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Size control and supporting of palladium nanoparticles made by laser ablation in saline solution as a facile route to heterogeneous catalysts

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ABSTRACT

In the literature many investigations on colloidal stability and size control of gold nanoparticles are shown but less for ligand-free palladium nanoparticles, which can be promising materials in various applications. Palladium nanoparticles are perspective materials for a manifold of energy application like photo- and electrocatalysis or hydrogen storage. For this purpose, size-controlled nanoparticles with clean surfaces and facile immobilization on catalyst supports are wanted. Laser ablation in saline solution yields ligand-free, charged colloidal palladium nanoparticles that are supported by titania and graphene nanosheets as model systems for photo- and electrocatalysis, respectively. By adjusting the ionic strength during laser ablation in liquid, it is possible to control stability and particle size without compromising subsequent nanoparticle adsorption of supporting materials. A quantitative deposition of nearly 100% yield with up to 18 wt% nanoparticle load was achieved. The average size of the laser-generated nanoparticles remains the same after immobilization on a support material, in contrast to other preparation methods of catalysts. The characterization by X-ray photoelectron spectroscopy reveals a redox reaction between the immobilized nanoparticles and the graphene support.

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1. Introduction

When palladium was named in 1805 by Pallas Athena [1], the Greek goddess of wisdom and science, the nomenclature resulted in real telling name. Today, palladium has a prominent role in research of materials, especially for the catalytic conversion of energy and materials like C—C cross coupling reactions [2–4]. The far most important application is yet dedicated to (heterogeneous) catalysis [5], represented by automotive exhaust cleaning [6,7] or electrocatalysis [8,9] either as elementary palladium or alloys [10,11]. For synthesis of palladium-based heterogeneous catalysts different approaches can be found in the literature. Besides classical impregnation techniques [12], flame processes [13] and precipitation methods [11], colloidal deposition is getting more and more attractive since it allows a better control of nanoparticle properties [14]. Nevertheless, conventional chemical synthesis always implies the use of ligands, surfactants and stabilizers. On the one hand, those additives are useful to control nanoparticle properties like size or morphology. On the other hand, ligands may block catalytic sites and should be removed from nanoparticle surface to increase the catalytic activity [15,16]. Subsequent removal of surfactants is cost intensive and yields often to particle growth and agglomeration resulting in losses of the catalytic activities.

Following this, the availability of ligand-free palladium nanoparticles omits any post-synthesis treatments and can be achieved by laser ablation in liquid. Consequently, a growing number of different working groups all around the world have recognized the potential of laser-generated palladium nanoparticles. In a pioneering work, Nishi and Suzuki reported about laser fabrication of palladium nanoparticles at air-suspension interface [17]. Further work on laser fabrication of palladium nanoparticles in water [18,19] and organic solvents [20,21] predominantly gives attention to particle characterization including size, morphology, crystallinity and surface chemistry. Besides catalysis, laser-generated palladium nanoparticles were also reported to be

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interesting for surface-enhanced Raman scattering (SERS) [20] or their magnetic properties [22].

Overall, laser ablation of palladium in water and organic solvents is well characterized but still lacks size control and stability, especially in pure water. This stability against aggregation is mandatory for a reproducible colloidal deposition in order to fabricate heterogeneous catalysts [23]. In the literature, the most common approach for size control and colloidal stability of laser-generated palladium nanoparticles is the use of ligands as shown for gold nanoparticles [24,25].

However, ligands and stabilizers play an ambivalent role in nanoparticle synthesis for catalytic application as already mentioned. For instance, Hwang et al. who laser-generated bare and ligand-stabilized palladium nanoparticles showed that catalytic activity was strongly enhanced for ligand-stabilized nanoparticles due to better size-control and smaller nanoparticles [26]. In contrast to this, Park et al. showed that surface coverage of platinum nanoparticles with polyvinylpyrrolidone or sulfate strongly decreased catalytic activity [27]. This antagonism is only solvable if one approaches nanoparticle size-control without use of potential deactivating ligands. For this purpose, the use of saline solution is a promising novel approach to stabilize ligand-free nanoparticles just by electrostatic means *via* surface charge delivery by anions [28–30]. However, the salt-stabilization works well for noble metals and was intensively studied on the model system of gold nanoparticles [30,31]. Optimal salt-to-nanoparticle surface ratio depends on type of anion with salinity in micromolar range. It was shown that the stabilization of gold is dominated by ion adsorption and not by surface oxidation [30]. But this charge delivery effect has been studied only for the most noble element gold [27,30]. Less noble elements may be oxidized by molecular oxygen in water, which leads to different initial states at the surface and therefore to different colloidal properties, notably if different surface charge situations of the material, *e.g.* Pd^{2+} and Pd^{4+}, exist.

In this paper, we demonstrate how palladium nanoparticle size and stability can be tuned by laser ablation in saline solution using different ionic strengths and different salts. Furthermore, we investigated the adsorption of colloidal palladium nanoparticles on different supports in order to synthesize heterogeneous catalysts.

2. Materials and methods

2.1. Laser ablation and nanoparticle adsorption

For nanoparticle fabrication an Nd:YAG picosecond laser (λ = 1064 nm, τ = 9.8 ps; Ekspla Atlantic 1064/532) operating at a repetition rate of 100 kHz and a pulse energy of 126 μJ was used. The laser beam was focused using an f-theta lens with 100.1 mm focal length onto a palladium target (99.99%, Alfa-Aesar) immersed in 30 mL liquid. By coupling the laser beam into a scanner optic a spiral pattern of 6 mm diameter was scanned on the target, which was fixed in a self-constructed batch-chamber made of steel (Fig. 1, see also [32]). The chamber was filled with Milli-Q water (resistivity of 18.2 MΩ cm at 25 °C) or with an electrolyte solution using different ionic strengths. Several electrolytes were chosen to study the size quenching effect and adsorption. Sodium phosphate buffer at pH 7 (PB, c = 0.00025–10 mmol/L, Sigma–Aldrich), sodium carbonate buffer at pH 9 (CB, c = 0.005–1 mmol/L, Merck) and sodium hydroxide (NaOH, c = 0.00025–1 mmol/L, VWR) were freshly prepared before laser ablation. The ablation time was 3 min and the palladium nanoparticle concentration was determined by weighing the target before and after ablation with a microbalance (PESA Weighting Systems).

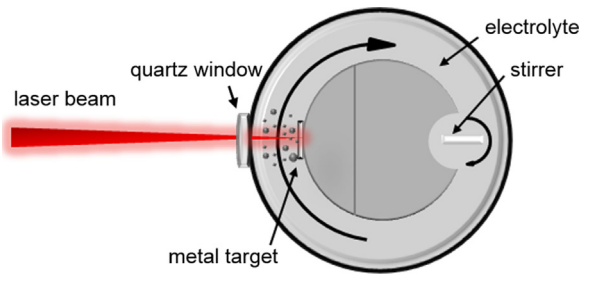

Fig. 1. Set-up for laser-fabrication of ligand-free palladium nanoparticles in aqueous, micromolar saline solution.

The nanoparticle adsorption experiments followed a procedure reported recently [33]. The carrier material TiO_2 (Hombikat Type II, Sachtleben), primary particle diameter (<15 nm, BET surface 90-120 m^2/g) or graphene nanosheets (GNS, synthesized according to Nakamura et al. [34]) were added to a certain amount of palladium colloid and the colloid-support suspension was shaken for several hours. After storing overnight, a sedimentation of the palladium-loaded TiO_2 (Pt/TiO_2) takes place and a clear supernatant results in case of a complete nanoparticle adsorption. In case of GNS, sometimes centrifugation (4000 min^{-1}, 5 min) was necessary to separate the support from the liquid because of the lower density of the support compared to titania. The supernatant was used for further analysis regarding adsorption efficiency.

2.2. Characterization of nanoparticle properties

The colloids were analyzed using UV–Vis extinction spectra on a Thermo Scientific Evolution 201 spectrometer (quartz cuvette with a 1 mm path length). UV–Vis spectra in a range of λ = 190–900 nm were measured directly after laser ablation and up to 27 days to evaluate the colloidal stability against aggregation over time. Furthermore, the colloidal stability was investigated by zeta-potential measurements using a Malvern Zetasizer "Nano ZS" in a disposal cell with a volume of 750 μL.

Particle size was investigated by measuring the hydrodynamic diameter using analytical disc centrifugation (ADC, DC 24000 from CPS instruments). A volume of 0.1 mL of the sample was injected and centrifuged against a saccharose gradient and an external standard (PVP particles at 0.239 μm) while the disc was operated at 24,000 rpm. Transmission Electron Microscopy (TEM) using a Philips CM12 microscope was performed after dropping the colloidal solution or the hybrid Pd/GNS (dispersed in Milli-Q water, resistivity of 18.2 MΩ cm at 25 °C) on a carbon-coated copper grid and drying in air. The particle size was measured with ImageJ software and determined by averaging over 350–2000 palladium nanoparticles. Electron images of Pd/TiO_2, deposited on a polished graphite carrier, were done by Scanning Electron Microscopy (SEM) measurements carried out with a Quanta 400FEG.

The colloidal palladium nanoparticles and the supported nanoparticles were characterized by X-ray photoelectron spectroscopy using JEOL, JPS 9010 TR with an Al K_α X-ray source (1486.6 eV). The sample was dropped on a Highly Ordered Pyrolytic Graphite (HOPG) substrate and dried in air. For analysis, the supported nanoparticles on GNS and TiO_2 were deposited on a graphite tape.

3. Results and discussion

3.1. Colloidal stability

As colloidal palladium nanoparticles do not represent the final product ready for application, a further processing is mandatory. This could be done by nanoparticle deposition on supports to form heterogeneous catalysts (see Section 3.3), embedding into

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