

Nanorods

Synthesis of gold nanorods

Gold nanorods were prepared by adopting a photochemical method that employs UV-irradiation to facilitate slow growth of rods [Kim, F.; Song, J. H.; Yang, P. D. J. Am. Chem. Soc. 2002, 124, 14316.] We used tetraoctylammonium bromide as a co-surfactant instead of tetradodecylammonium bromide. The growth solution was prepared by dissolving 440 mg of cetyltrimethylammonium bromide (CTAB) and 4.5 mg of tetraoctylammonium bromide (TOAB) in 15 mL of water and transferred to a cylindrical quartz tube (length 15 cm and diameter 2 cm). To this solution, 1.25 mL of 0.024 M HAuCl₄ solution was added along with 325 μ L of acetone and 225 μ L of cyclohexane. A small amount of AgNO₃ (250 μ L of 0.01 M) was also introduced. It is reported that the presence of AgNO₃ is essential for the growth of the Au nanorod and the length:diameter aspect ratio can be varied by varying the AgNO₃ concentration. The quartz tube was closed with a rubber stopper through which a glass rod was inserted (15 cm length and 1 cm diameter). The glass rod helps to reduce the effective thickness of the solution and facilitates uniform absorption the light through thin solution layer. The photochemical reaction was carried out using 300 nm irradiation in a Rayonet Photochemical Reactor for 18 h. Gold nanorods prepared by the photochemical method was first purified by centrifugation. The residue obtained after 10 min of centrifugation (7000 rpm) was dispersed in 2 mL of 0.7 M CTAB solution and kept undisturbed at 50°C for 12 h. Upon cooling, excess CTAB crystallized and was separated by filtration. The filtrate contains monodisperse Au nanorods and was used directly in subsequent studies.

The formation of the gold nanorod and its aspect ratio was confirmed from Transmission Electron Microscopic analysis. A drop of a dilute solution of Au nanorods was allowed to dry on a carbon coated copper grid and then probed using a JEOL JEM-100sx electron microscope. The average length and diameter of rods employed in the present investigation are 50.0 nm and 20.0 nm, respectively and an average aspect ratio of 2.5.

Surface functionalization of Au rods with Ru(bpy)₃²⁺-C₅-SH

The place exchange method has been widely employed to functionalize gold nanoparticles with thiol derivatives of organic molecules.[Badia, A.; Demers, L.; Dickinson, L.; Morin, F. G.; Lennox, R. B.; Reven, L. J. Am. Chem. Soc. 1997, 119, 11104.] A modified place exchange process was developed to link Ru(bpy)₃²⁺-C₅-SH to gold nanorods. Two methods were found to be successful in binding the Ru(bpy)₃²⁺-C₅-SH to the gold rods. In the first method, gold nanorods in aqueous solution were added to

a solution of $\text{Ru}(\text{bpy})_3^{2+}\text{-C}_5\text{-SH}$ dissolved in acetonitrile. The mixture was reacted at room temperature with constant stirring for 24 h, sonicating periodically. It was then washed 3 to 5 times with dichloromethane and supernatant was discarded to remove unbound dye molecules. The product was then resuspended in water. The UV-visible absorption of the suspension was measured to ensure the presence of absorption corresponding to the bound $\text{Ru}(\text{bpy})_3^{2+}\text{-C}_5\text{-SH}$.

In the second method the gold nanorods from water were first extracted into dodecanethiol/acetone. A mixture of 2:3:4 water:dodecanethiol:acetone ratio was able to transfer the nanorods into the organic layer. Formation of covalent bonds with the thiol group facilitated phase transfer of gold nanorods. It took approximately 5 hours for the nanorods to migrate from water to dodecanethiol layer. The upper organic layer was extracted and added to sodium sulfate to remove any residual water. The Au nanorods solution was then added to $\text{Ru}(\text{bpy})_3^{2+}\text{-C}_5\text{-SH}$, previously dissolved in a drop of acetone. The mixture was reacted for 24 h at room temperature with constant stirring and periodic sonication. To purify, the reaction mixture was washed with dichloromethane centrifuged at 5,000 rpm for 3 min to remove unbound $\text{Ru}(\text{bpy})_3^{2+}\text{-C}_5\text{-SH}$. This was repeated 3 to 5 times, until the supernatant removed after centrifugation did not show any unbound dye. The product can then be resuspended either in water or dichloromethane. (Note binding with $\text{Ru}(\text{bpy})_3^{2+}\text{-C}_5\text{-SH}$ facilitates dissolution of functionalized gold nanorods in polar solvents). The binding of $\text{Ru}(\text{bpy})_3^{2+}\text{-C}_5\text{-SH}$ to the surface of Au nanorods (Scheme 2) was confirmed by recording UV-visible absorption spectrum.

See following papers for further details:

Thomas, K. G.; Barazzouk, S.; Ipe, B. I.; Shibu Joseph, S. T.; Kamat, P. V., Unidirectional Plasmon Coupling through Longitudinal Self-assembly of Gold Nanorods. *J. Phys. Chem. B*, 2004, 108, 13066-13068.

Jebb, M.; Sudeep, P. K.; Pramod, P.; Thomas, K. G.; Kamat, P. V., Ru(II)trisbipyridine Functionalized Gold Nanorods. Morphological Changes and Excited-State Interactions *J. Phys. Chem. B*, 2007, 111, 6839 - 6844.