



## Novel Nanoparticle Catalysts for Catalytic Gas Sensing

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# Novel Nanoparticle Catalysts for Catalytic Gas Sensing

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## ABSTRACT

The state-of-the-art approach to stabilize nanoparticles (NPs) for heterogeneous phase applications is to support them on inert inorganic material, which is limited to low loadings of the catalytic component. However, applications such as catalytic gas sensing require a high density of catalytically active sites at a low total heat capacity. To offer an alternative to the supporting of NPs, the stabilization of catalytic NPs with organic ligands in solid state is presented. Therefore, the preparation strategy, consisting of NP synthesis and subsequent functionalization with mono- and bifunctional ligands, is introduced. The molecular linkage of Pt NPs with bifunctional amine ligands (ligand-linking) results in three-dimensional porous networks with ligand-free surface sites. The catalytic properties of ligand-stabilized NPs were investigated in a thermoelectric hydrogen sensor. In addition to an enhanced activity, the stability of the NPs can be significantly improved by ligand-linking. One reason may be that the bifunctional ligand is anchored on the NPs by two head groups. The criteria for ligand structures to enable a successful NP stabilization were identified. Para-phenylenediamine (PDA) combines the criteria and, consequently, by linking of Pt NPs with PDA a constant catalytic activity over more than 20 h on stream was achieved. Thus, ligand-stabilized NPs are presented as a novel catalyst for catalytic gas sensing.

## 1. INTRODUCTION

Due to the easy ignitability of gases like hydrogen or volatile organic compounds (VOCs), there is a need for fast and reliable detection of these gases wherever they are used on a larger scale. Most commercially available gas sensors are palladium gate field effective transistors, metal oxide semiconductors (MOS), and catalytic combustion devices.<sup>1-3</sup> A significant disadvantage of these established sensors is their high power consumption, because they require high operation temperatures ( $\sim 400$  °C) and are built in big dimensions. Additionally, the response time of these sensors is very long (up to several minutes) and a recovery modus is required for most of the MOS type sensors.<sup>1-3</sup> These aspects limit the applicability of these sensors as mobile safety monitoring devices, e.g. for the detection of leakages. A suitable strategy to overcome these limitations is micro-technologically based catalytic gas sensors with nano-structured materials applied as catalysts.<sup>4-10</sup> The reduction of the size of the sensor substrate decreases the power consumption at a constant operation temperature, and the nanostructured catalyst exhibits a high ratio of active sites to the material volume, which allows for a dynamic response to the target gas.

In gas-phase catalysis, often supported nanoparticles of the catalytically active material are employed. They exhibit a high surface energy, which results in their strong tendency toward sintering and coalescence.<sup>11</sup> Thus, the stabilization of NPs in order to maintain the nano-structure of particles is prerequisite for any application.<sup>12</sup> The state-of-the-art method to stabilize NPs is to support them on inert inorganic material with low loadings of the active component (single-digit weight percentages), restricting the density of catalytically active surface sites within the catalyst. For most applications, a low density of the catalytic compound is advantageous, because it enables for preventing mass transport limitations in catalytic applications and, hence, allows for an efficient utilization of the expensive catalytic component. However, in specific applications such as catalytic gas sensing based on a thermoelectric working principle, the sensitivity of the sensor is proportional to the

temperature difference induced by the catalytic conversion. A high density of active sites at a low total catalyst mass hence allows for a strong sensor signal (high sensitivity), combined with a fast response.<sup>13, 14</sup> Consequently, the supporting of the catalytic NPs on inert inorganic materials (e.g.  $\text{Al}_2\text{O}_3$ ) is not an ideal approach for catalytic gas sensing and alternative strategies toward NP stabilization are desired.

So far, the stabilization of NPs by ligands or capping agents (organic molecules bound to the NP surface) has been mainly reported in colloid chemistry in order to protect the NPs from sintering.<sup>15</sup> The approach of ligand-stabilization of NPs in solid state represents an alternative strategy to stabilize NPs and to enable a high density of active sites. Within this article, we show the potential of ligand-stabilized Pt NPs in solid state as a promising material for catalytic gas sensing, where a high density of the catalytic metal is desired. Therefore, we will start by introducing the strategy towards ligand-stabilized Pt NPs. The Pt NPs were functionalized with different mono- and di-amine ligands, since Pt exhibits a high catalytic activity for hydrogen oxidation, and amines are known to effectively bind to Pt.<sup>16</sup> Then, we describe the working principle of the applied thermoelectric gas sensor which was used to investigate the catalytic potential of the ligand-stabilized NP catalysts. Finally, gas-sensing tests performed with NPs stabilized by amine ligands are shown and the results are discussed with respect to the ligand properties.

## **2. SYNTHESIS AND STABILIZATION OF THE NANOPARTICLE COLLOIDS**

NPs can either be prepared by bottom-up (utilizing atomic precursors) or top-down approaches (macroscopic crystals serve as starting material). With respect to structural control, the advantages of bottom-up approaches outweigh their disadvantages, such as small batch sizes and difficulties in up-scaling of production processes.<sup>17</sup> Bottom-up wet-chemistry syntheses most often allow for an individual and effective adjustment of synthetic parameters.

Consequently, a precise control over particle size, size distribution, morphology, and composition as well as a high reproducibility can be achieved.<sup>18</sup> Colloidal syntheses are an example of a wet-chemistry bottom-up approach where the resulting NPs are stabilized in a solvent and any aggregation or sedimentation is suppressed.<sup>15</sup> Colloids are defined to be substances in a fine dispersed state with particle sizes below 100 nm so that dispersions of NPs in a solvent can be denoted as colloids.<sup>12, 19</sup>

## 2.1 Stabilization of NP colloids

Due to the high surface energy of NPs, the colloids have to be stabilized in order to prevent agglomeration and further growth of the individual particles. In general, stabilizing agents need to be applied already during synthesis. The different strategies toward stabilization of colloidal NPs, which all employ the help of stabilizing reactants, can be categorized into three main concepts, namely electrostatic repulsion, inhibited diffusion (e.g. synthesis in micelles), and steric hindrance (by binding capping agents or coordinating polymers to the NP surface). In this article, we will focus on stabilization by steric hindrance, as this concept was adapted for the NP catalysts.

Steric stabilization denotes the binding of molecules to the NPs that prevent approaching of two NPs. Most often, long-chained or branched hydrocarbons or polymers are applied to establish an organic shell around the NPs.<sup>20</sup> These molecules are coordinatively or even covalently bound to the surface *via* an anchoring or head group (a functional group that is able to bind to the NP), such as amines, thiols, or phosphines.<sup>20</sup> In the following, it will be distinguished between the terms "capping agent" and "ligands" to differentiate between applying adsorbates during NP synthesis to prevent coalescence (capping agent) and a target-oriented functionalization of NPs for specific applications (ligands). The application of capping agents during NP synthesis to prevent aggregation, precipitation, or to obtain shape

control is widely applied.<sup>21, 22</sup> A commonly used capping agent for Pt NPs is oleylamine (often in combination with oleic acid), due to the effective coordination of amines to Pt.<sup>23, 24</sup>

The reduction of the metal precursor has a strong influence on the nucleation and formation of NPs. The reactive metal species can be equivalent to the applied metal precursor or can be formed *in situ via* coordination of solvent molecules or capping agents to the metal ion.<sup>15</sup> In this way, the application of a capping agent directs the rate of precursor reduction and, as a result, influences the formation of nucleation seeds and their growth to nano-sized particles.<sup>15, 23</sup> As a result, the size, shape, crystallinity, and faceting of NPs can be adjusted by choice of the capping agent.<sup>25-27</sup> The preparation of NP colloids with the help of steric stabilization allows for versatile and tailored NP syntheses.

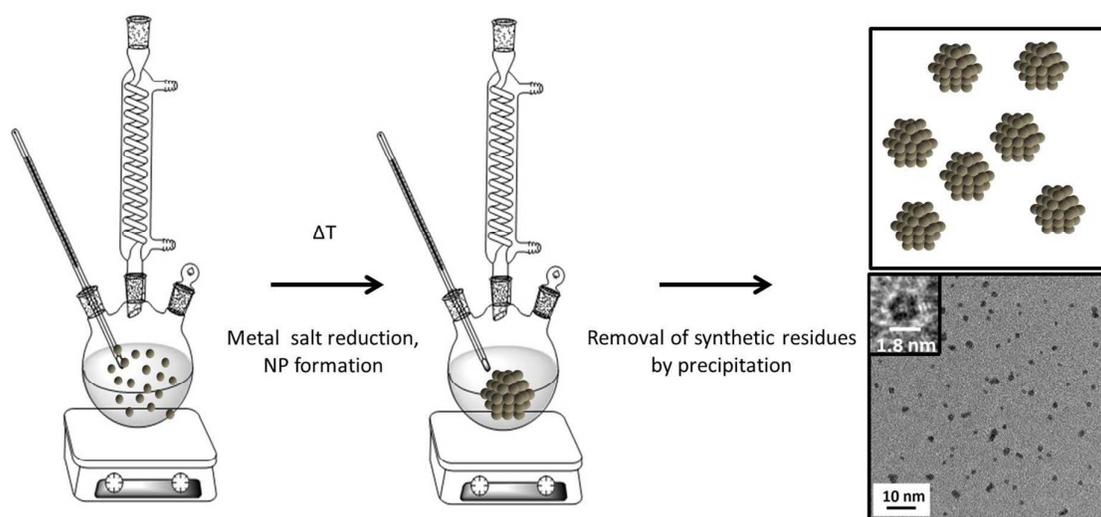
In order to investigate the influence of different ligands on the material's properties, one may exchange the capping agents with the desired ligands after synthesis (functionalization). The success of the ligand functionalization is determined by the different binding strengths of capping agent and ligand toward the NPs.<sup>28-30</sup> Strongly binding capping agents applied during synthesis may hinder effective and complete functionalization with ligands subsequent to the synthesis. In order to enable an effective functionalization with the desired ligand, a synthetic protocol is desired with minimum influence (weak binding) of capping agents which allows for an effective ligand exchange subsequent to NP synthesis. Furthermore, the separation of NP synthesis and functionalization into individual steps allows for investigation of the influence of the ligand on the material properties.

## 2.2 Polyol Synthesis of Pt Nanoparticles

In order to relate differences of the catalyst properties to the influence of the ligand, a preparation protocol has been chosen with minimal influence of capping agents during the synthesis which allows for the separation of NP synthesis and functionalization.<sup>31</sup> In this way, the ligand of interest can easily and effectively be bound to the NPs subsequent to their

synthesis, and differences in the catalytic properties can be related exclusively to the influence of the ligand.<sup>32</sup>

The so-called polyol synthesis is a synthesis strategy for colloidal NPs with its origin in the formation of  $\text{MeO}_x$  particles synthesized by reducing metal salts in ethylene glycol. However, these particles precipitate after synthesis due to their micrometer dimensions.<sup>33, 34</sup> The approach has been extended to the synthesis of noble metal particle colloids that are found to be successfully stabilized in alkaline polyol.<sup>35</sup> The main advantage of the polyol approach is that no strongly binding capping agents have to be added, as the polyol can fulfill three requirements: The polyol serves as solvent, reducing agent, and enables the colloid stabilization. In this way, only the metal precursor and the (alkaline) polyol are present in the reaction mixture. The polyol may stabilize small noble metal NPs, but however is not a strongly binding adsorbate. The most frequently used polyol is ethylene glycol (EG, ethane-1,2-diol), as it allows for reaction temperatures up to 200 °C and has the highest reduction potential as compared to oligo-ethylene glycols.<sup>36</sup>



*Figure 1: Polyol synthesis of platinum nanoparticles. Upon heating, the metal precursor  $\text{H}_2\text{PtCl}_6$  is reduced by alkaline ethylene glycol to form "unprotected" Pt NPs (the NPs are referred to as "unprotected" as no strongly binding adsorbates are added during synthesis). After synthesis, the NPs are washed and the synthesis residues are removed.<sup>37</sup>*

A preparation route for platinum NPs known from literature was applied for all particle syntheses.<sup>31</sup> A sketch of the synthesis strategy and a representative TEM image of the resulting Pt NPs are shown in Figure 1. Upon heating, the metal salt  $\text{H}_2\text{PtCl}_6$  is reduced in alkaline ethylene glycol to form Pt NPs. The resulting average NP size of 1.8 nm corresponds to a dispersion (ratio of surface atoms to total number of atoms per NP) of 0.56.<sup>37, 38</sup> The synthesis is highly reproducible and insensitive to disruptions of e.g. heating ramp or reaction temperature.

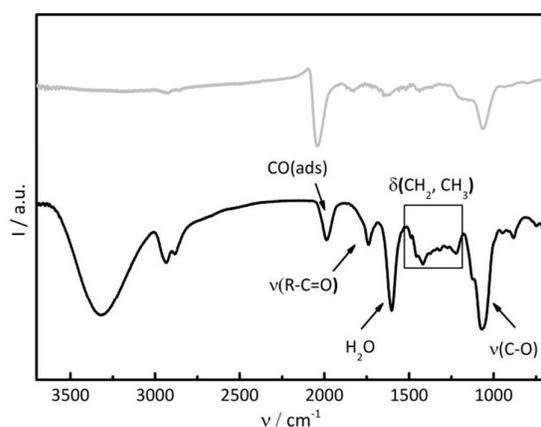


Figure 2: IR-Spectra of "unprotected" Pt NPs. Black: Isolation of Pt NPs by changing polarity of the solvent. Grey: Pt NPs precipitated with HCl and subsequent washing.<sup>37</sup>

The as-prepared NPs are referred to as "unprotected" due to the fact that no strongly binding capping agent is applied. However, a stable NP colloid requires an attractive interaction between solvent and NPs that is considered to be mediated by adsorbents on the NP surface. The precise mechanism of NP stabilization in the polyol approach is so far still not resolved. Possible adsorbates stabilizing the NP surface that are present in the reaction mixture are ethylene glycol or its oxidation products (glycolic and oxalic acid), carbon monoxide (side product of EG decomposition), OH- and chloride ions.<sup>31, 39</sup> IR spectra of "unprotected" Pt NPs isolated from the reaction mixture by precipitation with unpolar solvents (Fig. 2, black graph) reveal the large amount of molecules adsorbed on the NP surface. Parts of the organic

residues can be removed by precipitating and washing of the NPs with HCl and water (Fig. 2, grey graph). The remaining synthesis residues are no strongly binding adsorbates and, consequently, allow for subsequent functionalization.<sup>37</sup> After the washing procedure, redispersion of the NPs in polar solvents is possible as the solvents overcome the interparticle attraction by attractive interaction with the adsorbates on the NP surface.<sup>25</sup>

In summary, the major advantage of the polyol approach is the absence of strongly binding capping agents during NP synthesis that allows for subsequent manipulation of the surface. Residual adsorbates from synthesis can be exchanged by strongly binding ligands, e.g. amines, thiols, or phosphines, which is demonstrated in the following chapters. As a result, the "unprotected" NP colloids can serve as a basic building block for the selective functionalization with specific ligands subsequent to the synthesis.

### **3. STRATEGIES FOR NANOPARTICLE STABILIZATION AS SOLIDS**

Due to the high surface energy of NPs, stabilizing agents are required not only during synthesis, but especially for heterogeneous gas-phase or liquid-phase applications.<sup>11</sup> In this chapter, the state-of-the-art strategy for NP stabilization by supporting is introduced. Subsequently, the idea of stabilizing NPs with ligands, especially organic amines, is discussed.

#### **3.1 Deposition of NPs on inert support material**

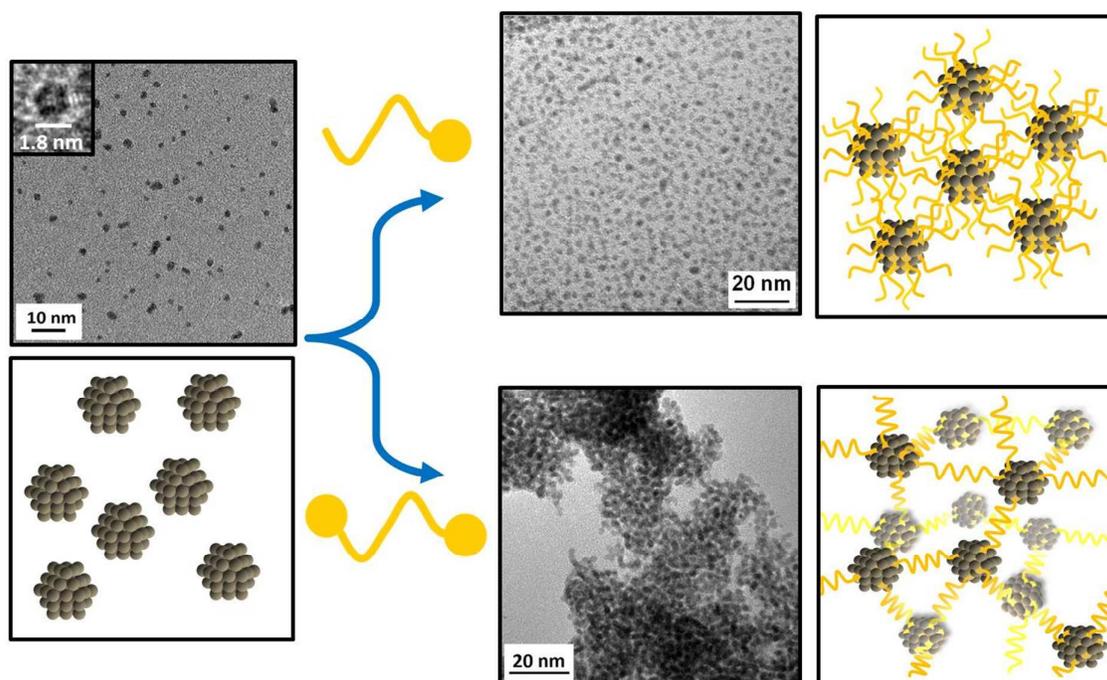
For applications in heterogeneous gas-phase or liquid-phase catalysis, NPs are mainly stabilized by supporting them on inert inorganic materials.<sup>40, 41</sup> Metal oxides like Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> are commonly used for gas-phase or liquid-phase catalysis, while high surface area carbons are state-of-the-art supports in electrocatalysis.<sup>42, 43</sup> At elevated temperatures, the deposited NPs may become mobile on the support.<sup>11</sup> In order to prevent the NPs from

agglomerating, which would result in a loss of the active surface area, the metal loadings in heterogeneous catalysis have to be kept low (< 10 wt%). Consequently, it is not possible to achieve a high ratio of catalytically active sites to total material weight.<sup>44</sup> For catalytic gas sensing, which requires high densities of active sites, the use of inorganic support materials thus is disadvantageous as it limits the sensitivity and deteriorates the response time of the sensor. An alternative approach for the stabilization of catalytic NPs was hence investigated, which is introduced in the following section.

### 3.2 Ligand-stabilized NPs as solids

In a dispersion, the attractive interaction between ligand and solvent prevents agglomeration of NPs. However, upon deposition of ligand-functionalized NPs onto a substrate and subsequent solvent evaporation, the ligand-ligand interactions between adjacent NPs become predominate. Alkyl chains as the simplest representative of hydrophobic ligands experience intermolecular *van-der-Waals* attraction, such that the deposited NPs locate themselves in close vicinity. It has been found that the distance between two adjacent alkyl stabilized NPs is less than twice the lengths of the linearly extended (*all-trans*) alkyl chains, which is explained by an interdigitation of the ligand tails.<sup>45-47</sup> An increase of the alkyl chain length leads to an increase of the attractive intermolecular interactions (around 4 kJ/mol per CH<sub>2</sub> unit) and, hence, supports a close arrangement.<sup>48</sup> Monodisperse NPs with long-chained hydrophobic ligands can even self-assemble into ordered superlattices with the closest packing of an hcp or fcc structure.<sup>47, 49</sup> The conformational flexibility of the alkyl chains enables space filling of the voids between the NP spheres.<sup>45</sup> However, the ligand interdigitation cannot proceed over the entire length of the alkyl chain for steric reasons. Consequently, the steric hindrance of the ligand tail still keeps the NPs apart from each other and, thereby, supports NP stabilization even as solids.

A second concept of sterical NP stabilization with ligands can be achieved with bifunctional ligands. The idea of the so-called concept of ligand-linking is to bind one ligand to two NPs to achieve a certain spacing between the NPs and, thereby, prevent agglomeration. Ligand-linking of NPs have been applied in a non-catalytic context. For example, thin films of dithiol-linked Au NPs have been prepared by layer-by-layer deposition and applied in resistive gas sensing by Joseph *et al.*<sup>50, 51</sup> The intermolecular interaction of volatile organic compounds (VOCs) with the linking ligands was found to change the electric resistance of the film and enables the detection of such molecules.<sup>51, 52</sup>



*Figure 3: Starting from "unprotected" NPs that result from the polyol process, the NPs can be functionalized with different mono- or bifunctional ligands. In this way, the material properties like its stability in catalytic applications can be related exclusively to the influence of the ligand.<sup>38</sup> "Reprinted with permission from Langmuir, 2014, 30, 5564-5573. Copyright 2015 American Chemical Society."*

The first example of linking catalytically active NPs with ligands was reported by Brauns *et al.*<sup>9, 10, 38, 53</sup>. Figure 3 sketches the applied preparation route toward ligand-stabilization. The synthesis of "unprotected" NPs *via* the polyol process allows for subsequent functionalization of the NPs with different mono- or bifunctional ligands in a separate step. In this way, different properties of ligand-functionalized NPs, e.g. their stability in catalytic applications, can be related exclusively to the influence of the ligand. Furthermore, materials can be prepared that exhibit a high density of the active component (around 70 wt% Pt NPs).<sup>37</sup>

#### 4. STABILIZATION OF PT NPS WITH MONO-AMINE LIGANDS

Pt NPs can be functionalized with mono-amines *via* replacement of weaker binding capping agents, which is denoted as functionalization. To readily indicate the success of ligand binding, functionalizations are often executed as phase transfer reactions.

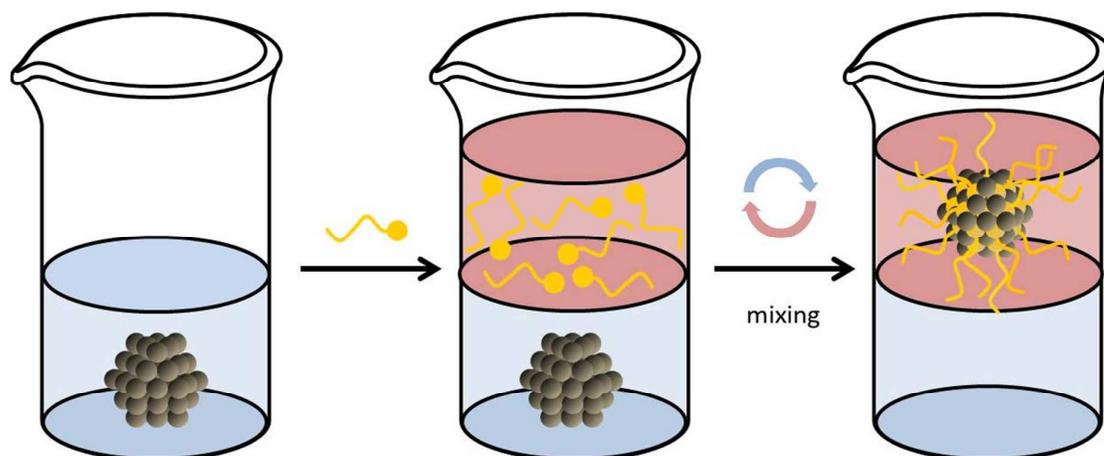


Figure 4: Functionalization of a Pt NP with mono-amines, accompanied by phase transfer of the functionalized NP.<sup>37</sup>

Figure 4 visualizes the functionalization of "unprotected" NPs with an alkylamine. The process of ligand binding is accompanied by a phase transfer of the NPs. The NPs are

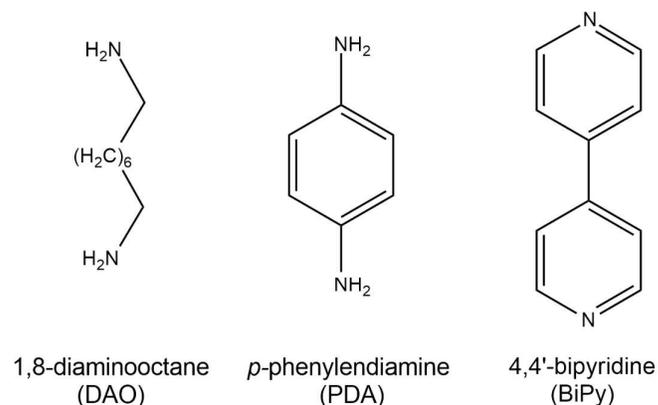
dispersed in a polar medium (e.g. ethylene glycol, utilizing the as-prepared NP colloid, here: blue), while the ligand (alkylamine) is dissolved in a nonpolar solvent (e.g. toluene, here: red) that is not miscible with the polar medium. Upon mixing of both phases, the ligands bind to the NPs. As a consequence of the nonpolar ligand tail, the functionalized NPs are transferred to the nonpolar phase which exhibits attractive interaction with the ligand shell. A color change of both phases indicates the successful phase transfer. The presented preparation route merely works for nonpolar ligands. However, an alternative preparation route that allows for the binding of polar ligands with thiol and amines as anchoring groups to “unprotected” Pt NPs can be found in the literature.<sup>54, 55</sup>

## 5. LIGAND-LINKED NANOPARTICLES

### 5.1 Concept of ligand-linking

As introduced above, the idea of ligand-linking is to bind one ligand to two NPs in order to keep them apart from each other and prevent agglomeration. Three-dimensional networks can be built from NPs and bifunctional ligands.<sup>38</sup> In literature, studies can be found about ligand-linked NP thin films and investigations about their optical and electrical properties.<sup>48, 50, 52, 56-58</sup> However, the concept of ligand-linking for the preparation of catalytic materials has only seldom been discussed, so far.<sup>38</sup> The linking ligands used in catalytic gas sensing so far consist of a hydrocarbon spacer, e.g. an alkyl chain or phenyl ring, and two amine head groups in *α,ω*- or *para*-position, respectively (see Figure 5 for structural formula of the ligands). The primary amines 1,8-diaminooctane (DAO) and *para*-phenylenediamine (PDA) have an alkyl or aryl spacer, respectively, and consequently differ in their conformational degrees of freedom and chemical stability of the backbone, while the hybridization of the amine group is similar. In contrast, 4,4'-bipyridine (BiPy) is a tertiary amine with the N

incorporated in the aromatic system, which leads to a  $sp^2$  hybridization of N. Consequently, the electron density is more localized at N as compared to the primary  $sp^3$  amine of DAO and PDA. In addition, BiPy has little conformational degrees of freedom due to the aromatic sub-units.



*Figure 5: Structural formula of the bifunctional amines used for ligand-linking.*

The approach used for linking starts with "unprotected" Pt NPs, as sketched in Figure 3. Both amine head groups of one ligand can bind to two individual NPs to link them. The linked NPs are, as a result, kept at a distance by the ligand. With proceeding linking, a three-dimensional network of NPs interconnected by bifunctional ligands is created (Fig. 3, right sketch).<sup>38</sup> Upon mixing a dispersion of "unprotected" NPs with a bifunctional ligand solution, the NPs will be linked, which eventually leads to precipitation. A colorless solvent indicates successful incorporation of all NPs into the network. The ligand-linking of Pt NPs with amines is not reversible and the ligand-linked NP networks are not soluble due to the anchoring of amines on Pt, as indicated by the precipitation.<sup>48</sup> In contrast to phase transfer reactions, functionalization with bifunctional ligands has consequently the advantage of a strong driving force toward the linked state.

## 5.2 Properties of ligand-linked Pt NPs

If multilayer NP assemblies are used for catalytic applications, not only the presence of ligand-free surface sites of individual NPs is relevant. In addition, the accessibility of the sites (e.g. by a porous morphology of the material) is an essential factor as diffusion limitations can lower the catalytic performance. The three-dimensional assembly of ligand-linked particles sketched in Figure 3 can be imaged by scanning electron microscopy (SEM). Figure 6 displays SEM micrographs of PDA-Pt NPs representative for ligand-linked NP networks.<sup>38</sup> The porous morphology of the network indicates the accessibility of the material for catalytic conversions. A high magnification image (Fig. 6 b)) enables even the resolution of individual NPs (bright spots), which verifies that the porous assembly does not consist of sintered NPs. Experimental tools besides SEM for the characterization of ligand-linked NPs that have already been applied successfully are IR spectroscopy to probe the ligand structure, elemental analysis and atomic absorption spectroscopy to estimate the ligand to metal ratio, and cyclic voltammetry for determining the number of ligand-free surface atoms (electrochemical surface area, ECSA).<sup>38,53</sup> ECSA did not show any strong deviation for the three linking ligands, but clearly evidences that more than 50 % of the metal surface atoms are ligand-free and therefore suitable to be catalytically active (see Table 1). In contrast, the use of monoamine ligands leads to very high ligand coverages (up to 100 %)<sup>59</sup> and therefore complete blocking of the catalytic surface as demonstrated for hexadecylamine (HDA) functionalized Pt NPs.

*Table 1 Electrochemical surface areas (ECSA) determined by from hydrogen under potential adsorption. HDA (hexadecylamine) is shown representative for a monofunctional ligand. For HDA-Pt NPs no ECSA was detectable. In contrast, more than 50 % of the Pt surface atoms are accessible for hydrogen adsorption evidencing the potential of these materials for catalytic conversions.*

	“unprotected”	HDA-	DAO-linked	PDA-linked	BiPy-linked
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	Pt NPs				
ESCA (m <sup>2</sup> /g)	100	-	61	53	66

Further methods that have yet not been applied for characterization of ligand-linked NPs but may be of interest for future studies are solid state NMR, Raman, or photoelectron spectroscopy.

As the minimal pore size is determined by the spacer length of the ligands, the accessibility of the porous structure may however be limited for larger reactants with sizes bigger than the dimensions of the ligands. This may enable for controlling selectivity by manipulating the accessibility of catalytic sites within the material. For further details on the quantification of the ligand-free surface area of the NP networks, the reader is referred to Morsbach *et al.*<sup>37,38</sup>

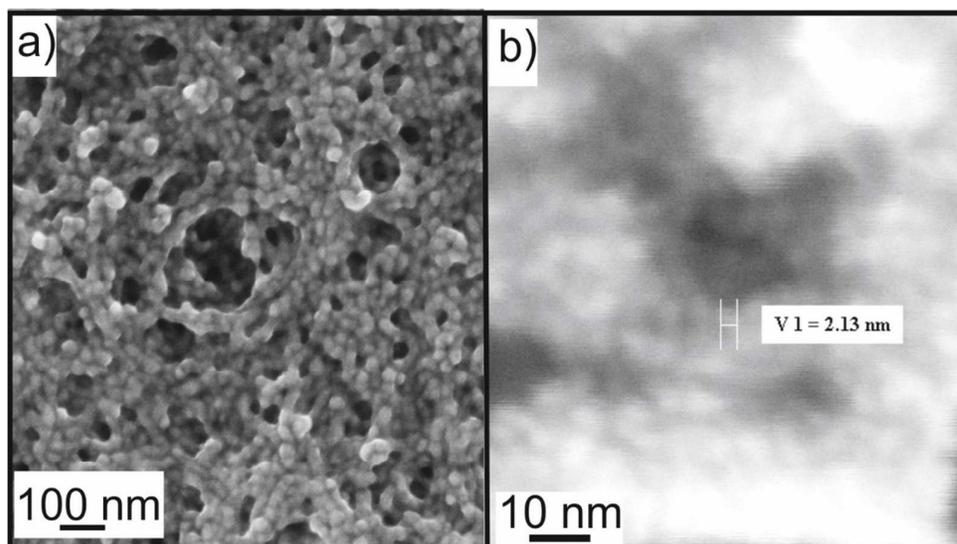


Figure 6: Scanning Electron Microscopy images of ligand-linked Pt NPs with a) low magnification and b) high magnification. The bright spots in b) correspond to individual NPs. "Reprinted with permission from Langmuir, 2014, 30, 5564-5573. Copyright 2015 American Chemical Society."

## 6 CATALYTIC HYDROGEN SENSING WITH PT NPs

Reports about catalytic gas sensors with NP catalysts merely concern NPs stabilized on an inorganic support, adopting strategies from gas phase catalysis.<sup>60-62</sup> However, the loading of the catalytically active metal on the support is usually limited to low weights, which limits the ratio of catalytic sites to the overall catalyst mass. In section 6.1 it will be discussed how this fact affects the overall sensor performance. As an alternative to supported NPs, ligand-stabilized Pt NPs were tested with respect to their performance in catalytic gas sensing, as the stabilization with ligands enables a high density of active sites in the material. In section 6.2, the benefits of the high density of active sites will be discussed.

### 6.1 Introduction into catalytic hydrogen sensing

Catalytic gas sensing denotes the detection (and quantification) of gases by catalytic conversion (combustion), which triggers the sensor signal. In general, gas sensing with Pt NPs as catalyst is possible for all volatile molecules that can be catalytically converted by Pt *via* an exothermic (or theoretically also endothermic) reaction. The main focus of the presented and discussed results lies on hydrogen sensing as one example for a gas with high industrial relevance.<sup>13</sup>

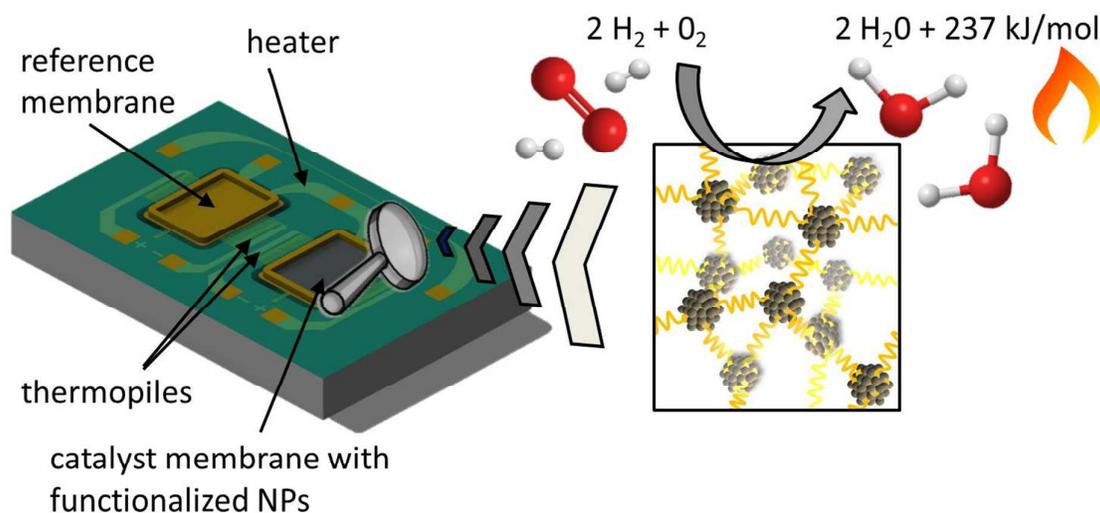


Figure 7: Catalytic gas sensor with functionalized NPs as catalyst. The reactant gases diffuse to the catalyst, where they are catalytically converted. As a result, the exothermic heat of reaction induces the sensor signal.<sup>37</sup>

Figure 7 illustrates the principle of a thermoelectric hydrogen sensor and its working principle. The sensor design and working principle were described in detail by Brauns *et al.*<sup>9</sup>

<sup>10</sup> The functionalized Pt NPs are deposited onto the catalyst membrane, which is connected to a heater and thermopiles. The heater ensures the stable operating temperature. Thermopiles are electronic devices in which an electric potential arises upon a temperature difference between both ends (junctions) of the thermopiles (Seebeck effect). The gas molecules - here hydrogen in synthetic air - diffuse into the catalyst. On the NP surface, the reactants ( $\text{H}_2 + \text{O}_2$ ) are converted to water. The exothermic heat of reaction induces a temperature difference at the thermopiles, which causes the sensor signal (electric potential) with the Seebeck coefficient being the constant of proportionality. As a result, there is a linear relationship between hydrogen conversion and height of the sensor signal.<sup>9</sup> The correlation between hydrogen partial pressure and sensor output has been investigated by stepwise increasing and subsequently decreasing the hydrogen partial pressure and recording the output signal. A clear resolution can be achieved down to 20 ppm  $\text{H}_2$ , while at around 10 ppm of  $\text{H}_2$  the electrical

noise becomes dominant.<sup>10</sup> The resolution of the sensor is independent from the ligand of the catalytic material.

Due to the sensor's operating principle, a good sensor performance requires a high temperature difference between catalytic material and sensor substrate. This is achieved by a good thermal isolation of the catalyst membrane and a high ratio of catalytic surface sites to the total catalyst mass in order to keep the heat capacity of the catalyst low,. A catalyst which fulfills these requirements enables a high sensitivity and short response times, as the heat of reaction is effectively converted into a temperature difference.<sup>10</sup> Of course, a good long-term stability of the catalyst is desired as well. The ligand-linked Pt NPs show a high weight ratio of the catalytic component (Pt ~70 wt%) to the material needed for the NP stabilization (ligands ~30 wt%). Furthermore, due to their small sizes the NPs exhibit a high surface-to-volume ratio (NP diameter ~ 1.8 nm). Due to these properties, ligand-linked NPs are promising materials for an application in catalytic gas sensors.

## 6.2 Gas-sensing with ligand-stabilized Pt NPs

Pt NPs stabilized with mono-amine ligands (HDA and aniline), di-amines (DAO, PDA, BiPy), and unprotected Pt NPs for comparison were applied as catalysts in hydrogen sensing in order to investigate the influence of the different stabilizing ligands on the long-term stability. The sensor measurements were performed with a constant stream of 1 vol% of hydrogen in synthetic air, and the sensor output was recorded over time. The results are displayed in Figure 8. The sensor signal has been converted from the electric potential to the generated temperature difference  $\Delta T$  to account for different Seebeck coefficients of individual sensors. Activation behavior, sensitivity (height of sensor signal for a given hydrogen partial pressure), and long-term stability are discussed in detail by Morsbach *et al.*<sup>53</sup>

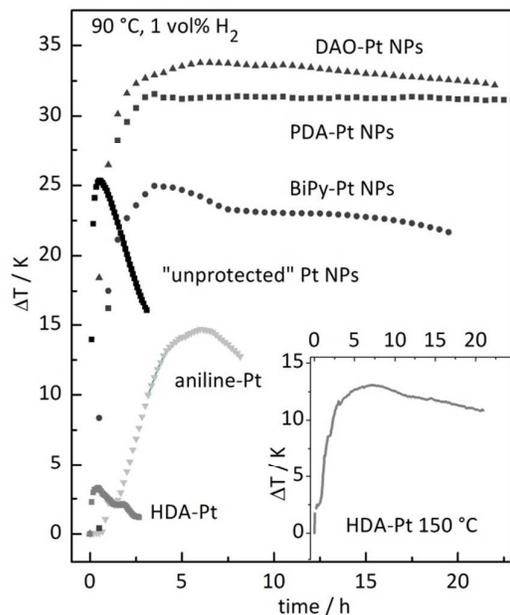
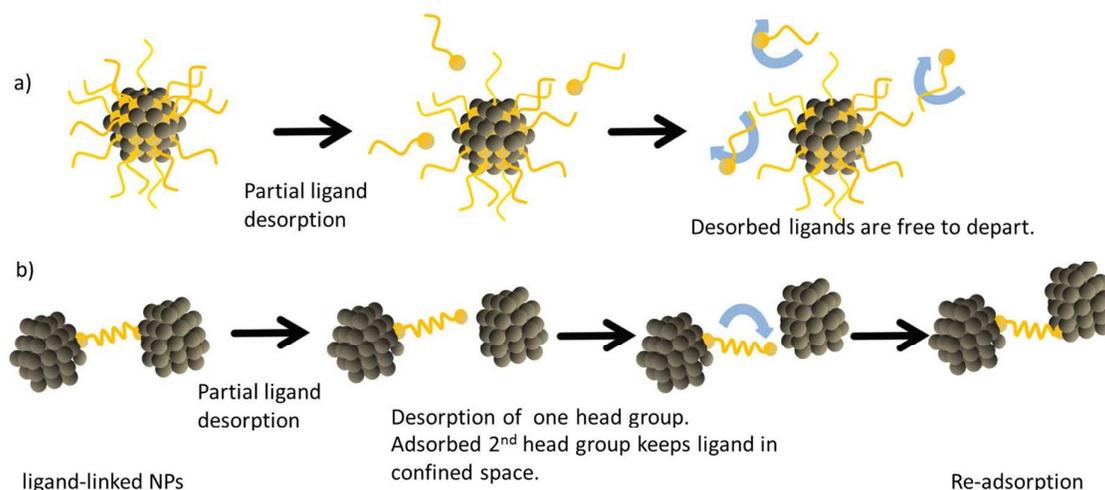


Figure 8: Sensor performance of functionalized NP catalysts. Sensor output under a constant stream of hydrogen at 90 °C for different NP catalysts. The inset displays the output of HDA-Pt at 150 °C operating temperature. Reproduced from Reference 53 with permission from Royal Society of Chemistry.

"Unprotected" Pt NPs as catalysts produce a high sensor signal after a very short activation phase, see Figure 8, while the stability is very poor and the sensor output drops rapidly. Due to the absence of any stabilizers, the NPs sinter rapidly, which reduces the catalytic surface area.<sup>11</sup> As a consequence, the reactant conversion is diminished, which leads to a deteriorated sensor signal.

The sensor signals of HDA-Pt catalysts (at 150 °C operating temperature) and aniline-Pt catalysts are moderate and decrease constantly and significantly after reaching a maximum.



*Figure 9: Partial ligand desorption of amines on Pt NPs. In the desorbed state, the stabilization effect on the NPs is diminished and the ligands may be decomposed in catalytic applications, an effect that leads to NP sintering. For monoamines, re-adsorption of desorbed ligands is made difficult due to the fact that ligands may depart from the vicinity of the NPs. In contrast, the bifunctionality may support re-adsorption of desorbed head groups, as the second anchoring group and conformational restrictions leave the desorbed head group in the vicinity of the NP which, in turn, enables re-adsorption. As a result, the NPs are effectively stabilized.*

After the activation phase, the output signal of BiPy-Pt and DAO-Pt slowly decreases over the course of the experiment, while the performance for PDA-Pt remains constant once the maximum activity is reached. The loss of activity of ligand-linked NPs occurs at a lower rate compared to monoamine-stabilized Pt NPs.

As discussed above, the stabilizing effect of ligands is only maintained as long as they are bound to the surface and their structure is intact. Figure 9a) sketches the effects of partial ligand desorption at elevated temperatures on the NP stabilization for monofunctional amines during catalytic applications. The ligands may partially desorb from the NP surface under catalytic conditions (middle sketch). In the desorbed state, the ligands are free to depart from the vicinity of the NP surface (right sketch) or may even get decomposed due to hydrogenolysis reactions. Consequently, re-adsorption is unlikely to occur once the ligands are desorbed from the NP and is prevented when the ligands are decomposed, which, in turn,

diminishes the stabilizing effect on the NPs and enables sintering. These results reveal that mono-amines cannot sufficiently stabilize Pt NPs for catalytic applications.

In contrast, for ligand-linked NPs partial amine desorption has a less negative impact, as illustrated in Figure 9b). An amine group may desorb from the NP surface as well. However, when one head group of a bifunctional ligand is desorbed, the ligand is still anchored to a NP *via* its second head group. Movements of the anchored ligand are restricted and limited to the intramolecular conformational degrees of freedom (see step 3). As a consequence of the anchoring, the ligand cannot depart from the vicinity of the NP and the desorbed head group is restricted to a confined volume close to the NP surface. A re-adsorption of the desorbed head group is hence fostered, which leads to maintenance of the stabilization and prevents ligand decomposition. As the simultaneous desorption of both head groups of one ligand molecule is unlikely to occur, linking ligands can be considered as more effective NP stabilizers in comparison to mono-functional amines.

In contrast to the other ligands, PDA-Pt generates a constant sensor output in a continuous stream of hydrogen. The PDA ligand on Pt may partially desorb as well, which challenges the stability. However, the rigid conformation of PDA may effectively support re-adsorption of desorbed head groups. Additionally, the aromatic backbone of PDA is chemically quite stable and is, thus, hardly oxidized or cleaved under the applied catalytic conditions.<sup>53</sup> As a result, the NPs are stabilized and sintering is prevented, such that no catalyst degradation was observed for more than 20 h on stream. The combination of a diamine and aromatic backbone as in PDA enables to stabilize NPs and create an active catalyst for hydrogen sensing. These results underline the potential of ligand-linking for NP stabilization in catalytic applications that require a high density of catalytically active centers.

## 7. PERSPECTIVE

Future studies on NP catalysts for gas sensing may investigate the implementation of selectivity toward gas mixtures by a sophisticated ligand choice. In addition to the stabilizing effect, the ligands direct the porosity of the NP network, as the minimum pore size is determined by the ligand length and its steric demand. The diffusion of reactants into a porous system depends on the ratio of pore diameter to reactant size. In this way, by adjusting the porosity of the ligand-linked NP network, it may be possible to manipulate selectivity by inhibiting the diffusion of larger molecules into the particle network. Further improvements of the long-term stability by the application of different ligand structures may be achievable. Although PDA-Pt is stable over more than 20 h of catalytic activity, the  $\sigma$ -bond between amine group and aromatic system is a site of fracture, as previously shown.<sup>53</sup> The key to further enhance the stability is to search for anchoring groups that bind stronger to Pt than amines. Also, by investigating further ligand structures it will be feasible to determine the probability of fracture for various chemical moieties and thus to rate their potential as building blocks for the design of stable ligands.

A further possibility to control selectivity and to improve stability may be the application of bimetallic NPs. The decomposition of ligands during sensor operations is expected to be assisted by larger Pt ensembles that are suitable for C-C cleavage.<sup>63</sup> The alloying of Pt with a catalytically inactive metal could dilute Pt surface atoms and, in this way, decrease the size of Pt ensembles. The active surface area of bimetallic NPs may be maintained by selective ligand functionalization. For example, carboxylates are known to strongly bind to Ag or Sn, while no stable bond is formed to Pt.<sup>64</sup> Thereby, ligand-linking of PtM NPs (M = Ag or Sn) with a bifunctional carboxylate ligand (*e.g.* terephthalic acid) could exclusively occur *via* carboxylate-M bonds and leave the Pt surface atoms ligand-free. An alloying of the catalytic NPs may also result in a different electronic structure. Thereby, selective adsorption of gases may be achieved and, in this way, a selective response toward one gas in a gas mixture.

## 8. CONCLUSIONS

Nanoparticles (NPs) are known to exhibit unique chemical and physical properties in comparison to the corresponding bulk materials. Due to their large surface-to-volume ratio and the resulting high surface energy, nanoparticles tend to aggregate and coalesce, which results in a loss of the nano-structure. Stabilization of NPs is hence prerequisite for usage in order to maintain the specific properties of nano-scaled materials. Applications such as thermoelectric gas sensing require a high density of catalytically active sites together with a low total heat capacity in order to achieve a short response time and a high sensitivity. In this review, novel NP catalysts that are stabilized by organic ligands are presented as an alternative approach to the supporting of NPs. The catalytic properties of NPs stabilized with mono- and diamines were discussed by their application in a thermoelectric hydrogen sensor. Investigation of the catalytic properties of mono-amine protected NPs however resulted in an insufficient activity and stability. The loss in stability is caused by partial desorption of the ligand, such that the stabilization effect is diminished. As a result, the NPs may aggregate and the surface area of the catalyst decreases. In conclusion, mono-amines are not suitable for stabilizing Pt NPs in catalytic gas sensors.

The concept of molecular linkage of nanoparticles with bifunctional amine ligands (ligand-linking) was introduced as an alternative to the use of monofunctional ligands. With the three-dimensional porous networks built by linking Pt NPs with diamines lead to high activities. Compared to mono-amine stabilized NPs, the stability can be significantly improved by ligand-linking. One reason may be that during a possible desorption of one head group the bifunctional ligand remains anchored on a NP *via* the second head group. This anchoring can enhance re-adsorption of the desorbed head group so that stabilization is maintained. To achieve a good stabilization, an aryl backbone with two primary amine head groups is beneficial. These criteria are best met by *para*-phenylenediamine (PDA) so that by linking of Pt NPs with PDA a constant catalytic activity over more than 20 h on stream was reached. It

is hence concluded that a novel NP catalyst for catalytic gas sensing could be introduced by stabilizing Pt NPs with organic diamines in solid state.

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