

SYNLETT Spotlight 166

Gold Nanoparticles: Synthesis and Applications

Compiled by Vanga R. Reddy



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

V. R. Reddy received his Master in Chemistry from the University of Hyderabad, India in 2000. Afterwards, he spent one and a half year as Junior Research Fellow with Prof. P. S. Zacharias working on the synthesis and application of chiral catalysts for enantioselective reactions at the same university. This summer he will finish his PhD thesis under the mentorship of Prof. G. Calzaferri and Dr. A. Currao at the University of Bern, Switzerland. He has been involved in the synthesis of gold and silver nanoparticles for sensitizing AgCl photoanodes used in water-splitting-related applications. His research interests include the synthesis, functionalization, and application of nanoparticles in various scientific disciplines.

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Introduction

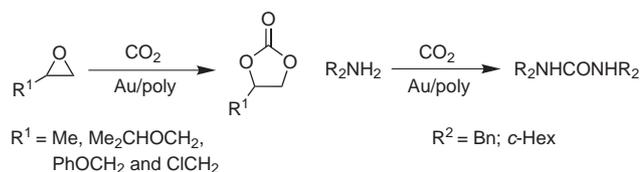
In the present scenario of nanotechnology, gold nanoparticles (Au NPs) are at the forefront due to their amazing chemical and physical properties, which can be exploited in various scientific disciplines. Au NPs have a wide range of applications in areas such as catalysis, medical diagnostics, and biological imaging.¹ Ease of chemical synthesis and less toxicity as compared to some other nanomaterials are advantages. Gold as well as silver nanoparticles have been known to mankind for several centuries. Interestingly, if we look at old cathedrals and churches, which were built few centuries ago, one can see color glass windows. The reason is that glassmakers of the medieval time added minute amounts of gold and silver salts to molten glass. Thus, they were able to incorporate gold and silver nanoparticles. The glassmakers were unknowingly the first nanotechnologists.² In a modern chemical aspect, Michael Faraday was the first scientist who made gold colloids, around 1857.³ Later on, the synthetic method was simplified by the pioneering work of

Turkevich⁴ and Frens.⁵ The properties of gold nanoparticles at the nano scale (1–100 nm) remarkably differ from those of the bulk counter part because of quantum size confinement imposed by the nano-size regime. As a result, gold nanoparticles show colors ranging from ruby red to blue, green, and orange, etc., depending on the size and shape.⁶ This prominent absorption in the visible is called surface plasmon absorption. The Au NPs show remarkable catalytic activity, whereas bulk gold is known to be catalytically inert.⁷

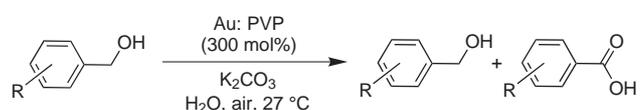
Gold nanoparticles can be synthesized by simple chemical reduction of a tetrachloroauric acid (HAuCl₄) solution with sodium citrate or sodium borohydride in both aqueous and organic media. Usually, SH- or NH-functional groups of organic moieties are known to bind to the surface of Au NPs. Colloidal solutions of Au NPs prepared by citrate⁴ and borohydride⁵ reduction have a red-wine color. Solutions of colloidal gold nanorods have a blue color⁸ with different optical properties.

Abstracts

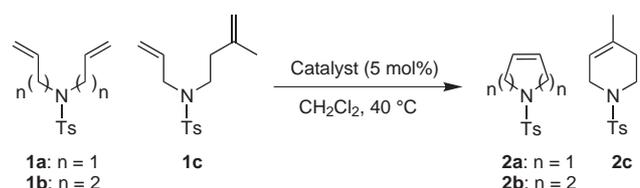
(A) Polymer-supported gold NPs have been used successfully to convert epoxides with CO₂ to carbamates as well as amines to amides.⁹



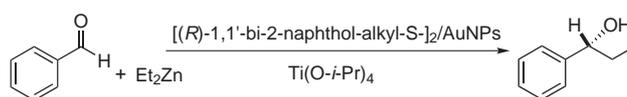
(B) Gold NPs stabilized in polyvinyl pyrrolidone were also used as catalyst in aerobic alcohol oxidation in water. A size effect was demonstrated, showing that O₂ adsorption onto the Au NPs is the key factor for the size-specific catalytic activity.¹⁰



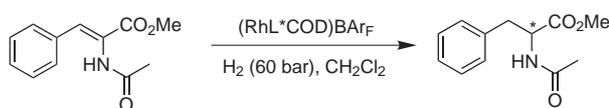
(C) Monolayer-protected gold clusters with a Ru-carbene complex have been synthesized and used as a catalyst in ring-closing olefin metathesis. The functionalized Au NPs can be reused several times and showed almost the same catalytic activity as simple Grubbs type or thioacetate-functionalized Ru-complexes.¹¹



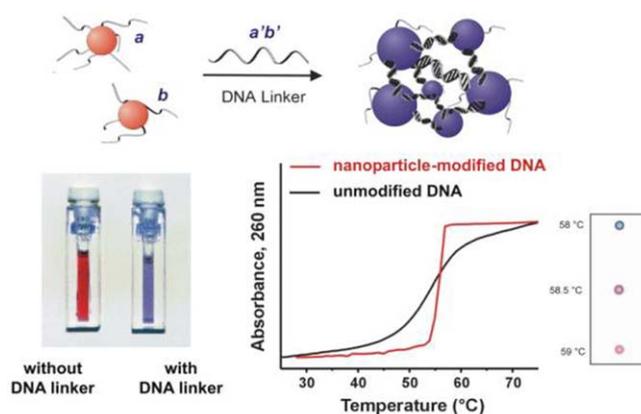
(D) Ti-BINOLate complex generated from the obtained monolayer-protected Au cluster (MPC) promoted catalytic asymmetric alkylation of benzaldehyde with Et_2Zn to afford the adduct in up to 98% yield with 86% ee. After the reaction, the BINOL-functionalized MPC was easily recovered.¹²



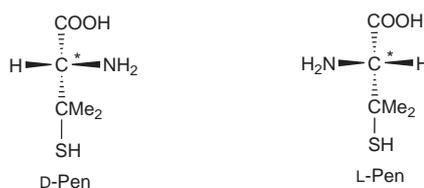
(E) Au NPs, coated with a mixed monolayer of *n*-octanethiolates and thiolates with chiral Rh diphosphine complexes as end groups, were studied as hydrogenation catalysts. With methyl (*R*)-acetamido cinnamate as substrate, virtually the same enantioselectivities (up to 93% ee) and full conversion were obtained as with the corresponding homogeneous catalyst. The colloids were easily recovered and reused as catalysts three times without loss of enantioselectivity.¹³



(F) Further studies indicated that the melting profiles of the nanoparticle-labelled DNA aggregates were extraordinarily sharp, occurring over a temperature range much narrower than the transition for unlabelled or conventional fluorophore-labelled DNA. These two observations created great interest in exploring the potential for designer nanomaterials in biodiagnostic applications.¹⁴



(G) A pair of gold nanocluster enantiomers protected by optically active thiols, D- and L-penicillamine (D-Pen and L-Pen), were successfully prepared. Circular-dichroism spectroscopy confirmed the mirror-image relationship between the D-Pen-capped and the L-Pen-capped gold NPs, suggesting that the surface modifier acts as a chiral selector, and that the nanoclusters have well-defined stereo structures like common chiral molecules. This finding will be important for various spectroscopic diagnostics and for chiral detection or molecular interaction analysis in biochemistry.¹⁵



(H) Silver chloride photoanodes have been used in water-oxidation and water-splitting experiments. Recent results show that AgCl electrodes modified with Au colloids have a higher photoactivity. The gold nanoparticles promote the charge-transfer process at the semiconductor/electrolyte interface, improving the photocatalytic oxidation capability of the AgCl.¹⁶



References and Notes

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