

Gold Nanoparticles as Catalysts for Polymerization of Alkylsilanes to Siloxane Nanowires, Filaments, and Tubes

B. L. V. Prasad,^{†,‡} Savka I. Stoeva,[†] Christopher M. Sorensen,[‡] Vladimir Zaikovski,[§] and Kenneth J. Klabunde^{*,†}

Departments of Chemistry and Physics, Kansas State University, Manhattan, Kansas 66502, and Borekov Institute of Catalysis, Novosibirsk 630090, Russia

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Small metallic particles have been used as catalysts for a long time.¹ The decrease in size, apart from increasing the surface area, is expected to make the catalytic active sites on the metal surface readily available to incoming reagents. Even noble metals such as gold, which are not very active in their bulk state, are found to be very good catalysts when their size is decreased to the nanometer level.² Gold nanoparticles have been actively targeted as oxidation catalysts for toxic fumes such as CO and NO.³ On the other hand, metallic nanoparticles such as gold, cobalt, and iron have also been shown to be good catalysts for preparing carbon and silicon nanotubes and other nanostructures.⁴ The mechanism for this high-temperature process is explained as vapor–liquid–solid (VLS) growth. This mechanism consists of three distinct stages: (i) metal alloying, (ii) crystal nucleation, and (iii) axial growth.⁵ However, utilization of gold nanoparticles as traditional polymerization catalysts, where the polymerization occurs at the particle surface, has been scarce. Here, we present a unique polymerization reaction of alkylsilanes and water in the presence of gold nanoparticles and the eventual formation of siloxane nanowires, filaments, and tubes. The yields of the final product are very high, and the reaction itself takes place at relatively low temperatures compared to those of semiconductor nanotube preparations.

Gold nanoparticles are known to be stabilized by a variety of ligands. We have previously reported that nearly monodisperse gold nanoparticles can be prepared by carrying out a digestive ripening (refluxing a polydisperse colloid suspended in a solvent with a suitable capping agent) protocol with different ligands such as alkanethiols, phosphines, amines, and silanes.⁶ Among these ligands, it was clearly established by Banaszak Holl and co-workers that when silanes are attached to gold surfaces they lose hydrogen, resulting in weak Au–Si covalent bonds.⁷ It has also been demonstrated that large amounts of gold and other metal colloids can be prepared in polar solvents such as acetone, butanone, and pentanone.⁸ Transmission electron microscopy (TEM) pictures of the as-prepared colloids reveal that the gold nanoparticles are highly polydisperse and also highly defective in nature (Figure 1a).

In an effort to make narrower size-distributed colloids, we have been trying to digestively ripen these Au-ketone-stabilized colloids with various ligands. Indeed, we have shown that digestively ripening these colloids with ligands such as dodecanethiol leads to a highly monodisperse colloid which forms beautiful superlattices.⁹ Similarly, digestive ripening of a Au-butanone or Au-pentanone colloid with $C_{18}H_{37}SiH_3$ leads to a decrease in the size of the as-prepared gold nanoparticles with a narrower size distribution (Figure 1b). However, when the same reaction (refluxing a Au-butanone

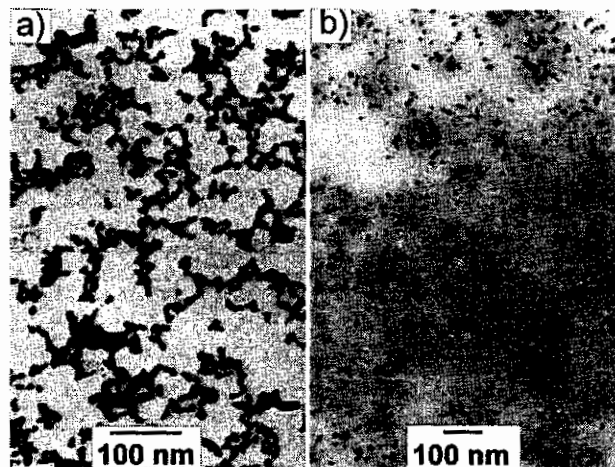


Figure 1. (a) TEM pictures of as-prepared Au-pentanone (in 2-pentanone) and (b) after digestive ripening with $C_{18}H_{37}SiH_3$ in the absence of water.

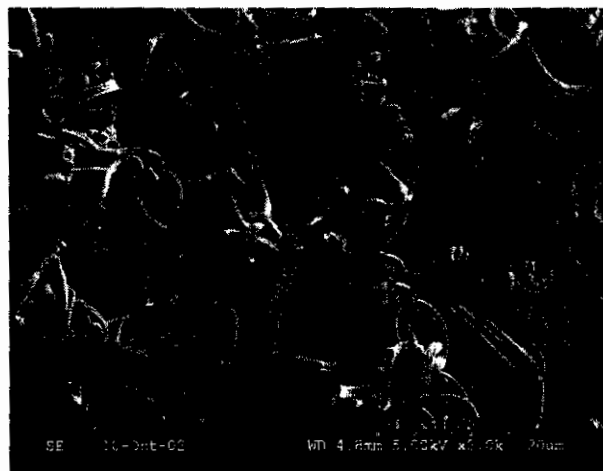


Figure 2. SEM picture of siloxane nanowires, filaments, and tubes resulting from the reflux of Au-pentanone colloid with $C_{18}H_{37}SiH_3$ with water present.

or Au-pentanone colloid with $C_{18}H_{37}SiH_3$) was carried out in the presence of small amounts of water, a dramatic formation of nanowires, filaments, and tubes is observed (Figure 2).¹⁰ The average diameters of these wires and tubes are in the 50–100 nm range, and the lengths are almost into millimeters. Interestingly, many of these nanostructures adopt highly helical structures. High-resolution TEM (HRTEM) micrographs clearly reveal the presence of a gold nanoparticle at the tip of each of these nanostructures (Figure 3a). Elemental and energy-dispersive X-ray studies suggest the elemental composition of these nanostructures to be $C_{18}H_{37}SiO_{1.5}$, with trace amounts of gold.¹¹ HRTEM photographs (Figure 3b) and selected area electron diffractions also suggest these

[†] Departments of Chemistry and Physics, Kansas State University.

[‡] Departments of Chemistry and Physics, Kansas State University.

[§] Borekov Institute of Catalysis.

[‡] Present address: Materials Chemistry Division, National Chemical Laboratory, Pune 411008, India.

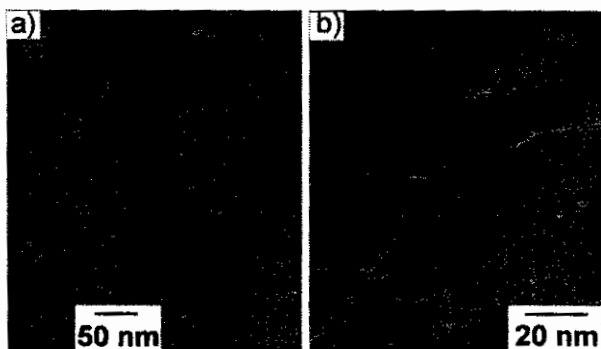
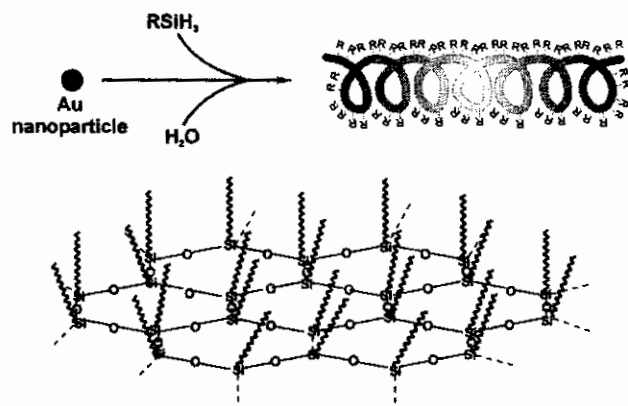


Figure 3. High-resolution TEM photographs (a) clearly depicting a gold nanoparticle at the tip of the nanowires and (b) showing the amorphous nature of these structures.

Scheme 1. Schematic of the Polymerization Reaction and a Probable Structure for the Siloxane Polymer Obtained^a



^a The R groups are randomly tilted to give a better view.

structures to be without any crystalline order. Indeed, when we recorded the powder X-ray pattern of these structures, we did not find any peak other than that corresponding to SiO_2 .

On the basis of the elemental analysis and the observed structures, we propose a tentative structure for these polymers (Scheme 1). Each Si atom is bound to three oxygen atoms and to one R group coming from the alkylsilane. The structure satisfies the elemental composition found by both elemental analysis and EDX ($\text{C}_{18}\text{H}_{37}\text{SiO}_{1.5}$). The proposed structure of the polymer also agrees with the mechanism suggested below. When the alkylsilane is attached to the gold nanoparticle surface, it loses hydrogen, forming three weak Au–Si bonds. In support of the Au–Si bonds formation during the polymerization process are the reports of the well-established reaction of silanes with gold⁷ and the finding that R_4Si could lead to weak Au–Si bonds,^{7c} which indeed may play a role in this polymerization reaction. The weak Au–Si bonds are easily attacked by water molecules, leading to the formation of $\text{RSi}(\text{OH})_x$. The $\text{RSi}(\text{OH})_x$ molecules then react with themselves (similar reactions are known to occur during silica gel formations in the presence of acid or base), leading to the observed nanostructures. The gold nanoparticles which catalyze these reactions also function as templates, restricting the polymer structures to mostly one dimension. It is important to note that control experiments were carried out when no Au nanoparticles were added to the solution and no formation of nanowires or any other one-dimensional structures was observed. Since the reaction occurs very rapidly, the structures are highly amorphous. The remnant large hydrocarbon groups (R) on the Si atom probably force the polymers to adopt

the helical structures observed. It is also found that these one-dimensional nanostructures are attracted to hydrophilic substrates. For example, when a solution containing these nanowires was allowed to dry on a hydrophilic surface such as mica or normal glass, the nanostructures were found to lose their wirelike morphology, and a glassy structure was observed (see Supporting Information Figure 1). On the other hand, on any hydrophobic surface such as carbon film (on a TEM grid), graphite, and hydrocarbon-coated glass, the wire structures are well preserved (see Supporting Information Figures 2–6).

In summary, a unique polymerization reaction involving alkylsilanes and water catalyzed by gold nanoparticle surfaces is reported. A large quantity of siloxane nanowires, filaments, and tubes are readily prepared through a simple reflux reaction. Although their structures are highly amorphous and defective, they could be easily stabilized on hydrophobic surfaces and isolated in a powder form. Efforts are currently underway to isolate large quantities of these nanowires to investigate their detailed structure and physical properties.

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Supporting Information Available: SEM picture of nanowires converted to glassy structure on a hydrophilic surface (mica) and SEM pictures of nanowires on several hydrophobic supports (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) In a typical reaction, 300 mg of $\text{C}_{18}\text{H}_{37}\text{SiH}_3$ was added to 3 mL of Au colloid in butanone or 2-pentanone containing approximately 12 mg of Au (Au:ligand molar ratio approximately 1:20). Ten microliters of water was added to the gold colloid itself before addition of the ligand. The mixture was then allowed to reflux under an Ar atmosphere for 90 min. In fact, we found that if we left both gold colloid and $\text{C}_{18}\text{H}_{37}\text{SiH}_3$ ligand under ambient atmospheric conditions for some time, they picked up enough moisture and no addition of water was required. In a control experiment we prepared the colloid in very carefully controlled conditions under an Ar atmosphere and added the ligand in a drybox. Refluxing this mixture did not show the formation of any wires. Addition of a little water (10 μL) to this mixture, followed by reflux, immediately led to the formation of wires, signifying the importance of water/moisture in this reaction.
- (11) Elemental analysis was carried out at Galbraith Laboratories by isolating the wires in powder form by centrifuge and washing them with 2-pentanone several times. We also carried out EDAX from single filaments, where the localization was near 100 Å, and it has shown that the stoichiometry is close to $\text{C}_{18}\text{H}_{37}\text{SiO}_{1.5}$.

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