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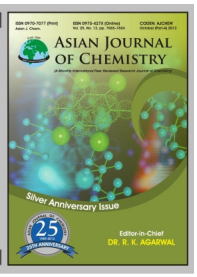

# Synthesis of Gold Nanoparticles in Presence of Ionic Liquid [Bmin][$CF_3SO_3$] with Humic Acid under Microwave Irradiation and Its Application as a Nanocatalyst

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Gold nanoparticles were synthesized in the presence of ionic liquid [Bmin][$CF_3SO_3$] with humic acid for 90 s under microwave irradiation. The resulting gold nanoparticles were confirmed by UV-visible spectroscopy, X-ray diffraction and transmission electron microscopy. The catalytic effect of gold nanoparticles was investigated for the oxidation of 2-hydroxybenzyl alcohol to produce 2-hydroxybenzaldehyde in the presence of 3-chloroperoxybenzoic acid and hydrogen peroxide in methanol. The reaction was completed after 160 min using these gold nanoparticles as a catalyst and the product was identified by high performance liquid chromatography (HPLC) with UV-visible detector.

**Key Words: Gold nanoparticles, Humic acid, 2-Hydroxybenzaldehyde, Microwave irradiation.**

## INTRODUCTION

Nanotechnology is a branch of science and engineering dedicated to materials with dimensions in the order of 100 nm or less[1]. Nanoparticles have been shown to be highly efficient as supports in heterogeneous catalysis owing to their high specific surface area[2]. Gold nanoparticles, in particular, not only exhibit unique optical and catalytic properties but also have excellent chemical stability and biocompatibility[3]. These characteristics lead to many potential applications, such as optics, electrochemistry, catalysis and biochemical sensing[4-6]. Different methods for the synthesis of supported gold nanoparticles have been reported to obtain well-dispersed particles with nanometer sizes. Among these methods, the microwave and sonochemical synthetic methods are unique and unconventional method[7].

In this study, an eco-friendly ionic liquid, ([Bmin][$CF_3SO_3$]) was used for the reaction instead of an organic solvent. The ionic liquid has the characteristics of liquid within a wide temperature range. Because most of ionic liquids have a vapour pressure close to zero, they can exist safely at high temperature (400 ºC) at which general solvents vaporize. Therefore, ionic liquids are attractive material as eco-friendly alternative solvents and are used in a range of areas, including nanoparticles synthesis[8].

A variety of reducing agents have been used in nanomaterial synthesis. In particular, sodium borohydride is a famous material for the syntheses of nanoparticles as a reducing reagent. In this experiment, humic acid as a reducing agent was applied to the synthesis of gold nanoparticles. Humic acid is a principal component of humic substances, which are the major organic constituents of soil (humus), peat, coal, many upland streams, dystrophic lakes and ocean water[9]. The reducing properties and the polyelectrolyte nature of humic acid is due to the presence of polar functional groups, such as phenols, hydroxyls, carbohydrate subunit and the presence of carboxylic acid[10,11]. Many attempts have been made to synthesize nanoparticles using humic acid because of the presence of aromatic and aliphatic moieties that affect its interaction with metals/organics formatting nanostructures[12-14]. This paper reports the use of humic acid as a reduction material in the single-step synthesis of gold nanoparticles in the presence of an ionic liquid under microwave irradiation and the catalytic activity of gold nanoparticles in the oxidation of 2-hydroxybenzyl alcohol to 2-hydroxybenzaldehyde with oxidizing agents.

## EXPERIMENTAL

For synthesis of gold nanoparticles, 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmin] [$CF_3SO_3$], 95 %), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.999 %), humic acid, 2-hydroxybenzyl alcohol (99 %) and 2-hydroxybenzaldehyde (98 %) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 3-chloroperoxybenzoic acid was obtained from Acros (75 %, Beel, Belgium) and hydrogen peroxide was purchased from Samchun (34.5 %, ACS reagent,

Seoul, Korea). HPLC grade methanol (Sigma-Aldrich, St. Louis, MO, USA) was used as a mobile phase and deionized water was also used (18 MΩ).

For the synthesis of gold nanoparticles, microwave irradiation was conducted in multimode with continuous heating using a model MDS-2100 microwave oven (CEM Corporation, CEM, Matthews, NC)). The power range (maximum 950 W) of the microwave oven was adjusted to 42 %. UV-visible spectroscopy (400-800 nm) was performed using a Shimadzu UV-1601 PC spectrophotometer at room temperature and a 1-cm optical length cuvette. For TEM analysis, gold nanoparticles dispersed in an aqueous medium were placed on a carbon-coated copper grid. The particle size and morphology of the samples were examined by TEM (JEOL Ltd, JEM-200, Tokyo, Japan) at an acceleration voltage of 300 kV. XRD (Bruker D8 Advance, Germany) was performed to examine the crystal structures and crystallite sizes. For application, 2-hydroxybenzaldehyde was confirmed using HPLC SI-2 series (Shiseido, Tokyo, Japan) with a 3001 pump, 3002 UV-visible detector and 3004 oven. The mobile phase was deionized water and methanol 5:3 (v/v). The column used was a Xterra RP-18 5 μm, 3.9 mm × 150 mm. The temperature of column was 30 ºC. The volume of injection was 20 μL and the flow rate was 500 μL/min. The wavelength of detector used was 254 nm. The peak of retention time of 2-hydroxybenzyl alcohol and 2-hydroxybenzaldehyde was 3.24 and 6.92 min, respectively.

**Synthesis of gold nanoparticles:** Gold nanoparticles were synthesized in the presence of [Bmin][$CF_3SO_3$] by the reduction of hydrogen tetrachloroaurate(III)trihydrate ($HAuCl_4{\cdot}3H_2O$) with humic acid. The synthesis of gold nanoparticles can be summarized as follows: 5mL of deionized water containing 3 g of humic acid was mixed with 2 mg of hydrogen tetrachloroaurate(III)trihydrate ($HAuCl_4{\cdot}3H_2O$) and irradiated microwave for 90 s. The colour of solution was changed into purple.

**Test of catalytic activity of gold nanoparticles by HPLC:** The catalytic effect of the fabricated gold nanoparticles was examined by monitoring the change in the 2-hydroxybenzyl alcohols to 2-hydroxybenzaldehyde by HPLC. 3 mg of gold nanoparticles, 0.6 mg of $K_2CO_3$, 1 mL of $H_2O_2$, 0.02 g of 3-chloroperoxybenzoic acid and 0.6 mg of 2-hydroxybenzyl alcohol were added to a 100 mL vial. The catalytic activity was examined at 343 K in a shaking incubator. Also, the experiment which was removed only gold nanoparticles were performed as a control factor at the same time.

## RESULTS AND DISCUSSION

The gold nanoparticles were characterized by UV-visible spectroscopy, powder XRD, TEM. Fig. 1(a) shows that a typical surface plasmon band of gold nanoparticles after reduction with humic acid appeared at $\lambda_{max}$ = 577 nm. Fig. 1(b) is the peak of humic acid and Fig. 1(c) is the peak of $HAuCl_4{\cdot}3H_2O$, itself. From the UV-visible spectrum, the formation of gold nanoparticles from humic acid under microwave irradiation was confirmed.

Fig. 2 shows an XRD pattern of the typical gold nanoparticles. The characteristic peak for gold nanoparticles

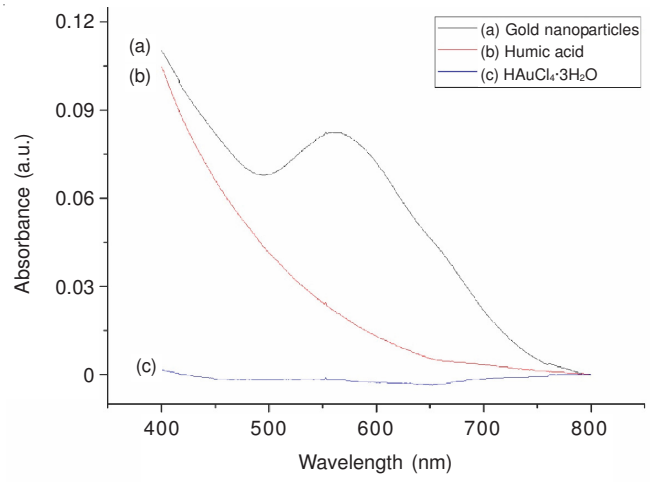


Fig. 1. UV-VIS spectrum of (a) gold nanoparticles, (b) humic acid and (c) $HAuCl_4{\cdot}3H_2O$

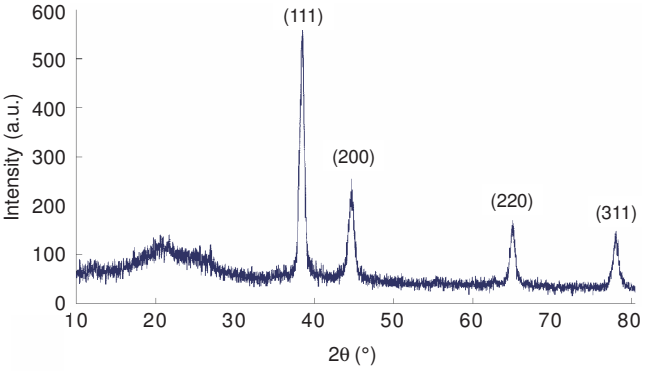


Fig. 2. XRD pattern of the gold nanoparticles produced in the presence of ionic liquid of [Bmin][$CF_3SO_3$] with humic acid under microwave irradiation

(2θ = 38.35, 44.36, 64.73, 77.63), marked by indices [(1 1 1), (2 0 0), (2 2 0), (3 1 1)], showed that the resulting gold nanoparticles were essentially crystalline. The crystallite sizes can be estimated from the XRD data using Scherrer's equation[15]:

$$D = \frac{K\lambda}{B\cos\theta}$$

where λ is the X-ray wavelength (0.154 nm) and θ is the Bragg angle of the peak. B is based on the peak width (FWHM in radians), the crystallite size, D was calculated using the Scherrer's equation. The K is Scherrer's constant in the above equation accounts for the shape of the particle and is generally taken to have a value of 0.9. The size obtained from the Scherrer's equation yielded the apparent or mean crystallite size of a material. The average crystallite size was 10.5 nm in Table-1, as determined from the XRD data by Scherrer's equation, which was smaller than the particle sizes calculated from the TEM images (20-50 nm). This might be due to overlap of the gold nanoparticles.

Fig. 3 shows a TEM image of the gold nanoparticles synthesized in deionized water solution under microwave irradiation. All nanoparticles had the shapes of triangle, hexagon, quasi-spherical type. The size of gold nanoparticles was obtained with a diameter range of 20-50 nm under microwave irradiation.

TABLE-1
MEAN CRYSTALLITE SIZE OF GOLD NANOPARTICLES BY SCHERRER'S EQUATION

| Peak | 2-Theta | FWHM (B) | δ (nm) |
|---|---|---|---|
| G1 | 38.35 | 0.751 | 11.2 |
| G2 | 44.36 | 0.913 | 9.4 |
| G3 | 64.73 | 0.852 | 11.0 |
| G4 | 77.63 | 0.994 | 10.3 |
| Average | – | – | 10.5 |

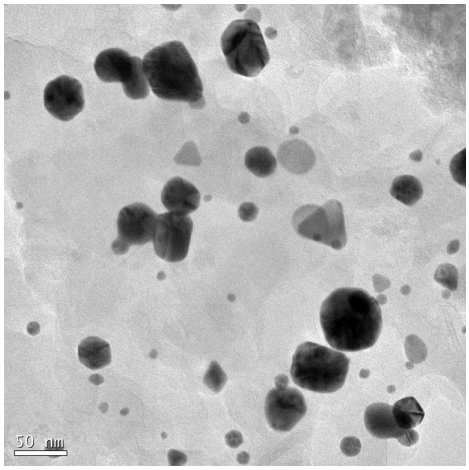


Fig. 3. TEM image of the gold nanoparticles produced in the presence of ionic liquid of [Bmin][$CF_3SO_3$] with humic acid under microwave irradiation

Also, the catalytic effect of gold nanoparticles in oxidation of 2-hydroxybenzyl alcohol was examined by HPLC. Fig. 4 shows that the content of 2-hydroxybenzyl alcohol decreased gradually for 160 min, whereas the quantity of 2-hydroxybenzaldehyde increased gradually. On the other hand, when the hydrogen peroxide and 3-chloroperoxybenzoic acid, were used for the reaction without gold nanoparticles, the concentration of 2-hydroxybenzyl alcohol barely changed over a 160 min period. This suggests that gold nanoparticles acted as an excellent nanocatalyst for the oxidation of 2-hydroxybenzyl alcohol to 2-hydroxybenzaldehyde.

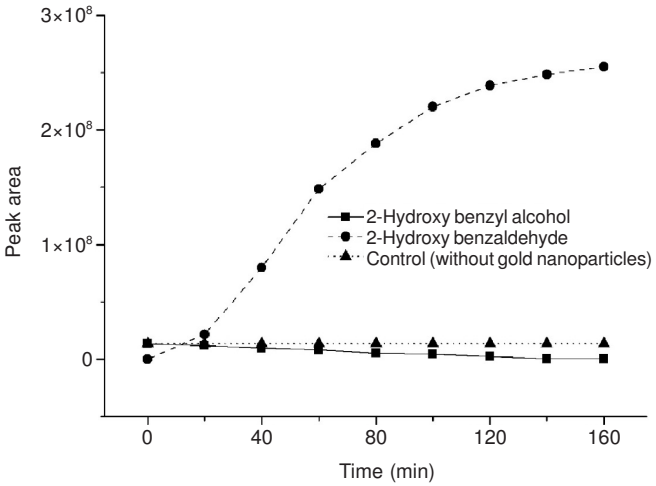


Fig. 4. Monitoring of catalytic activity of gold nanoparticles by HPLC for the oxidation of 2-hydroxybenzyl alcohol

## Conclusion

Gold nanoparticles were synthesized in the presence of ionic liquid of [Bmin][$CF_3SO_3$] with humic acid as a reducing agent and hydrogen tetrachloroaurate(III)trihydrate in an aqueous solution under microwave irradiation for 90 s. XRD pattern of gold nanoparticles shows (2θ = 38.35, 44.36, 64.73 and 77.63), which were assigned to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) planes, respectively.The size of the gold nanoparticles ranged from 20 to 50 nm, the shape of gold nanoparticles observed at triangle, hexagon, quasi-sphere type in TEM. As we compared the size of gold nanoparticles with TEM and XRD, the difference of gold nanoparticle size, it may be due to the overlap of the gold nanoparticles when they were grown as a nanoparticle status.The synthesized gold nanoparticles were used as a nanocatalyst for the oxidation of 2-hydroxybenzyl alcohol to 2-hydroxybenzaldehyde, we confirmed the catalytic effect of gold nanoparticles as a nanocatalyst by HPLC. The 2-hydroxybenzyl alcohol was converted successfully to 2-hydroxybenzaldehyde and the time of oxidation was taken for 160 min.

## ACKNOWLEDGEMENTS

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