



Short communication

Spontaneous hydrolysis of borohydride required before its catalytic activation by metal nanoparticles

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ABSTRACT

Though borohydride has been frequently used as a hydrogen source in the nanoparticle-catalyzed chemical reduction, the explanation for a delay of the reaction is still under debate. Here we investigated the mechanism of the catalytic borohydride reduction and found that the negative charge of borohydride prevented it from approaching the negatively charged nanoparticles, resulting in a delay of reactions. Spontaneous hydrolysis of borohydride was critical to the start of the reaction. A universal method was introduced to dramatically increase the catalytic efficiency. Our experiment suggested a guideline for designing efficient catalysts and reducing agents in future.

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1. Introduction

Metal nanoparticles are useful catalysts thanks to their large surface area and unique scale range that enable pseudohomogeneous catalytic reactions in solution while retaining excellent sustainability and activity [1–3]. They are considered to be excellent hydride carrier with lower activation energy in hydrogenation [4–6], which benefits applications for both the chemical reduction and the chemical hydrogen storage [7–9]. Borohydride and its derivatives are frequently used as a hydrogen source [10–14]. Meanwhile, the reduction of 4-nitrophenol (4NP) by borohydride has been frequently used to examine the catalytic activity of metal nanoparticles, in which a decrease in the characteristic absorption peak of nitrophenolate at 400 nm indicates the accomplishment of the reduction reaction.[15–17] However, the mechanism of these reactions is not very clear yet. For example, such reactions are mostly accompanied by a time lag in any visible absorbance change, *i.e.*, induction time [6,16,18–23]. The cause of the delay and the science beneath the delay is still under debate [22]. Various models have been reported to explain the delay, such as the time required for borohydride molecules to diffuse to the nanoparticle surface, for the removal of surface oxidized layers [19], for the scavenging of the dissolved oxygen [20], for the decomposition of borohydride on the surface of nanoparticles [21], or the reconstruction of nanoparticles [18]. A better

understanding of the underlying mechanisms is needed to promote catalytic efficiency [22].

In order to understand how the reaction starts as well as how the activated hydride subsequently reacts for the chemical synthesis or for the hydrogen gas generation, we screened the catalytic activity of metal nanoparticles, and found that the spontaneous hydrolysis of borohydride anions played a more important role in determining the catalytic reaction than the metal nanoparticles. The intermediate from the hydrolysis was able to donate active hydride to nanoparticles instantly upon contact.

2. Experimental

2.1. Preparation of stock solutions

Metal ion stock solutions (14 mM) and poly(acrylic acid) (PA) stock solution (1.1 mM) were prepared in deionized water. Sodium borohydride stock solution (1 mg/mL) and 4-nitrophenol stock solution (6 mg/10 mL) were prepared in deionized and used instantly.

2.2. Synthesis of PA-AgNDs

AgNO₃ and 3-aminopropyl trimethoxysilane were mixed at a 3-aminopropyl trimethoxysilane/Ag⁺ ratio of 2:1 in methanol and left in the dark with stirring for 2–3 h. The silane-silver stock solution (65 μL) and 1.1 mM Poly(acrylic acid) stock solution (63 μL) were mixed in DI water (2900 μL) and left in the dark with stirring for 1 h, followed by reducing with fresh sodium borohydride stock solution

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(35 μL) [24]. The sample was used after an overnight incubation in the dark.

2.3. Synthesis of PA-AgNPs

AgNO_3 solution (3 mM, 630 μL) and poly(acrylic acid) (1.1 mg) were mixed in DI water (5370 μL) and left in the dark with stirring for 1 h, followed by reducing with fresh sodium borohydride stock solution (210 μL). The sample was used after an overnight incubation in the dark.

2.4. Synthesis of citrate-AgNPs

A mixture of AgNO_3 solution (1 mM) and sodium citrate tribasic dihydrate (1 mM) were heated at 75 $^\circ\text{C}$ in the dark with stirring for 10 min. The sample was used after cooling down for 1 h in the dark.

2.5. Synthesis of AgNPs without organic protection groups

Sodium borohydride (2 mM) was added dropwise into AgNO_3 solution (5 mM) under stirring at a sodium borohydride/ Ag^+ volume ratio of 3:1.

2.6. Comparison of catalytic ability

The concentrations of each component were kept constant throughout the experiments except where indicated. All the 4NP reductions took place at 25 $^\circ\text{C}$. In a quartz cuvette (10 mm), DI water (1 mL), catalyst (0.3 mM, 1 mL) and 4-nitrophenol stock solution (30 μL) were mixed. Sodium borohydride stock solution (50 μL) for 4NP reduction was then added into the mixture, followed by a quick shake of the cuvette. The absorption spectra were then recorded on a SCINCO S-4100 Scan UV–visible spectrophotometer at room temperature. The concentration of silver ions was decreased to 0.1 mM to show the significance of aging time when comparing the impact of the aging time on the induction time.

The reduction can be visualized by the vanishing of the 400 nm peak of 4NP with the appearance of a new peak at 300 nm of 4-aminophenol (4AP). We observed the kinetics of the reaction by recording the change in the absorbance (not A/A_0) of the p-nitrophenolate ions at 400 nm (Fig. S1).

3. Results and discussion

The size of nanoparticles is a key parameter for efficient catalysis, given the size-dependence of catalytic activity and surface area [1]. With its few-atom cluster feature, we considered the silver nanodot, a luminescent ligand-stabilized silver cluster, to be a good catalyst for

the reduction of 4-nitrophenol with sodium borohydride [3,24–26]. With only a 15-fold molar excess of freshly prepared sodium borohydride (60 mM) to 4-nitrophenol (4 mM), the characteristic absorption of 4-nitrophenolate at 400 nm decreased sharply after a short delay in the presence of the poly(acrylic acid)-stabilized silver nanodot (PA-NDs, 300 μM silver, Fig. S1). The solution of 4-nitrophenol became colorless subsequently. The absorbance at 400 nm remained in the absence of silver species. Contrary to our expectations, the poly(acrylic acid)-protected silver nanodot was not the best catalyst. It exhibited a similar reaction constant to that of the silver nanoparticles (AgNPs) without any organic protection group and the citrate-stabilized silver nanoparticles (citrate-AgNPs), but showed a longer induction time. However, the poly(acrylic acid)-stabilized silver nanoparticles (PA-AgNPs) catalyzed the reaction faster to finish within a few seconds (Fig. 1a), exhibiting no induction time. It was plausible to explain the difference by the particle size. Large nanoparticles with a diameter of more than 100 nm were obviously found among the poly(acrylic acid)-stabilized silver nanodots agglomerated heavily to form sub-micrometer aggregates (Fig. S2a), the citrate-stabilized silver nanoparticles formed micrometer-long crystal filaments (Fig. S2b), and the un-stabilized silver nanoparticles (Fig. S2c). All of them exhibited significantly smaller surface areas per mass than the poly(acrylic acid)-stabilized silver nanoparticles, which showed well-dispersed particles (Fig. 1b). However, we found some other reasons causing the difference that will be explained later.

Both nanoparticles and corresponding metal ions could be catalytic precursors, but nanoparticles/clusters that were reduced from metal ions acted as catalysts. It has been reported that the catalytic centers might involve the un-reduced silver ions adsorbed on the nanoparticle surface [27]. We therefore removed free silver ions by collecting the silver nanoparticles after centrifugal ultrafiltration. These nanoparticles showed catalytic activity similar to the original solution, suggesting that it was the nanoparticles, not the ions, catalyzed the reaction. Interestingly, the supernatant catalyzed the reduction of 4-nitrophenol as well, just with a longer induction time and a smaller reaction constant. ICP-AES confirmed that there were about 10 μM of un-reduced silver ions in the supernatant of citrate-stabilized silver nanoparticles and 1 μM in the poly(acrylic acid)-stabilized silver nanoparticles. As demonstrated above, the nanoparticles, not the ions, acted as catalysts. It was possible that such ions were first reduced to metal clusters/nanoparticles and then catalyzed the reactions, [28] given that the strong reducing environment would transform most silver ions to clusters/nanoparticles. Indeed, the formation of metal clusters/nanoparticles was critical for the catalysis. No reactions were observed in the presence of a peptide, HDCNKDKHDCNKDKHDCN (HDCN) as the strong affinity of HDCN for silver or gold ions stopped the formation of metal clusters [29]. Other heavy metal ions, such as gold ions, platinum ions, and

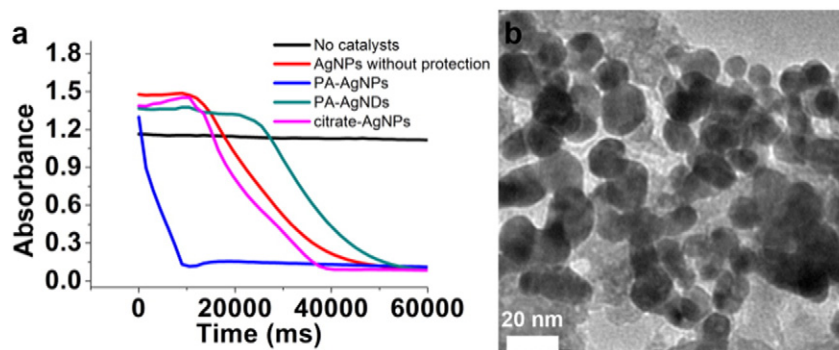


Fig. 1. Catalytic reduction of 4-nitrophenol with sodium borohydride. **a**, Absorbance at the peak position for 4-nitrophenol (400 nm) as a function of time in the absence (No catalysts) or presence of silver nanoparticles without stabilization agents (AgNPs without protection), poly(acrylic acid)-stabilized silver nanoparticles (PA-AgNPs), poly(acrylic acid)-stabilized silver nanodots (PA-AgNDs), and citrate-stabilized silver nanoparticles (citrate-AgNPs). In all cases, the concentrations of 4-nitrophenol and borohydride were 4.3 mM and 63 mM, respectively. The concentration of silver in the Ag-based catalyst was 0.3 mM. **b**, TEM images of poly(acrylic acid)-stabilized silver nanoparticles. Scale bar: 20 nm.

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