The Effect of Annealing Metallic Nanoparticles on their Catalytic Efficiency

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Abstract:

The electron transfer reaction between thiosulfate and hexacyanoferrate (III) catalyzed by gold nanostructures has been studied as a function of nanoparticle shape. Gold nanoprisms were prepared on substrates and their catalytic activities were compared to nanoprisms that had been annealed by various methods and to various degrees. The activation energies were also found for both roughened and smooth thin gold films. The activation energies for the reactions were found in order to determine the catalytic ability over the temperature range 23-60°C. An analysis of the results suggests that unannealed surface atoms with unsaturated valency (e.g. those present on unannealed prisms bound to a substrate or on roughened thin film surfaces) have the highest catalytic activities, and annealing of the prisms leads to an increase in the activation energy and thus a lowering of their catalytic efficiencies.

Introduction:

Recent excitement in nanoparticle catalysis has partly been due to the discovery of shape and size dependent nanoparticle properties. A variation in catalytic activity has been reported between nanoparticles of different crystal surfaces and thus different ratios of available atoms to react with on the crystals' faces, edges, and corners [5]. Colloidally synthesized platinum nanoparticles have shown varying degrees of catalytic activity during the electron transfer reaction between thiosulfate and hexacyanoferrate (III) depending on the nanoparticle's shape. The activation energies for the reaction increase as the particle shape changes from a tetrahedral, to a cube, and then to a sphere, which correlate with a decrease in catalytic activity [4]. Surface plasmon resonance absorption occurs when incident light oscillates the conduction band electrons of the metal particle and is highly dependent on the particle's shape, size, surface quality, and medium. For this reason, changes in the particle's surface plasmon resonance absorption were spectrally followed to qualitatively track the physical changes that occurred during the annealing processes [2].

For this work, nanosphere lithography [1,3] was utilized to make gold nanoprisms stabilized on quartz and annealed to varying degrees in order to study the effect of the nanoparticle's physical properties in the reaction between hexacyanoferrate (III) [$Fe(CN)_6^{3-}$] and thiosulfate [$S_2O_3^{2-}$] (shown in Figure 1). All nanoparticles were used uncapped and all reactions were done in triplicate to catalyze the reaction at a 1:15 ratio of [$Fe(CN)_6^{3-}$]: [$S_2O_3^{2-}$] at three different temperatures.

$$2Fe(CN)_6^{3-} + 2S_2O_3^{2-} \rightarrow 2Fe(CN)_6^{4-} + S_4O_6^{2-}$$

Figure 1: The gentle electron transfer reaction between thiosulfate and hexacyanoferrate III.

Experimental Procedure:

Gold nanoparticles were initially fabricated using nano-sphere lithography which has been developed within the literature [1,3]. Briefly, quartz slides were cleaned and rendered hydrophilic. A mask was created on the substrate by self-assembling a monolayer of sub-micron polystyrene spheres. Using a PVD filament evaporator, 35 nm of gold was deposited normal to the substrate surface, creating gold nanoprisms within the interstitial areas between spheres. The polystyrene spheres were then removed via sonication in ethanol. By thermally heating some of these nanoprisms at 930°C for 30 seconds in an AET RTP, the particles melted into near spherical nanoparticles. A third sample of nanoparticle catalysts was created by transferring the substrate-bound nanoprisms into DDI water via a femtosecond laser pulse. The nanoparticles were analyzed before and after transfer using SEM and TEM techniques (Figures 2 and 3, respectively) and a slight annealing of the particle's surface were observed. Thin film gold surfaces were prepared by depositing gold onto clean quartz and smooth mica surfaces for the rough and smooth films, respectively. The surfaces were analyzed by AFM to verify a distinction between film roughnesses.

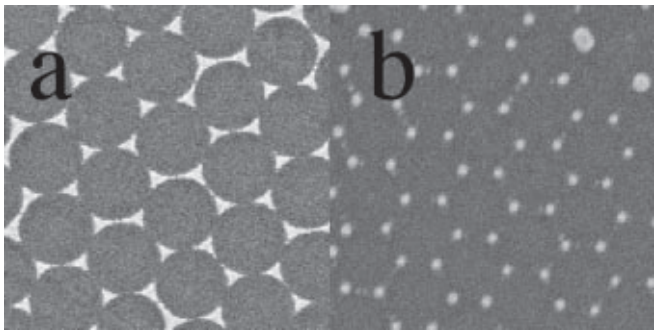

Figure 2: SEM images of a) nanoprisms on quartz, and b) nanospheres on quartz.

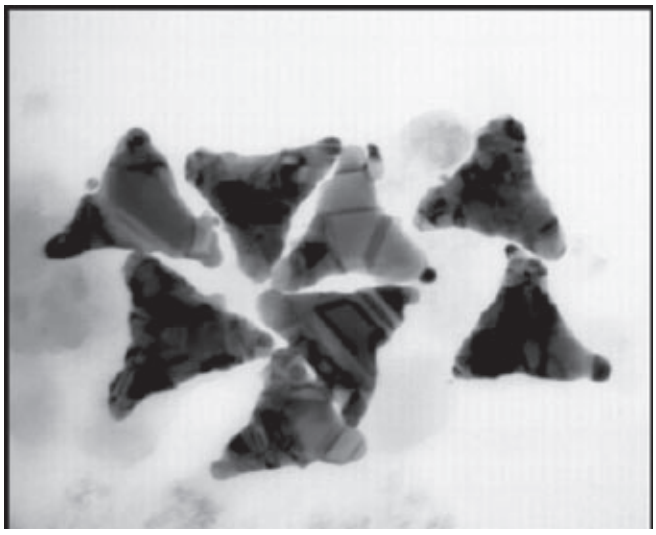

Figure 3: A TEM image of nanoprisms in deionized water.

The rate of the reaction was measured by spectrally following the decrease in the concentration of the reactant hexacyanoferrate (III) at 420 nm. The rate was assumed to be pseudo-first order by using a 15:1 ratio of $[S_2O_3^{2-}]$: $[Fe(CN)_6^{3-}]$, and rate constants were obtained using the Beer-Lambert Law for 23, 45, and 60°C. The natural logs of the rate constants were plotted against inverse temperatures to produce an Arrhenius plot (Figure 4) from which the activation energies for each gold catalyst were obtained.

Results and Conclusions:

By analyzing different surfaces of nanoparticles and thin films in the chemical reaction in Figure 1, we have shown that surfaces exposed to the least amount of annealing have large catalytic activities. The substrate bound prisms were the most catalytically active with an activation energy of 30.2 ± 2.6; followed by prisms suspended in solution, 33.0 ± 3.4; rough thin film surface, 37.1 ± 2.5; spheres supported on the quartz, 37.9 ± 3.2; the smooth thin film surface, 48.4 ± 1.9; and lastly the uncatalyzed reaction, 56.7 ± 5.0. Consequently, the nanoparticles with rougher surfaces and thus unsaturated atoms were better catalysts than surfaces that were annealed by heating, which results in saturated atomic valency.

Future Work:

Additional investigation for this research includes examining the recycling potential of these gold nanoparticles, using same-sized and same-shaped nanocatalysts in other types of chemical reactions, and continuing to control the shape and size of the nanoparticles while making them smaller.

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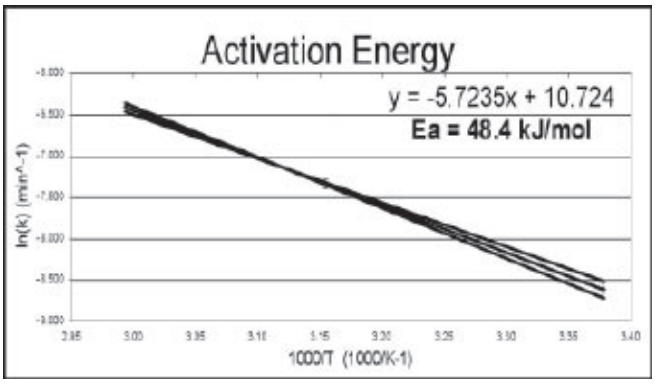

Figure 4: Arrhenius plots were used to derive the activation energy.