

## Effectively Catalytic Decomposition of Acetaldehydes in Spirits by Using Chitosan-Capped Gold Nanoparticles

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**ABSTRACT:** As shown in the literature, chitosan (Ch) can react easily with acetaldehydes to form Schiff bases with high yields at room temperature. Therefore, in this work, we report an innovative idea to prepare nanocomposites (NCs) of Ch-capped gold NPs (NPs) for effectively catalytic decomposition of acetaldehyde in spirits. Ch of NCs can easily catch acetaldehydes in spirits. Thus the caught acetaldehydes were therefore concentrated on NCs. Subsequently, the concentrated acetaldehydes were catalytically decomposed on catalysts of Au NPs in Ch/Au NCs. Experimental results indicate that the acetaldehyde was significantly decomposed by ca. 40 % in 120 ppm acetaldehyde-containing white spirits by adding 0.05 ppm Ch-capped Au NPs after three days. This efficiency for catalytic decomposition of acetaldehyde is a marked increase by ca. 200 % of magnitude, as compared with that based on commercial Au NPs with similar sizes at the same Au concentration. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 86–91, 2013

**KEYWORDS:** catalysts; composites; nanoparticles; nanowires and nanocrystals

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### INTRODUCTION

Recently, noble metal nanoparticles (NPs) of gold, silver and platinum have been extensively investigated<sup>1,2</sup> due to their unusually plasmonic,<sup>3</sup> optical,<sup>4</sup> chemical,<sup>5</sup> photoelectrochemical,<sup>6</sup> and electronic<sup>7</sup> properties. The number of potential applications for nanomaterials, especially in the field of proteins detection,<sup>8</sup> and catalysts modification,<sup>9</sup> are rapidly growing because of their unique electronic structure and extremely large surface areas. Moreover, metal/metal nanocomposites (NCs) are synthesized to further improve their specific properties.<sup>10,11</sup> In other nanoscale fields, silica and titania are most popularly used supporting materials for enhancing catalytic activities of supported gold and silver NPs.<sup>12,13</sup> As shown in the literature, the developed methods for noble metal NPs fabrications include chemical,<sup>14</sup> sonochemical,<sup>15</sup> and sonoelectrochemical<sup>16</sup> reductions, laser ablation,<sup>17</sup> annealing from high-temperature solutions,<sup>18</sup> metal evaporation,<sup>19</sup> and Ar<sup>+</sup> ion sputtering.<sup>20</sup> Meanwhile, some stabilizers, like sodium dodecyl sulfate,<sup>21</sup> sugar ball,<sup>22</sup> and poly(vinylpyrrolidone)<sup>23</sup> were used, and some stabilization technologies of thiol-ligand coatings<sup>24</sup> and polymer capping agents<sup>25</sup> were developed to prevent the prepared NPs from aggregating. Tan et al.<sup>26</sup> reported a synthesis of positively

charged silver NPs via photoreduction of AgNO<sub>3</sub> in branched polyethyleneimine/HEPES solution. Importantly, these positively charged Ag NPs demonstrate superior surface-enhanced Raman scattering (SERS) activity over negatively charged Ag NPs for the detection of a variety of negatively charged analytes in aqueous solutions. Brinas et al.<sup>27</sup> developed a method for preparing size-controllable Au NPs capped with glutathione by varying the pH of the solution before reduction. This method is based on the formation of polymeric NPs precursors, Au(I)-glutathione polymers, which change size and density depending on the pH.

It is well known, chitosan (Ch) is a ubiquitous biopolymer with good biocompatibility and low cytotoxicity.<sup>28</sup> It is a linear polysaccharide obtained by deacetylation of chitin. By replacing the majority of aminoacetyl groups in chitin by the amine moieties Ch molecules can be dissolved in acidic water. In such solution, Ch can be a positively charged polyelectrolyte due to the protonation of the amine groups. Biological Ch is attractive for many potential applications in food, pharmaceutical and cosmetic industries, and bioengineering.<sup>29</sup> Moreover, the amine groups are also responsible for several easy and site-selective methods on chemical modification of Ch, such as Schiff base formation, N-acylation, and reductive alkylation.<sup>30</sup> Therein, Ch reacts easily

with acetaldehydes to form Schiff bases with high yields at room temperature. This easy chemical modification favors the continuous development of Ch derivatives in many application fields.<sup>31</sup> Therefore, these specially chemical properties of Ch encourage us to prepare Ch-based NCs for efficiently decomposing toxic reagents of acetaldehydes in spirits. In our previous study,<sup>32</sup> we reported a green pathway to prepare Au NPs via aid of Ch at room temperature. However, the whole experiment needed to be performed for 7 days. In this work, we report an innovative and fast pathway to prepare Ch/Au NCs in neutral solutions from bulk Au substrates without addition of other stabilizer and reducing agent. Application of the prepared NCs on effectively catalytic decomposition of toxic acetaldehydes in spirits is examined.

## EXPERIMENTAL

### Chemical Reagents

The NaCl electrolytes (p.a. grade) purchased from Acros Organics were used as received without further purification. Commercial water soluble Ch powders with a degree of deacetylation of 0.82 were purchased from First Chemical Works, Taiwan. This value of degree of deacetylation was provided by the First Chemical Works and was not experimentally evaluated further. All of the solutions were prepared using deionized 18.2 M $\Omega$  cm water provided from a MilliQ system.

### Preparation of Chitosan/Gold Nanocomposites

All of the electrochemical experiments were performed in a three-compartment cell at room temperature, 22°C, and were controlled by a potentiostat (model PGSTAT30, Eco Chemie). First, a sheet of gold with bare surface area of 4 cm<sup>2</sup>, a sheet of 2 × 4 cm<sup>2</sup> platinum, and a KCl-saturated silver-silver chloride (Ag/AgCl) rod were employed as working, counter and reference electrodes, respectively. Before the oxidation-reduction cycles (ORC) treatment, the gold electrode was mechanically polished (model Minimet 1000, Buehler) successively with 1 and 0.05  $\mu$ m of alumina slurries to a mirror finish. Then the electrode was cycled from -0.28 to +1.22 V vs. Ag/AgCl at 500 mV/s for 500 scans in a deoxygenated solution (40 mL) containing 0.1 N NaCl and 1 g/L Ch under slight stirring. The durations at the cathodic and anodic vertices are 10 and 5 s, respectively. After this roughening procedure, positively charged Au- and Ch-containing complexes were left in this aqueous solution at pH 6.5. Immediately, the solution was heated from room temperature to boiling (100°C) on a thermal heater at a heating rate of 6°C/min in air to synthesize Ch/elemental Au NCs. Finally, nondissolved Ch powders were removed from solutions by filtering.

### Catalytic Decomposition of Acetaldehydes

Before measurement prepared Ch-capped Au NPs-containing solutions were added in commercial white spirits (58 % ethanol, v/v %), which contain 120 ppm acetaldehydes. The final concentrations of Au NPs in the spirits were controlled at ca. 0.05 ppm (In Taiwan, the drinking water quality standards for heavy metals are limited to below 0.05 ppm.). The corresponding experiments were performed in dark sealed cells at room temperature for three days. Then the degree of the decomposition of acetaldehyde in spirits was analyzed by using gas chromatog-

raphy-mass spectrometer (GC-MS; Micromass TRIO-2000). Each extract (1  $\mu$ m) was injected into a capillary column (DB-WAX 30 m length × 0.25 mm i.d. × 0.25  $\mu$ m film thickness). Helium was used as carrier gas with a flow rate of 1 mL/min. The temperature program used was as follows: 50°C for 5 min. The temperature was then increased to 280°C at 10°C/min, and the final temperature was held for 5 min. The temperatures of injector and detector were 280 and 300°C, respectively. Chromatographic peaks were identified by comparing the mass spectrum of each component with the U.S. National Institute of Standards and Technology (NIST) Mass spectral Library and Wiley Database provided by the spectrometer. Quantification of acetaldehydes (peak area ratio) was based on comparison of peak area to the peak area of the external standard.

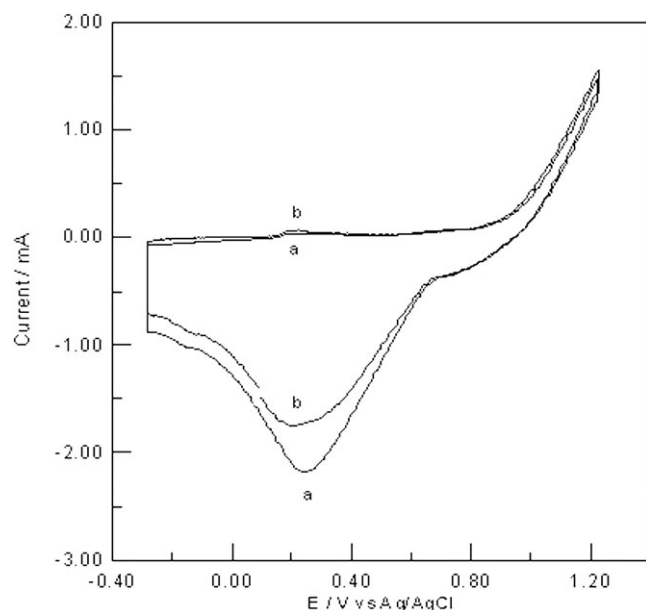
### Characteristics of Chitosan/Gold Nanocomposites

A single drop of the sample-containing solution was placed on a 300 mesh Cu/carbon film transmission electron microscopy (TEM) sample grid and was allowed to be dried in a vacuum oven. Then the sample was examined by using a Philips Tecnai G2 F20 electron microscope with an acceleration voltage of 200 kV. Ultraviolet-visible absorption spectroscopic measurements were carried out on a Perkin-Elmer Lambda 35 spectrophotometer in 1 cm quartz cuvettes. For X-ray diffraction (XRD) measurements, instrument of ARL X'TRA Thermo with a supplemental capillary was used to examine the liquid sample. High resolution X-ray photoelectron spectroscopy (HRXPS) was recorded during measuring powder samples. These powder samples were obtained by using centrifugation collections at 15000 rpm for 3 min. Then the powders were rinsed with deionized water. The whole procedures were performed for three cycles. For HRXPS measurements, a ULVAC PHI Quantera SXM spectrometer with monochromatized Al K $\alpha$  radiation, 15 kV and 25 W, and an energy resolution of 0.1 eV was used. To compensate for surface charging effects, all HRXPS spectra are referred to the C 1s neutral carbon peak at 284.8 eV. The complex HRXPS peaks are deconvoluted into component Gaussian peaks using a peak separation and analysis software (PeakFit v4.0, AISN Software).

## RESULTS AND DISCUSSION

### Preparation of Chitosan/Gold Nanocomposites

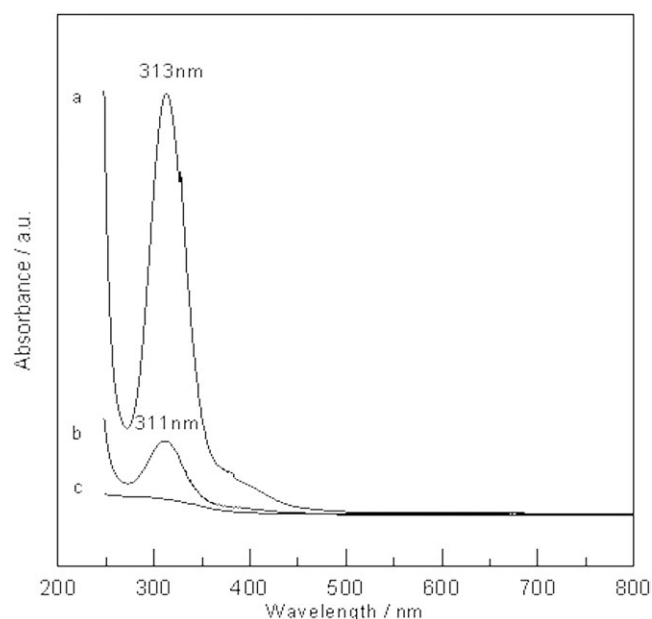
Because Ch reacts easily with acetaldehydes to form Schiff bases with high yields at room temperature,<sup>30</sup> we aim to prepare Ch/Au NCs to effectively decompose adsorbed acetaldehydes on Ch by using catalysts of Au NPs. In this work, Ch was added in a neutral 0.1N NaCl solution to prepare red Ch/Au NCs. We also made an attempt on synthesizing Ch/Au NCs in a 0.1N HCl solution containing 1 g/L Ch by using the same procedure, as described in the experimental section, but it did not succeed. Therefore, protonated Ch in acid solutions is unsuitable for the preparation of Ch/Au NCs. It may be ascribed to different types of Au-containing complexes, which are precursors of Au NPs, are formed in solutions with different pH values.<sup>33</sup> In the ORC treatment, the chloride electrolyte was selected since this facilitates the metal dissolution-deposition process that is known to produce SERS-active roughened surfaces.<sup>34</sup> Figure 1 shows the results of the 100th scan of cyclic voltammograms for the dissolution and redeposition of Au substrates in 0.1N NaCl solutions



**Figure 1.** Cyclic voltammogram at 500 mV/s of the 100th scan for electrochemically roughened gold substrates in different solutions: (a) 0.1N NaCl; (b) 0.1 N NaCl containing 1 g/L chitosan.

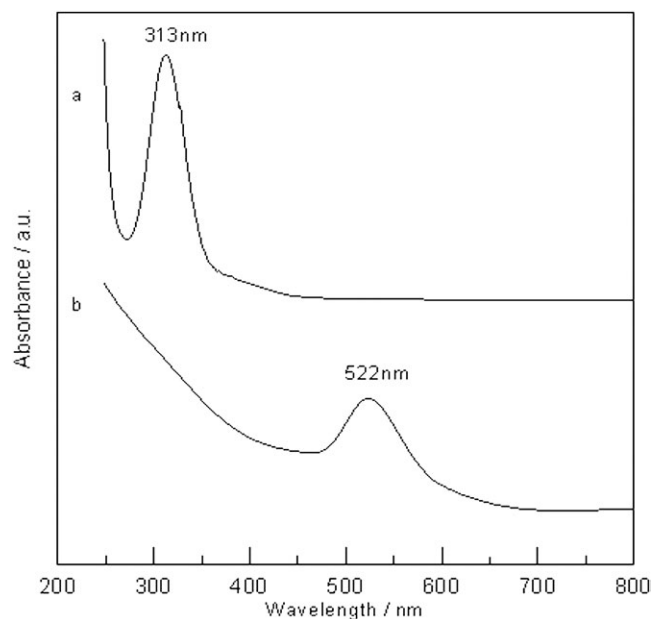
with and without the addition of Ch. Basically, these I-E curves are quite similar, but the area of the cathodic peak is decreased due to the addition of Ch, as demonstrated in curve b. It indicates that the presence of Ch is unfavorable for the redeposition of Au NPs on the Au substrates. As shown in our previous study,<sup>35</sup> complexes of  $\text{AuCl}_4^-$  would be present in the solution after roughening the Au substrate by using ORC procedure. Then  $\text{AuCl}_4^-$  can be adsorbed on the nitrogen of Ch to form self-assembled monolayers (SAMs).<sup>36,37</sup> As expected, white Ch suspensions were changed to yellow ones after the ORC procedure. It reveals that  $\text{AuCl}_4^-$  is readily adsorbed on Ch as a precursor for the subsequent preparation of red Au NPs in solutions.

As shown in spectra a and b of Figure 2, the absorbance maximum bands of  $\text{AuCl}_4^-$  nanocomplexes appear approximately at 311 and 313 nm for prepared nanocomplexes in solutions<sup>35</sup> with and without Ch, respectively. These results of similar absorbance maximum bands indicate that Ch is not a necessity for preparing  $\text{AuCl}_4^-$  nanocomplexes in solutions via the ORC procedure. However, it plays an important role in the subsequent reduction for preparation of elemental Au NPs in solutions. Moreover, these absorbance maximum bands are markedly different from those of elemental Au NPs located at ca. 520 nm.<sup>38</sup> Spectrum c of Figure 2 represents a blank experiment. It represents the absorbance maximum band of 1 g/L Ch in 0.1N NaCl. Clearly, Ch did not cause any interference in examining the formation of  $\text{AuCl}_4^-$ . As shown in spectrum a of Figure 3, after heating the  $\text{AuCl}_4^-$  nanocomplexes-containing solution without the Ch for obtaining elemental Au NPs, the absorbance maximum band of the solution still appears approximately at 313 nm. Also, the solution color maintains yellow. These phenomena reveal that elemental Au NPs can not be obtained in absence of Ch. Encouragingly, as shown in spectrum b of Figure

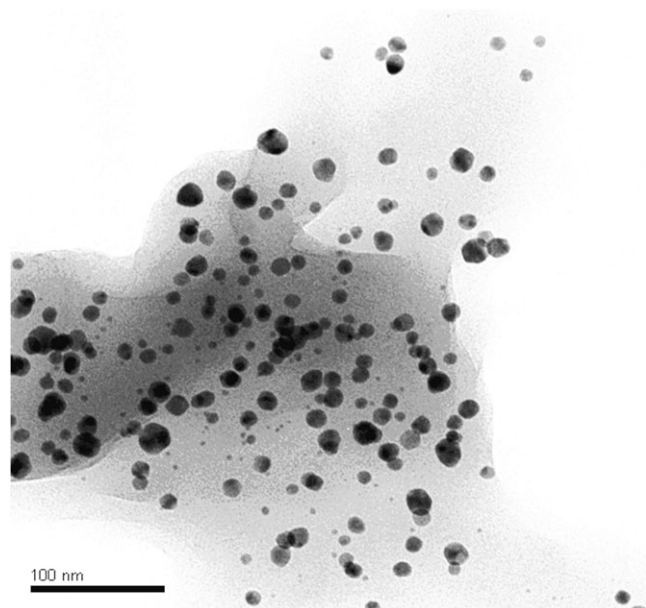


**Figure 2.** UV-vis spectra of Au-containing complexes in solutions after roughening the Au substrates in different solutions: (a) 0.1N NaCl; (b) 0.1N NaCl containing 1 g/L chitosan. Spectrum c represents a blank experiment of 0.1N NaCl containing 1 g/L chitosan.

3, the wavelength of the absorbance maximum band of the solution changes from 311 nm to 522 nm after heating the  $\text{AuCl}_4^-$  nanocomplexes-containing solution in presence of Ch. Also, the solution color changes from yellow to red after heating. These results indicate that elemental Au NPs are successfully synthesized.<sup>38</sup> Meanwhile, non-dissolved yellow Ch



**Figure 3.** UV-vis spectra of Au-containing colloidal solutions after reducing the positively charged Au-containing complexes in solutions prepared in different solutions: (a) 0.1N NaCl; (b) 0.1N NaCl containing 1 g/L chitosan.



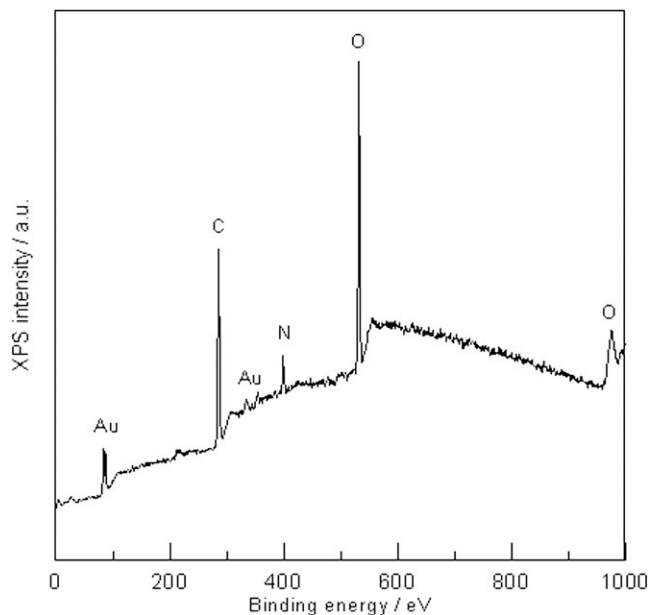
**Figure 4.** TEM micrograph of prepared Au NPs in the Ch/Au NCs, showing size and dispersion; scale of nano-bar being 100 nm.

settlements were also changed into red ones after heating due to the adsorption of Au NPs. Further inductively coupled plasma-mass spectrometer (ICP-MS) analysis indicates that the concentration of Au NPs in the synthesized Ch/Au NCs is ca. 70 ppm.

#### Characteristics of Chitosan/Gold Nanocomposites

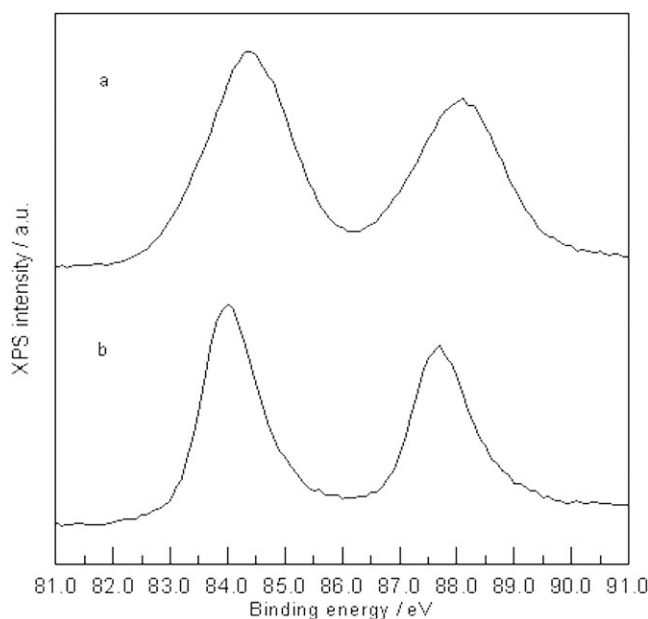
The dispersion and the particle size of prepared Au NPs adsorbed on Ch were examined by using TEM images. As shown in Figure 4, the Au NPs with a mean diameter of ca. 15 nm demonstrate no aggregation and fairly even dispersion. Also, moiré patterns of the Au NPs exhibit one-dimensional fringe lattices due to moiré interference. It indicates that these NPs are crystalline.<sup>39</sup>

Meanwhile, we use HRXPS to further examine the oxidation states of the main components of the prepared Ch/Au NCs. Figure 5 shows the HRXPS survey spectrum of the prepared NCs. The signals of Au, N, C and O are clearly shown. Generally, Ch is composed of H, C, N and O. It confirms that the prepared Ch/Au NCs are indeed composed of Au and Ch. Subsequently, investigations of the oxidation states were further performed on the components of Au and N of the NCs. Figure 6 displays the HRXPS Au  $4f_{7/2-5/2}$  core-level spectra of the prepared Au NPs on Ch before and after the reduction of positively charged Au complexes. As shown in spectrum b, after heating the solution for reducing positively charged Au complexes to prepare Ch/Au NCs, the doublet peaks are located at 84.0 and 87.7 eV, which can be assigned to Au(0).<sup>40</sup> It confirms that the Au NPs on Ch are elemental states. As comparing spectrum a (representing the positively charged Au-containing complexes before reduction) with spectrum b (representing the elemental Au(0) NPs), it is found that there are additional components of Au shown in the region of higher binding energy for the positively charged Au-containing complexes. The oxidized Au shown at 85.2 and 86.7 eV in spectrum a can be assigned to monovalent Au(I) and



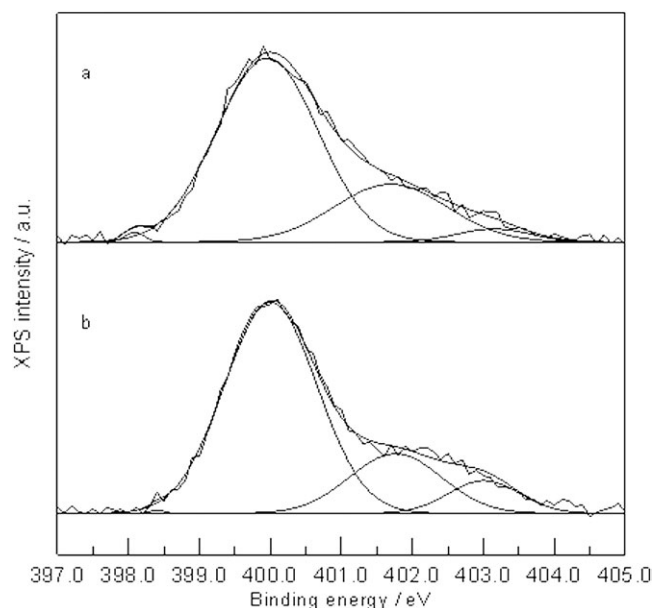
**Figure 5.** HRXPS survey spectrum of prepared Ch/Au NCs.

trivalent Au(III), respectively.<sup>41</sup> Moreover, the full width at half maximum (FWHM) of HRXPS Au  $4f_{7/2}$  core-level spectra are 1.7 and 1.1 eV for Ch/Au NCs before and after heating treatment. These results also confirm their different oxidation states. Figure 7 shows the XPS N 1s spectra of Ch with the adsorbates of Au before and after reduction via heating treatment. As shown in the literature,<sup>42</sup> after further deconvolution of N 1s spectra into four component peaks, the positively charged nitrogen ( $-N^+H-$ ) species with the higher binding energy (BE) tail (BE > 401 eV) can be used to determine the oxidation level of conductive polypyrrole (PPy). This oxidation level is calculated



**Figure 6.** HRXPS Au  $4f_{7/2-5/2}$  core-level spectra of prepared Ch/Au NCs before (spectrum a) and after (spectrum b) heating at a rate of 6°C/min.





**Figure 7.** HRXPS N 1s core-level spectra of prepared Ch/Au NCs before (spectrum a) and after (spectrum b) and after heating at a rate of 6°C/min.

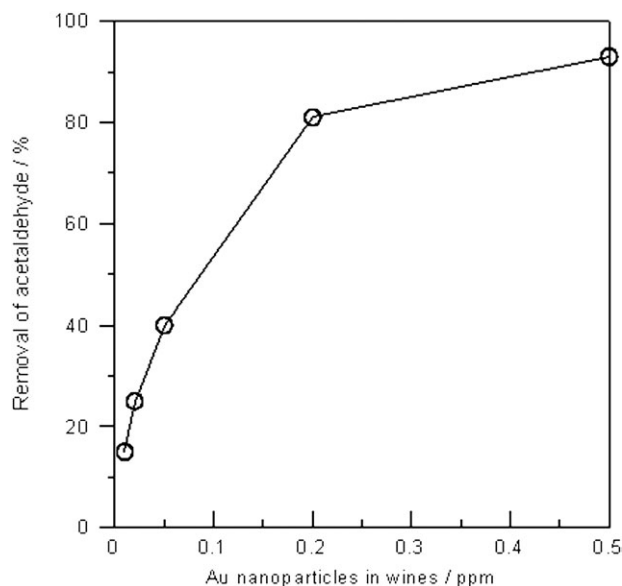
from the ratio of the peak area of  $N^+$  ( $BE > 401$  eV) to that of the total N 1s shown in the XPS spectrum. Here we employ the similar deconvolution treatment to distinguish the oxidation states of N of Ch before and after the formations of Au (0) NPs on Ch. The results show that the oxidation levels of N of Ch before and after the formations of Au (0) NPs all are 0.28. Thus, it certifies that the reduction via heating only works on the positively charged Au. The charge transfer between Au and N during heating treatment didn't occur.

#### Catalytically testing of Chitosan/Gold Nanocomposites

As shown in the literature, the most well known catalytic activity of Au NPs is their capability for instantaneously oxidizing CO into  $CO_2$  at low and room temperatures.<sup>43,44</sup> In our previous study,<sup>45</sup> we found that the sonoelectrochemically prepared Au NPs are active catalysts for the decomposition of 2000 ppm acetaldehyde in 40% (v/v %) ethanol solutions. In this work, to investigate the effects of the prepared Ch-capped Au NPs on the enhanced decompositions of acetaldehydes at room temperature, prepared Ch-capped Au NPs-containing solutions were added in commercial white spirits (58% ethanol, v/v %) with 120 ppm acetaldehydes, as described in the experimental section. The final concentrations of Au NPs in spirits were controlled at 0.05 ppm. Experimental analyses indicated that the acetaldehydes in spirits were decomposed by ca. 40% and 13% based on Ch-capped Au NPs and commercial ones with similar particle sizes of ca. 12 nm in the same Au concentration, respectively, after testing for three days. It is a marked increase in catalytic decomposition of acetaldehydes by ca. 200% of magnitude by using Ch-capped Au NPs, as compared with commercial Au NPs. Recently, Wu et al.<sup>46</sup> also reported photoinitiated oxidation degradation of gaseous acetaldehyde by using  $TiO_2$ -based photocatalysts. In their report, UV or visible lights are necessary for initiating the photocatalysts. It is noticeable the decomposition

of acetaldehyde in spirits by using Ch-capped Au NPs in this work was performed in dark cells. To study the mechanism of the improved catalytic activities for toxic acetaldehyde based on Ch/Au NCs, a control solution containing 0.1N NaCl and 1 g/L Ch (the same solutes in preparing Ch/Au NCs) was also prepared. Then the same experiment for removing acetaldehyde was performed in the control solution. Experimental result indicates that the acetaldehydes in spirits can be removed by ca. 8%. This phenomenon can be ascribed to the easy formation of Schiff bases between Ch and acetaldehydes.<sup>30</sup> Thus, it is favorable for the subsequent decomposition of acetaldehydes by the Au NPs capped on the Ch. Therefore, the mechanism of the improved activity observed on Ch/Au NCs for the catalytic decomposition of toxic acetaldehyde is proposed as follows. Acetaldehyde can be concentrated onto the Ch matrix by the Schiff reaction. Then it is decomposed by the Au NPs capped on the Ch. Meanwhile, catalytic activities for decomposition of acetaldehydes of Ch/Au NCs with low and high concentrations of Au NPs in spirits were also examined. Experimental analyses indicated that the acetaldehydes in spirits were decomposed by ca. 15 % and 93 % based on Ch-capped Au NPs with Au concentrations of 0.01 and 0.5 ppm, respectively, after testing for three days. The detailed correlation of Au NPs concentration to acetaldehyde removals was demonstrated in Figure 8.

Moreover, further experimental results indicate that concentrations of ethanol (58% ethanol, v/v%), acetic acid (4100 ppm) and acetic ester (5500 ppm) in spirits were unchanged after experiments for catalytic decomposition of acetaldehyde in spirits for three days. Therefore, the mechanism of the catalytic oxidation decomposition of acetaldehyde on Ch/Au NCs in this work is proposed as follows.



**Figure 8.** Removals of acetaldehyde in spirits after adding Ch-capped Au NPs with different concentrations of Au for 3 days.

## CONCLUSIONS

In this work, a new pathway to prepare Ch/Au NCs is successfully developed. Ch works as a medium for the adsorbed positively charged Au complexes. Then the complexes can be further reduced to elemental Au NPs on Ch in solutions. The efficiency of the catalytic decomposition of acetaldehyde in spirits by using Ch-capped Au NCs is significantly increased by 200% of magnitudes, as compared with that by using commercial Au NPs. The mechanism of the improved activity observed on Ch/Au NCs for the catalytic decomposition of toxic acetaldehyde is proposed as that acetaldehyde can be concentrated onto the Ch matrix by the Schiff reaction. Then it is decomposed by the Au NPs capped on the Ch.

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