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Preparation and Catalytic Activity of Gold Nanoparticles Stabilized by Poly(N-Vinylpyrrolidone) and Deposited onto Aluminum Oxide

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Abstract Gold nanoparticles (AuNPs) stabilized by poly(N-vinylpyrrolidone) (PVP) were prepared by "one-pot" synthetic protocol and characterized by UV-Vis spectroscopy, DLS and TEM. According to DLS measurements the average size of AuNPs stabilized by PVP in aqueous solution is varied from 10 to 25nm. The PVP stabilized AuNPs (AuNPs-PVP) were deposited on the surface of aluminum oxide (Al_2O_3/AuNPs-PVP) and its catalytic activity was evaluated with respect to decomposition of hydrogen peroxide. It was found that the amount of AuNPs-PVP deposited onto Al_2O_3 is extremely low and in the range of 0.06-0.1%. TEM images reveal that the average size of AuNPs-PVP deposited on the surface of Al_2O_3 is equal to 10-30 nm. The rate of H_2O_2 decomposition in the presence of Al_2O_3/AuNPs-PVP exhibits induction period in dependence of the molecular weight of PVP and increases in the following order PVP-$350{\cdot}10^3$ > PVP-$40{\cdot}10^3$ > PVP-$10{\cdot}10^3$.

Keywords: *gold nanoparticles, poly(N-vinylpyrrolidone), stabilization, deposition, aluminium oxide, catalysis*

1. Introduction

Nowadays, gold nanoparticles (AuNPs) due to their unique properties such as optical, mechanical, electrical and catalytic activity play crucial role for industries [1,2,3]. Catalytic activity of AuNPs is well known since 1980's when the work of Haruta has been published [4]. Catalysts based on AuNPs and supported on metal oxides have attracted researcher's attention because of their high catalytic activity for various oxidation and reduction reactions under mild conditions [5]. For instance, authors [6] used AuNPs supported on ceria oxide for oxidation of carbon monoxide at low temperature. A catalytic property of gold nanoparticles deposited on aluminum oxide depends on stabilizing method of AuNPs and their dimensions. There are many researches devoted to investigation of catalytic properties of gold nanoparticles which are deposited on different supporting agents such as non-reducible (Al_2O_3, SiO_2 etc.) and reducible oxides (Fe_2O_3, CeO_2, TiO_2, MnO_x etc.) [7,8,9]. AuNPs can also be deposited at the poly(ethyleneterephlate) surface by ion-beam irradiation [10].

In the present work we stabilized AuNPs with poly(N-vinylpyrrolidone) having different molecular weights, determined their sizes, prepared aqueous solutions of AuNPs, immobilized them on aluminum oxide by impregnation method and studied the catalytic activity.

2. Experimental

2.1. Materials

Standard aqueous solution of tetrachloauric acid $HAuCl_4$ with concentration 100mg·L^{-1} was purchased from Sigma-Aldrich. Poly(N-vinylpyrrolidone) (PVP) with different molecular weights $10{\cdot}10^3$, $40{\cdot}10^3$, $350{\cdot}10^3$ and aluminum oxide were also purchased from Sigma-Aldrich.

2.2. Methods

Absorption spectra of AuNPs were determined at room temperature by UV-Vis spectroscopy (Specord 210 plus BU, Germany). The sizes of AuNPs were determined with the help of DLS device Malvern Zetasizer Nano ZS90 (UK). Concentration of Au in supernatant was determined by ion-coupled plasma atomic emission spectroscopy ICP-AES "Optima 5100DV" (Perkin Elmer, USA). Transmission electron microscopy (TEM) image was recorded on a JEOL JEM–1011LA (Japan).

2.3. Preparation of Gold Nanoparticles

PVP stabilized AuNPs were obtained by "one-pot" synthetic protocol [11]. Aqueous solutions of $HAuCl_4$ (5mL), 0.5M KOH (4mL), and 4% PVP (5mL) were mixed, stirred and heated up to 100°C during several minutes. As a result the colored solutions of AuNPs stabilized by PVP (PVP-AuNPs) were obtained as shown in Figure 1.

2.4. Deposition of PVP-AuNPs on Aluminum Oxide

PVP-AuNPs were supported on Al_2O_3 by impregnation method. For this 0.5g of Al_2O_3 was added to 5mL of PVP-AuNPs and stirred during 5 hours. After the precipitate was separated by preparative centrifuge "Eppendorf 5810R" (Germany) at $10{\cdot}10^3$rpm, then it was washed out 5 times with distilled water. The content of Au in supernatant was determined by the ICP-AES. The precipitate was dried at 50 ℃. The powders of Al_2O_3 with supported PVP-AuNPs (Al_2O_3/PVP-AuNPs) were used as catalysts for decomposition of H_2O_2 (Figure 2).

Figure 1. Samples of AuNPs stabilized by PVP with $M_n = 10{\cdot}10^3$ (1), $40{\cdot}10^3$ (2) and $350{\cdot}10^3$ (3)

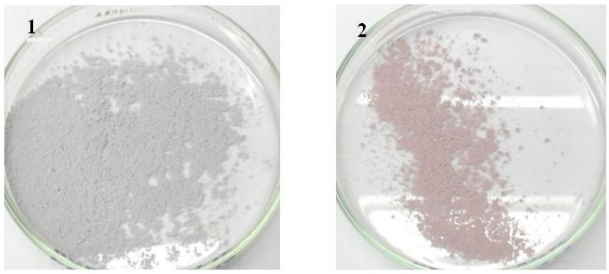

Figure 2. Samples of Al_2O_3 with immobilized PVP-AuNPs. $M_n = 40{\cdot}10^3$ (1) and $350{\cdot}10^3$ (2)

3. Results and Discussion

3.1. Characterizations of AuNPs

Visible spectra of freshly prepared PVP-AuNPs show the absorption bands with maxima at 520-550nm corresponding to so-called "plasmon resonance" spectra that are specific for AuNPs [12].

Figure 3 represents the size distribution of AuNPs stabilized by PVP with various molecular weights. In dependence of the molecular weights of PVP the size distribution of PVP-AuNPs is varied from 10 to 25nm.

TEM image of AuNPs-PVP deposited onto Al_2O_3 reveals that there are no big agglomerates of the gold nanoparticles (Figure 4). TEM micrograph clearly shows the attached to the surface of Al_2O_3 gold nanoparticles with average size varying from 10 to 30nm. TEM results are in good agreement with hydrodynamic sizes of AuNPs measured by DLS.

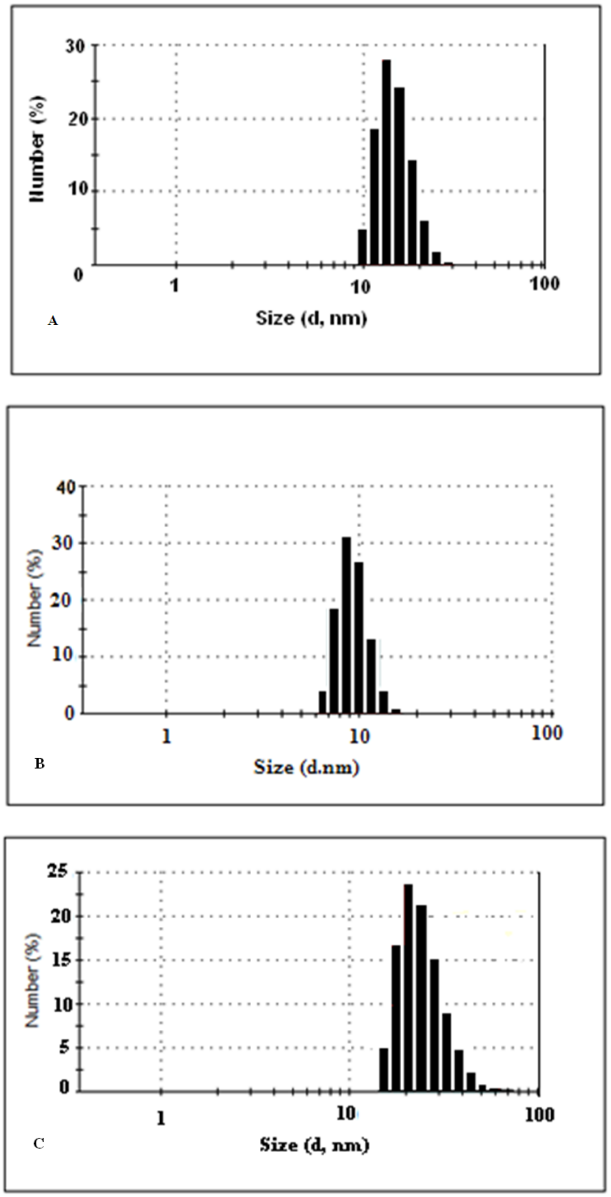

Figure 3. Size distribution of AuNPs stabilized by PVP with $M_n = 10{\cdot}10^3$ (A) $40{\cdot}10^3$ (B) and $350{\cdot}10^3$ (C)

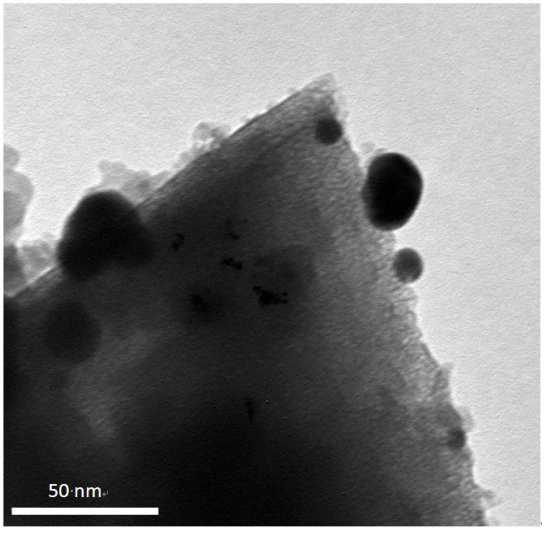

Figure 4. TEM image of AuNPs-PVP-$40{\cdot}10^3$ supported on Al_2O_3

3.2. Decomposition of Hydrogen Peroxide

The catalytic activity of AuNPs depends on the size of gold nanoparticles, e.g. the smaller AuNPs size the higher catalytic activity [3]. However, in our case the catalytic activity of AuNPs also depends on the amount of gold nanoparticles deposited on the surface of Al_2O_3. We have found that the concentration of Au nanoparticles deposited on Al_2O_3 is very small and equal to 0.06-0.1%. Despite of this fact, as illustrated in Figure 6, the rate of H_2O_2 decomposition changes exponentially while Al_2O_3 itself and PVP supported onto Al_2O_3 do not show any catalytic activity in decomposition of H_2O_2.

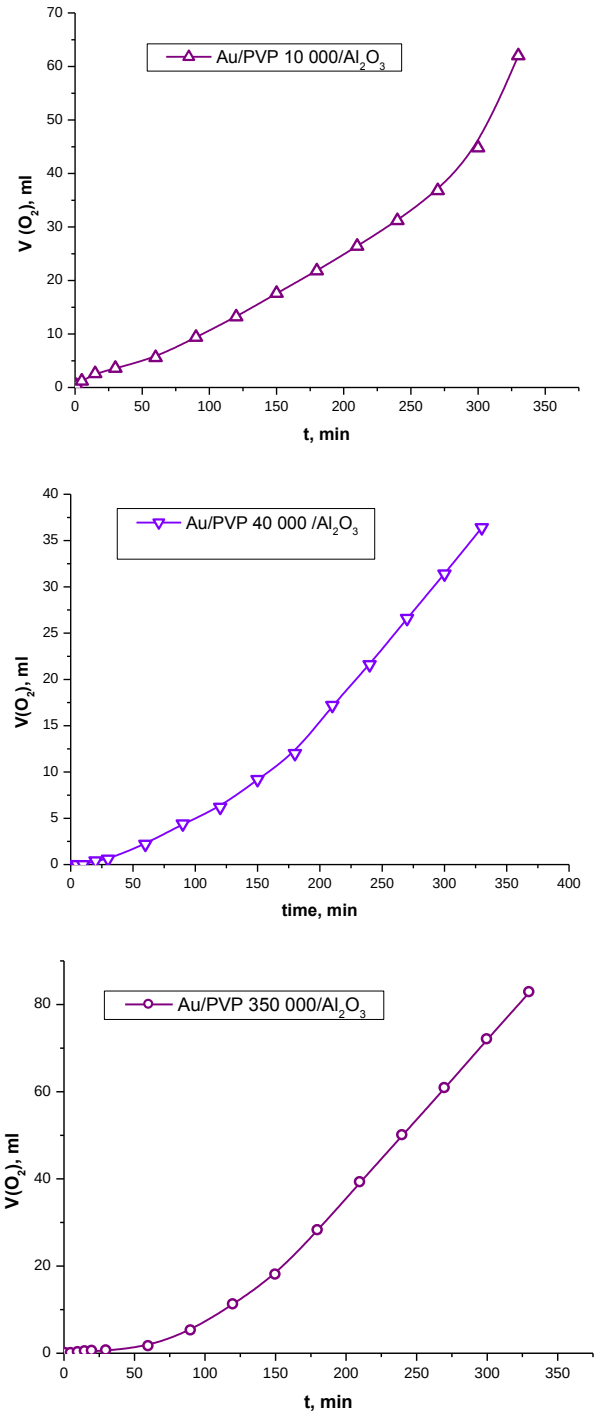

Figure 5. Time dependent decomposition of hydrogen peroxide in the presence of gold nanocatalysts

It should be noted that in the presence of Al_2O_3/AuNPs-PVP the rate of H_2O_2 decomposition exhibits an induction period that depends on the molecular weight of PVP and changes in the following order PVP-$350{\cdot}10^3$ > PVP-$40{\cdot}10^3$ > PVP-$10{\cdot}10^3$. As seen from Figure 5, decomposition of H_2O_2 in the presence of Al_2O_3/AuNPs-PVP-$350{\cdot}10^3$ starts after 1h while the same reaction starts immediately in the presence of Al_2O_3/AuNPs-PVP-$10{\cdot}10^3$. This is probably explained by less accessibility of gold nanoparticles to substrate due to surrounding of catalytic centers by high molecular weight PVP.

4. Conclusion

Poly(N-vinylpyrrolidone) protected gold nanoparticles were prepared by "one-pot" method and impregnated on the surface of Al_2O_3. The average size of AuNPs stabilized by PVP is varied from 10 to 25nm. The amount of deposited onto Al_2O_3 gold nanoparticles is extremely low and in the range of 0.06-0.1%. TEM results show that the average size of gold nanoparticles attached to the surface of Al_2O_3 is varied from 10 to 30nm. The catalytic activity of Al_2O_3/AuNPs-PVP nanocatalysts increases exponentially with induction period of time in dependence of molecular weight of PVP.

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References

[1] Motoyuki I., Hidehiro K, "Surface modification for improving the stability of nanoparticles in liquid media," *KONA Powder and particle journal*, 119-129, 2009.

[2] Suresh K. Balasubramanian, Liming Yang, Lin-Yue L. Yung, Choon-Nam Ong, Wei-Yi Ong, Liya E. Yu, "Characterization, purification and stability of gold nanoparticles," *Biomaterials*, 31, 9023-9030, 2010.

[3] Jingfang Zhou, John Ralston, Rossen Sedev, David A. Beattie, "Functionalized gold nanoparticles: Synthesis, structure and colloid stability," *Journal of Colloid and Interface Science*, 331, 251-262, 2009.

[4] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, "Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature far Below 0 ℃," Chemistry Letters, 16, 405-408, 1987.

[5] Lu-Cun Wang, Xin-Song Huang, Qian Liu, Yong-Mei Liu, Yong Cao, He-Yong He, Kang-Nian Fan, Ji-Hua Zhuang, "Gold nanoparticles deposited on manganese(III) oxide as novel efficient catalyst for low temperature CO oxidation," *Journal of Catalysis*, 259, 66-74, 2008.

[6] S.A.C. Carabineiro, A.M.T. Silva, G. Drazic, P.B. Tavares, J.L. Figueiredo, "Gold nanoparticles on ceria supports for the oxidation of carbon monoxide," Catalysis Today, 154, 21-30, 2010.

[7] Lu-Cun Wang, Qian Liu, Xin-Song Huang, Yong-Mei Liu, Yong Cao, Kang-Nian Fan, "Gold nanoparticles supported on manganese oxides for low-temperature CO oxidation," *Applied Catalysis B: Environmental*, 88, 204-212, 2009.

[8] V. Costa, M. Estrada, Y. Demidova, I. Prosvirin, V. Kriventsov ,R. Cotta, S. Fuentes, A. Simakov, E. Gusevskaya, "Gold nanoparticles supported on magnesium oxide as catalysts for the aerobic oxidation of alcohols under alkali-free conditions," *Journal of Catalysis*, 292, 148-156, 2012.

[9] K.Y. Ho and K.L. Yeung, "Properties of TiO2 support and the performance of Au/TiO2 catalyst for CO oxidation reaction," *Gold Bull.*, 40, 15-30, 2007.

[10] Jai Prakash, A.Tripathi, V Rigato, J C Pivin, etc. "Synthesis of Au nanoparticles at the surface and embedded in carbonaceous matrix by 150 keV ion irradiation," *Journal of Physics D: Applied Physics*, 44(12), 2011.

[11] S. Ram, L. Agrawal, A. Mishra, S. Roy, "Synthesis and optical properties of surface stabilized gold nanoparticles with poly(vinyl pyrrolidone). Polymer molecules of a nanofluid," *Advanced Science Letters*, 4, 3431-3438, 2011.

[12] D.L. Feldheim, C.A. Foss, *Metal Nanoparticles: Synthesis, Characterization and Applications*, Basel Marsel Dekker Inc., New York, 2002.

[13] B.K. Min, C.M. Friend, "Heterogeneous gold-based catalysis for green chemistry: Low-temperature CO oxidation and propene oxidation," *Chemical Reviews* 107, 2709-24, 2007.