEM picture of recovered Au:Chit catalysts, after third cycle, (b) high resolution TEM image of (a), (c) histogram plots of (b) and (d) X-ray diffraction pattern of (a).

as Au:Chit, metal NCs are efficiently entrapped on chitosan matrix.

UV–vis spectra of AuPd:Chit and AuPt:Chit are shown in Fig. 4c and d. An exponentially increasing absorbance toward higher energy due to the interband transition of newly formed bimetallic alloy structure of AuPd NCs is observed [23]. The absence of SPR band of Au also indicates the alloy form rather than the formation of segregation. On the contrary, bimetallic AuPt:Chit shows a broad band at ~ 502 nm, which is ascribable as the segregation of gold in the AuPt NCs.

The thus-prepared bimetallic clusters were tested for aerobic alcohol oxidation, which showed that both AuPd:Chit and AuPt:Chit have comparable catalytic activity to Au:Chit (Table 2). All the reactions were carried out in water in the presence of 2 atom% of M:Chit and 300 mol% of K_2CO_3 at 300 K under aerobic conditions. As shown in Entries 1–3, in the oxidation of benzyl alcohol (**1a**) to benzoic acid, AuPt:Chit took a longer time (10 h, 95% yield) than either AuPd:Chit (8 h, 97% yield) or Au:Chit (8 h, 96% yield). In contrast, oxidations of **1b**, **1c** and **1d** were completed within 4, or 26, or 0.5 h and 8, or 29, or 1.5 h by AuPt:Chit and AuPd:Chit,

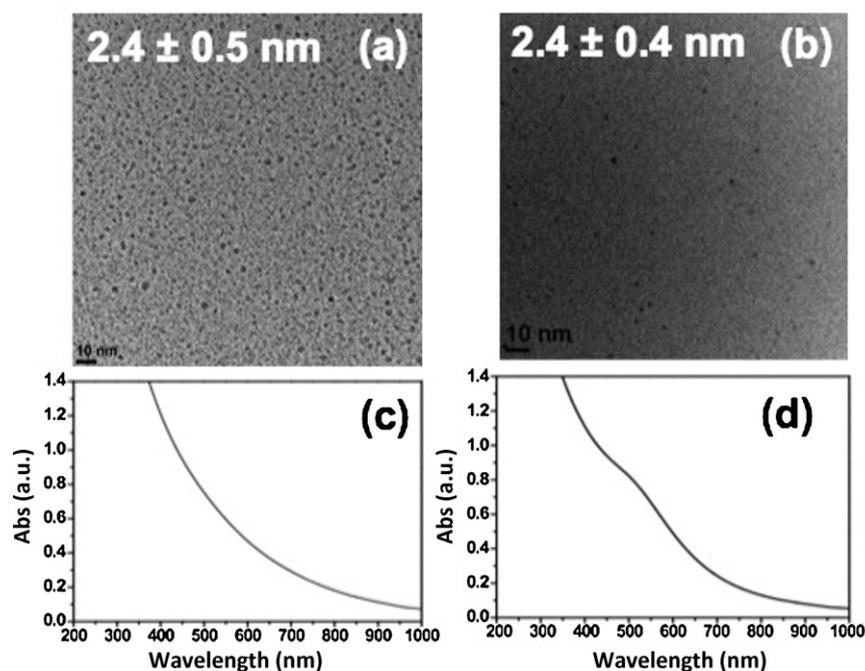
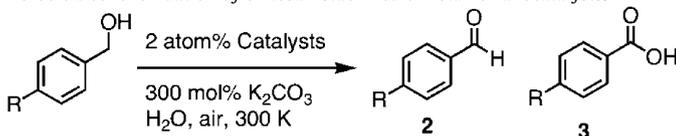


Fig. 4. (a) TEM images of AuPd:Chit and (b) AuPt:Chit. (c) and (d) are UV–vis spectra of AuPd:Chit and AuPt:Chit, respectively.

Table 2
Aerobic alcohol oxidation by chitosan-stabilized bimetallic nanocatalysts.



1a: R = H

1b: R = *p*-OH

1c: R = *p*-NO₂

1d: 1-Indanol



Entry	Substrate	Catalysts	Time (h)	Yield (%)	
				2	3
1	1a	Chit–Au NCs	8	0	96
2	1a	Chit–AuPd NCs	8	0	97
3	1a	Chit–AuPt NCs	10	0	95
4	1b	Chit–Au NCs	8	98	0
5	1b	Chit–AuPd NCs	6	96	0
6	1b	Chit–AuPt NCs	4	98	0
7	1c	Chit–Au NCs	30	0	98
8	1c	Chit–AuPd NCs	29	0	97
9	1c	Chit–AuPt NCs	26	0	98
10	1d	Chit–Au NCs	1.5	96	0
11	1d	Chit–AuPd NCs	1.5	95	0
12	1d	Chit–AuPt NCs	0.5	95	0

respectively, while a slightly longer time was required to complete the reaction with Au:Chit (Entries 4–12).

4. Conclusion

We have developed simple preparative methods for Au, AuPd and AuPt NCs protected by chitosan, which behave as heterogeneous catalysts under basic aqueous conditions and show comparable catalytic activity toward the aerobic oxidation of various alcohols to *quasi*-homogeneous Au:PVP catalyst. Thanks to their heterogeneous characters, these catalysts are easily recovered through a simple centrifugation process, and no aggregation is observed after the third reuse. Although the reason for such high activity of these chitosan-protected NCs has not yet been determined, these catalysts are expected to be practically useful catalysts because of their simple preparation, availability, and reusability. Furthermore, since chitosan can be made into any form of beads, fibers and membranes, the application potential of Au:Chit is even more versatile.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.03.019.

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