ChemComm

Novel dendron-stabilized gold nanoparticles with high stability and narrow size distribution†

Min-Kyu Kim,[a] You-Moon Jeon,[a] Woo Sung Jeon,[a] Hee-Joon Kim,[a] Seung Gab Hong,[b] Chan Gyung Park[b] and Kimoon Kim*[a]

[a] *National Creative Research Initiative Center for Smart Supramolecules and Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea. E-mail: kkim@postech.ac.kr*

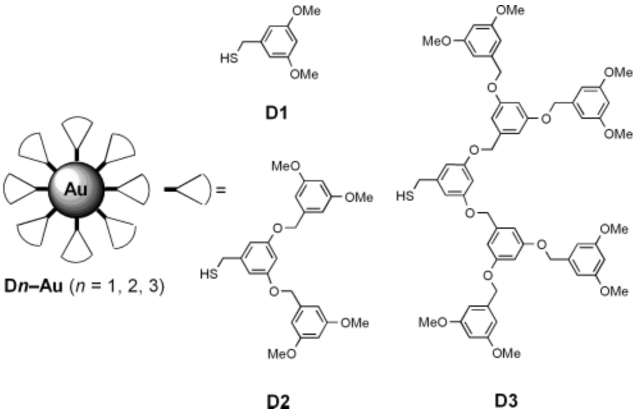
[b] *Center for Advanced Aerospace Materials, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea*

Received (in Cambridge, UK) 16th January 2001, Accepted 28th February 2001
First published as an Advance Article on the web 21st March 2001

Dendron-stabilized gold nanoparticles synthesized with Fréchet-type dendrons possessing a single thiol group at the focal point have small cores (average diameters of 2.4–3.1 nm) with narrow size distribution and remarkably high stability; in particular, the nanoparticles synthesized with the second generation dendron has an almost monodisperse core (2.4 ± 0.2 nm).

The chemistry of metal nanoparticles is one of the rapidly emerging research fields because of their potential applications to sensor devices, catalysis, nanoelectronics and many other area.[1] In particular, synthesis of large quantities of monodisperse nanoparticles of diameter < 10 nm is important for many of their applications. Following the seminal work of Schiffrin and coworkers[2] on stable gold clusters coated with alkanethiolate monolayers, many monolayer-stabilized gold nanoparticles have been reported.[3] Among them, dendrimer-stabilized gold nanoparticles, in which dendrimers play dual roles as a stabilizer and a permselective organic shell, have drawn considerable attention: early examples include gold colloids coated with poly(amidoamine) (PAMAM) dendrimers containing terminal amines.[4,5] However, they are only stable in solution and in the presence of excess of free dendrimers owing to the low affinity of the terminal amine groups for gold. Subsequently, PAMAM dendrimers partially functionalized with thiol groups have been used to enhance the stability of the dendrimer-stabilized gold nanoparticles.[6] Despite the enhanced stability, however, the resulting gold nanoparticles exhibit a rather broad size distribution because the degree of functionalization of the dendrimers is difficult to control precisely. Herein we report a new strategy where dendrons with a single thiol group at the focal point are used as a stabilizer and a permselective organic shell is employed to produce Au nanoparticles. This affords highly stable Au nanoparticles with smaller cores (ave. diam., 2.4–3.1 nm) and narrower size distribution. In fact, the nanoparticles synthesized with the second generation dendron has an almost monodisperse core (2.4 ± 0.2 nm). To our knowledge, this is the first set of examples of dendron-stabilized metal nanoparticles.[7]

First, second and third generation dendron-thiols (**D1**, **D2**, and **D3**, respectively; Scheme 1)[8] were prepared from the reaction of the corresponding Fréchet-type dendron-bromides[9] with thioacetic acid, followed by reduction with $LiAlH_4$.† Dendron-stabilized gold nanoparticles (**D1–Au**, **D2–Au**, and **D3–Au**) were synthesized by the two-phase method reported by Schiffrin with some modification.[2] More specifically, a two-phase mixture containing $HAuCl_4$ in water and tetraoctylammonium bromide in toluene was stirred, the organic layer separated and treated with dendron-thiol (dendron-thiol : Au = 2 : 1) and finally allowed to stir vigorously with an aqueous solution of $NaBH_4$ which afforded the crude product. Purification of the crude products by several cycles of precipitation–filtration–dissolution from toluene–ethanol solution yields **D1–Au** and **D2–Au** as black powders, and **D3–Au** as a black waxy powder. All of the nanoparticles are soluble in common organic solvents such as toluene, acetone, dichloromethane, chloroform or THF. They are remarkably stable both in solution, as well as in the solid state. Little decomposition or aggregation occurs even after several months in solution, as judged by their solubilities and UV–VIS spectra. Furthermore, these nanoparticles remain unchanged after standing overnight at elevated temperatures (at 50 °C in solution and at 160 °C in the solid state). The origin of the remarkable stabilities of these dendron-stabilized Au nanoparticles remains to be established.



Scheme 1 Schematic illustration of dendron-stabilized Au nanoparticles.

The core size and size distribution of the dendron-stabilized Au nanoparticles were examined by high resolution transmission electron microscopy (HR-TEM) (Fig. 1). In general, the present Au nanoparticles have a narrower size distribution than most of the previously known alkanethiolate-,[3a] arylthiolate-,[3b] or dendrimer-stabilized gold nanoparticles.[4–6] For example, **D1–Au**, having an average core size of 2.8 ± 0.3 nm, shows a narrower size distribution compared with the gold nanoparticles prepared with arylthiols of similar sizes.[3b] Most remarkably, **D2–Au** is nearly monodisperse with an average core size of 2.4 ± 0.2 nm. The core size and dispersity are not significantly affected by use of different molar ratios of **D2** : $HAuCl_4$ such as 0.5 and 6. Such monodispersity is seldom observed in unfractionated metal nanoparticles.[10] On the other hand, **D3–Au** has a larger and less narrow-disperse core (3.1 ± 0.6 nm) compared with **D1–Au** and **D2–Au**. The larger core size of **D3–Au** over those of **D1–Au** and **D2–Au** is in contrast to the earlier observation that the cores of dendrimer-stabilized Au nanoparticles decrease in size and dispersity with increasing dendrimer generation.[4,5] At present, we do not understand why

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† Electronic supplementary information (ESI) available: synthetic procedures and characterization data for dendron-thiols (**D1**–**D3**) and their gold nanoparticles. See http://www.rsc.org/suppdata/cc/b1/b100575h/

DOI: 10.1039/b100575h

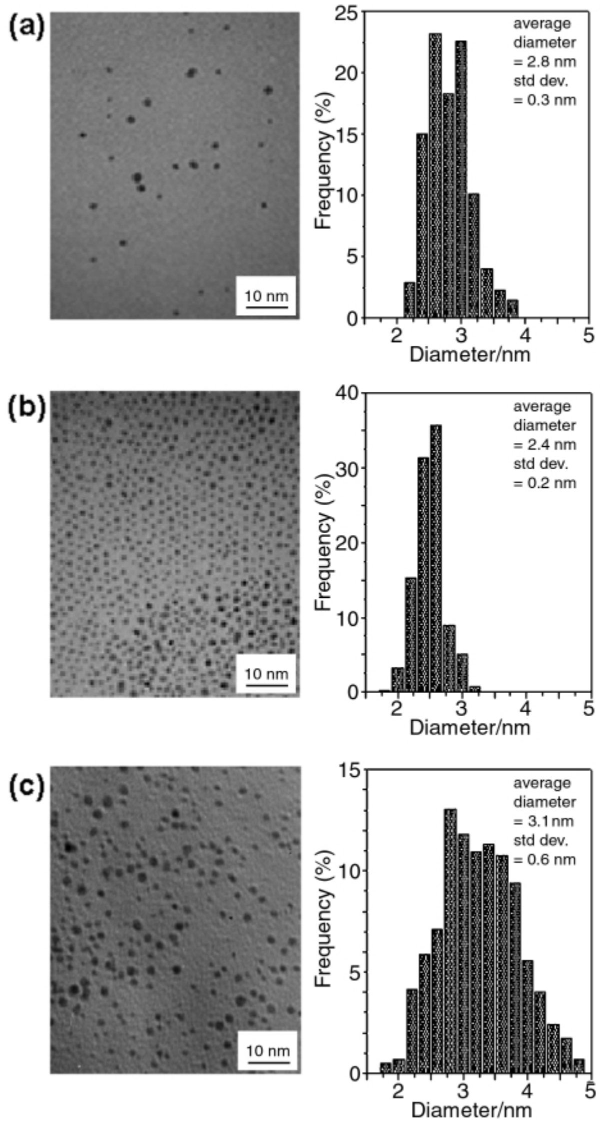

Fig. 1 TEM micrographs and histograms of size distribution for the dendron-stabilized Au nanoparticles: (a) **D1–Au**, (b) **D2–Au** and (c) **D3–Au**. The average core sizes and distribution were determined by counting 345 (**D1–Au**), 598 (**D2–Au**) and 819 (**D3–Au**) particles.

there is apparently no correlation between dendron generation and particle size. However, we suspect that the second generation dendron **D2** may have a 'magic' size to protect Au particles with the particular size leading to monodispersity. We are currently investigating in depth the effect of dendron size on the size and dispersity of Au nanoparticles. As seen in Fig. 2, **D1–Au** and **D3–Au** exhibit a typical surface plasmon (sp) band at 530–540 nm in their UV–Vis spectra, whereas **D2–Au** displays a very weak sp band, which is consistent with its smaller particle size and narrower distribution.[11] Further characterization of the dendron-stabilized Au nanoparticles is in progress.

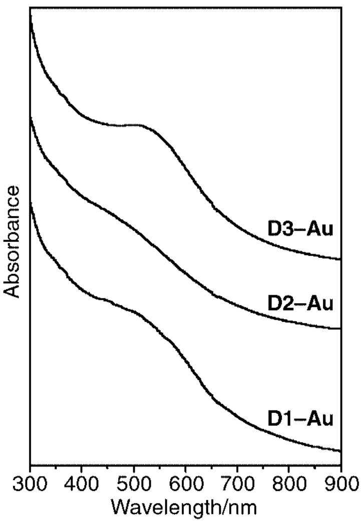

Fig. 2 UV–Vis spectra of the dendron-stabilized Au nanoparticles in THF.

In summary, we present the first dendron-stabilized Au nanoparticles synthesized with Fréchet-type dendrons possessing a single thiol group at the focal point, which have remarkably high stability and narrow size distribution. Particularly, the results on **D2–Au** suggest that this method may provide a convenient way to synthesize stable, monodisperse Au nanoparticles with small cores. Furthermore, this work should be easily expanded to the synthesis of other dendron-stabilized metal nanoparticles which may find useful applications in many areas including chemical sensing and catalysis.

We gratefully acknowledge Creative Research Initiative Program of the Korean Ministry of Science and Technology for support of this work, Brain Korea 21 Program of the Korean Ministry of Education for graduate studentships to M.-K. K., and Professor P. K. Bharadwaj for reading the manuscript.

Notes and references

1 A. C. Templeton, W. P. Wuelfing and R. W. Murray, *Acc. Chem. Res.*, 2000, **33**, 27; A. N. Shipway, E. Katz and I. Willner, *ChemPhysChem.*, 2000, **1**, 18.

2 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.

3 (*a*) M. J. Hostetler, J. E. Wingate, C.-J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans and R. W. Murray, *Langmuir*, 1998, **14**, 17; (*b*) S. Chen and R. W. Murray, *Langmuir*, 1999, **15**, 682; (*c*) T. G. Schaaff, G. Knight, M. N. Shafigullin, R. F. Borkman and R. L. Whetten, *J. Phys. Chem. B*, 1998, **102**, 10 643; (*d*) S. Chen and K. Kimura, *Langmuir*, 1999, **15**, 1075; (*e*) L. O. Brown and J. E. Hutchison, *J. Am. Chem. Soc.*, 1997, **119**, 12 384.

4 K. Esumi, A. Suzuki, N. Aihara, K. Usui and K. Torigoe, *Langmuir*, 1998, **14**, 3157; K. Esumi, A. Suzuki, A. Yamahira and K. Torigoe, *Langmuir*, 2000, **16**, 2604.

5 M. E. Garcia, L. A. Baker and R. M. Crooks, *Anal. Chem.*, 1999, **71**, 256.

6 V. Chechik and R. M. Crooks, *Langmuir*, 1999, **15**, 6364.

7 After submission of this paper, a report on Au nanoparticles stabilized with 4-pyridone-based dendrons was published: R. Wang, J. Yang, Z. Zheng, M. D. Carducci, J. Jiao and S. Seraphin, *Angew. Chem., Int. Ed.*, 2001, **40**, 549.

8 Y. Takaguchi, S. Suzuki, T. Mori, J. Motoyoshiya and H. Aoyama, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1857.

9 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638; R. Sadamoto, N. Tomioka and T. Aida, *J. Am. Chem. Soc.*, 1996, **118**, 3978.

10 Dendrimer-encapsulated Pd and Pt nanoparticles were reported to be almost monodisperse (1.4 ± 0.2 nm): M. Zhao and R. M. Crooks, *Angew. Chem., Int. Ed.*, 1999, **38**, 364.

11 M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. N. Shafigullin, I. Vezmar and R. L. Whetten, *J. Phys. Chem. B*, 1997, **101**, 3706.