

ALKYL CHAIN MODIFIED GOLD NANOPARTICLES FOR CATALYSIS

ŘEZANKA Michal, PETRŽÍLKOVÁ Michaela, STIBOR Ivan

Technical University of Liberec, Liberec, Czech Republic, EU, michal.rezanka@tul.cz

Abstract

Attachment of organic molecules is usually accomplished through the thiol functionality, but it would be desirable to have alternatives. Herein we would like to report preparation of gold nanoparticles with diameter of a few nanometers and their modification by alkyl chains. Such functionalization was achieved by direct attachment of organic moieties present in organo-tin compounds. The modified nanoparticles are expected to be more stable than the thiolated ones thus providing broader field of use in the catalysis of chemical reactions.

Keywords: Gold, nanoparticles, alkyl, catalysis

1. INTRODUCTION

In last few years, reports on gold-based catalysts have increased significantly, because various organic transformations can be performed under mild conditions with high regio- and chemo-selectivities. [1] Bulk gold metal is considered inactive, however, gold in the form of nanometer size particles possesses a higher surface to volume ratio and this leads to high chemical reactivity. The extent of these properties depends strongly on the size, morphology, and nanoparticle stabilization, and is therefore linked to the nanoparticles' synthesis conditions. [2]

There also arises a need to prepare gold nanoparticles (AuNPs) modified with suitable ligand on their surface, which can be subsequently exchanged with alkyl chain. One of the possibilities is to prepare triphenylphosphine-stabilized AuNPs. [3]

Common approach how to modify AuNPs is to functionalize them with thiol-based ligands. [4] However, thiol-based ligands are not very stable under oxidation condition, which is a great disadvantage if the AuNPs are to be used to catalyze chemical reactions. Therefore it is better to use the ligands attached to the particles by C-Au bond. This type of monolayer on gold surface has also better permeability, which is an absolute requirement for the high catalytic activity of AuNPs.

C-Au bond functionalization of AuNPs has been done through carbon atoms of a terminal acetylene moiety [5] and of alkyl groups. [6] Even before these recent developments, it was discovered [7] that treatment of cleaned gold surfaces with solutions of covalent trialkylstannyl tosylates, trifluoroacetates, and triflates in organic solvents under ambient conditions leads to self-limiting growth of organic monolayers with distinctly different properties. These monolayers are more resistant to heat and to oxidative agents, less ordered, and more permeable. It was further found that the number of leaving groups such as tosylate is unimportant and that tetraalkylstannanes and dialkylstannadiyl ditosylates also produce the same monolayers as trialkylstannyl monotosylates. *n*-Butyl and *n*-octadecyl monolayers were also prepared *via* the solution deposition of *n*-butylmercury tosylate (C₄H₉HgOTs) and *n*-octadecylmercury tosylate (C₁₈H₃₇HgOTs) on Au, followed by a thermal annealing cycle for Hg removal. [8]

Herein we would like to report for the first time the preparation of butyl modified AuNPs by modification of nanoparticles with organo-tin compounds.

2. RESULTS AND DISCUSSION

At the outset, triphenylphosphine-stabilized AuNPs were prepared according to Hutchison et al. [3] procedure in a good yield. Attachment of ligands was confirmed by ¹H-NMR (in CDCl₃), where protons from triphenylphosphine appeared in aromatic region (**Fig. 1**).

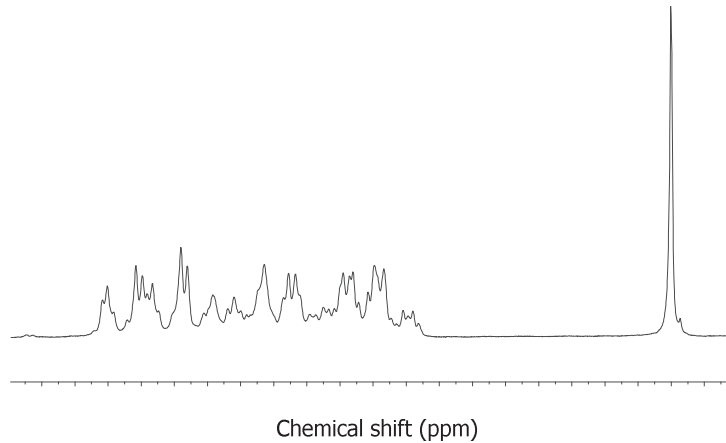


Fig. 1 ¹H-NMR (in CDCl₃) of triphenylphosphine-stabilized AuNPs

A pilot study of the ligand exchange of triphenylphosphine AuNPs was done by dodecanethiol. [4] Product was characterized by TEM and ¹H-NMR. TEM did not indicate any aggregation possibly occurred during the process (**Fig. 2a**). Aromatic signals are not present in ¹H-NMR while aliphatic signals appeared (**Fig. 2b**), which indicates successful completion of ligand exchange.

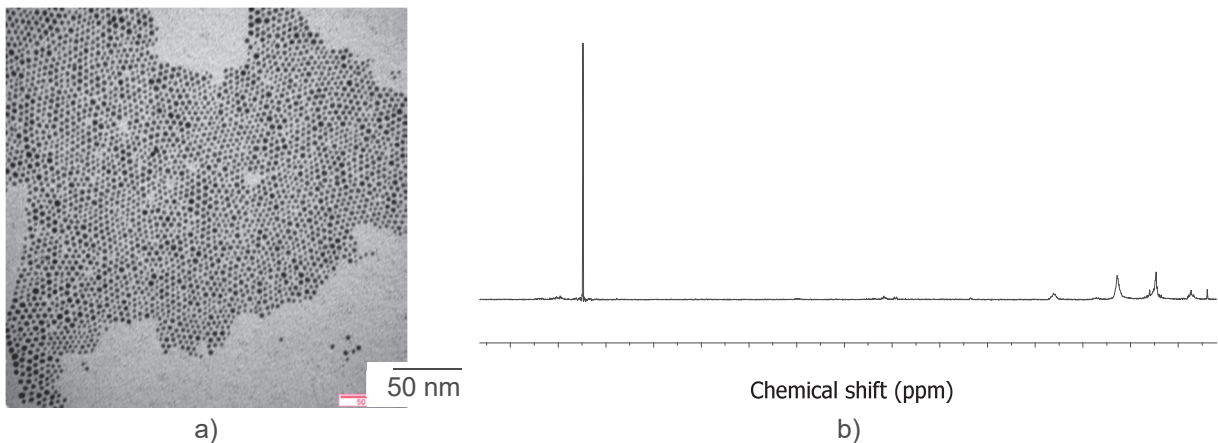


Fig. 2 Characterization of dodecanethiolated AuNPs a) by TEM; b) by ¹H-NMR

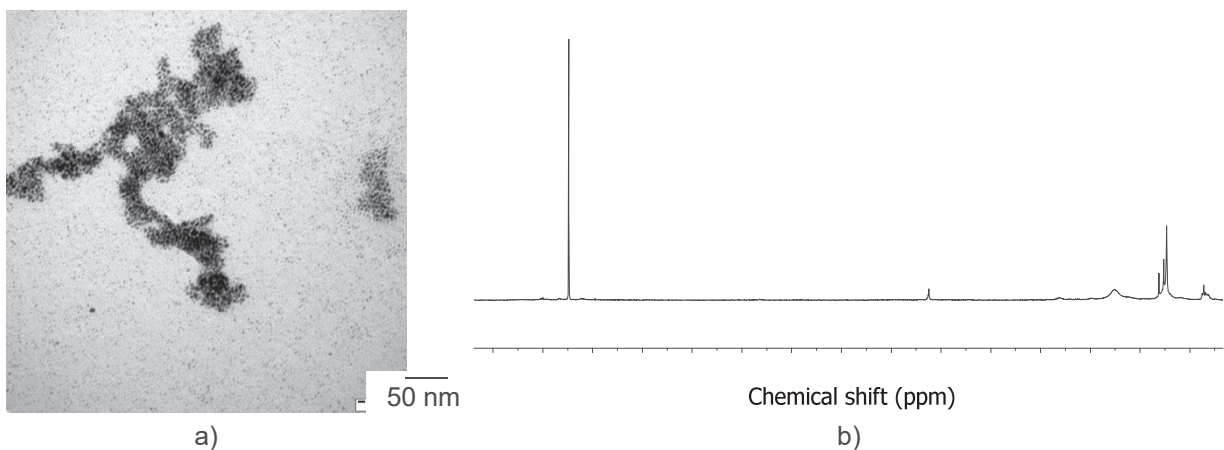


Fig. 3 Characterization of butylated AuNPs a) by TEM; b) by ¹H-NMR

Similarly, dibutyltin ditosylate was used for introducing butyl group attached to gold directly by C-Au bond. However, this reaction led only to degradation of reactants. Therefore toluene was used as a solvent and the reaction yielded butyl-AuNPs, which was characterized by TEM and ¹H-NMR. Average diameter of AuNPs is 3 nm and butyl signals are present in aliphatic region in NMR (**Fig. 3**).

3. EXPERIMENTAL

3.1. Triphenylphosphine-stabilized AuNPs

Procedure according to Hutchison et al.(3) started from 750 mg of HAuCl₄ · 3 H₂O yielded 273 mg of triphenylphosphine-stabilized AuNPs.

3.2. Dodecanthiolated AuNPs

The procedure for preparation of dodecanthiolated AuNPs was adapted from literature. [4] Briefly: A mixture of triphenylphosphine-stabilized AuNPs (10 mg) and octadecanethiol (11 μl, 45 μmol) dissolved in CHCl₃ (30 mL) was stirred for 24 h at 55 °C. After removal of the solvent, the crude product was dissolved in *i*-PrOH and purified by gel chromatography on Sephadex LH-20 with *i*-PrOH as eluent.

3.3. Butylated AuNPs

The procedure for preparation of butylated AuNPs was adapted from literature. [4] Briefly: A mixture of triphenylphosphine-stabilized AuNPs (10 mg) and dibutyltin ditosylate (26 mg, 45 μmol) dissolved in toluene (30 mL) was stirred for 24 h at 55 °C. After removal of the solvent, the crude product was dissolved in *i*-PrOH and purified by gel chromatography on Sephadex LH-20 with *i*-PrOH as eluent.

4. CONCLUSION

Triphenylphosphine-stabilized gold nanoparticles were prepared and ligand exchange to butyl group was achieved by reaction with dibutyltin ditosylate. The modified nanoparticles are expected to be more stable than the thiolated ones thus providing broader field of use in the catalysis of chemical reactions.

ACKNOWLEDGEMENTS

This work was supported by the Project LO1201 obtained through the financial support of the Ministry of Education, Youth and Sports in the framework of the targeted support of the “National Programme for Sustainability I”, the OPR&DI project Centre for Nanomaterials, Advanced Technologies and Innovation CZ.1.05/2.1.00/01.0005 and by the Project 14-02337S of Czech Grant Agency.

REFERENCES

- [1] TAKALE B. S., BAO M. YAMAMOTO Y. Gold nanoparticle (AuNPs) and gold nanopore (AuNPore) catalysts in organic synthesis. *Organic & Biomolecular Chemistry*. Vol. 12, No. 13, 2014, pp. 2005-2027.
- [2] JIMENEZ-RUIZ A., PEREZ-TEJEDA P., GRUESO E., CASTILLO P. M., PRADO-GOTOR R. Nonfunctionalized Gold Nanoparticles: Synthetic Routes and Synthesis Condition Dependence. *Chemistry - A European Journal*. Vol. 21, No. 27, 2015, pp. 9596-9609.
- [3] WANG R., ZHENG Z., KOKNAT F. W., MARKO D. J., MÜLLER A., DAS S. K., KRICKEMEYER E., KUHLMANN C., THERRIEN B., PLASSERAUD L., SÜSS-FINK G., PASQUALE A. D., LEI X., FEHLNER T. P., DIZ E. L., HAAK S., CARIATI E., DRAGONETTI C., LUCENTI E., ROBERTO D., LEE C. Y., SONG H., LEE K., PARK B. K., PARK J. T., HUTCHISON J. E., FOSTER E. W., WARNER M. G., REED S. M., WEARE W. W. Cluster and Polynuclear Compounds. *Inorganic Syntheses*. John Wiley & Sons, Inc., 2004., pp. 184-232.

- [4] WOEHRLE G. H., WARNER M. G., HUTCHISON J. E. Ligand Exchange Reactions Yield Subnanometer, Thiol-Stabilized Gold Particles with Defined Optical Transitions. *The Journal of Physical Chemistry B*, Vol. 106, No. 39, 2002, pp. 9979-9981.
- [5] HONG W., LI H., LIU S.-X., FU Y., LI J., KALIGINEDI V., DECURTINS S., WANDLOWSKI T. Trimethylsilyl-Terminated Oligo(phenylene ethynylene)s: An Approach to Single-Molecule Junctions with Covalent Au-C σ -Bonds. *Journal of the American Chemical Society*, Vol. 134, No. 47, 2012, pp. 19425-19431.
- [6] CHEN W., WIDAWSKY J. R., VÁZQUEZ H., SCHNEEBELI S. T., HYBERTSEN M. S., BRESLOW R., VENKATARAMAN L. Highly Conducting π -Conjugated Molecular Junctions Covalently Bonded to Gold Electrodes. *Journal of the American Chemical Society*, Vol. 133, No. 43, 2011, pp. 17160-17163.
- [7] KHOBRAGADE D., STENSRUD E. S., MUCHA M., SMITH J. R., POHL R., STIBOR I., MICHL J. Preparation of Covalent Long-Chain Trialkylstannyl and Trialkylsilyl Salts and an Examination of their Adsorption on Gold. *Langmuir*, Vol. 26, No. 11, 2010, pp. 8483-8490.
- [8] SCHOLZ F., KALETOVÁ E., STENSRUD E. S., FORD W. E., KOHUTOVÁ A., MUCHA M., STIBOR I. MICHL J., VON WROCHEM F. Formation of n-Alkyl Monolayers by Organomercury Deposition on Gold. *The Journal of Physical Chemistry Letters*, Vol. 4, No. 16, 2013, pp. 2624-2629.