

## Surface Functionalization

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# A General Approach for Monolayer Adsorption of High Weight Loadings of Uniform Nanocrystals on Oxide Supports

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Abstract: Monodispersed metal and semiconductor nanocrystals have attracted great attention in fundamental and applied research due to their tunable size, morphology, and well-defined chemical composition. Utilizing these nanocrystals in a controllable way is highly desirable especially when using them as building blocks for the preparation of nanostructured materials. Their deposition onto oxide materials provide them with wide applicability in many areas, including catalysis. However, so far deposition methods are limited and do not provide control to achieve high particle loadings. This study demonstrates a general approach for the deposition of hydrophobic ligand-stabilized nanocrystals on hydrophilic oxide supports without ligand-exchange. Surface functionalization of the supports with primary amine groups either using an organosilane ((3-aminopropyl)trimethoxysilane) or bonding with aminoalcohols (3-amino-1,2-propanediol) were found to significantly improve the interaction between nanocrystals and supports achieving high loadings (>10 wt.%). The bonding method with aminoalcohols guarantees the opportunity to remove the binding molecules thus allowing clean metal/ oxide materials to be obtained, which is of great importance in the preparation of supported nanocrystals for heterogeneous catalysis.

### Introduction

Colloidal nanocrystals (NCs) with dimensions below 100 nm possess unique electronic, magnetic, optical, and chemical properties distinct from their bulk counterparts playing an important role in modern science and technology.<sup>[1]</sup> Incorporating NCs into materials and devices allows a variety of novel applications in sensing,<sup>[2]</sup> optoelectronic,<sup>[3]</sup> biomedicine,<sup>[4]</sup> and catalysis.<sup>[5]</sup> Nowadays, monodisperse NCs of many metals and semiconductors are synthesized through solution chemistry approaches.<sup>[6]</sup> To utilize these colloidal NCs in a variety of applications, their controlled immobilization on a surface is usually the important first step. For example, in heterogeneous catalysis, the distribution of adsorbed NCs and the nanoscale geometry and interfacial

structure between NCs and oxide support are key parameters that determine the observable catalytic properties and stability of the catalysts.<sup>[5e,7]</sup> Therefore, developing methods to controllably and reliably deposit uniform NCs on support surfaces is crucial for preparing advanced materials and devices for many applications especially in catalysis<sup>[5e,7b]</sup> and sensing.<sup>[8]</sup>

When impregnating NCs from aqueous solutions, surface charges are the most common parameters used to tune the electrostatic interaction between NCs and supports and develop attractive force between them aimed at NC deposition.<sup>[9]</sup> Surface modification of supports with functional groups such as amines, phosphates and carboxylates is a typical way to match their Zeta potential to NCs at a certain range of pH.<sup>[9c]</sup> However, a variety of uniform NCs are produced in non-aqueous conditions capped with long chain alkyl surfactants, and multiple steps of ligand exchange or surface coating may be required to make NCs dispersible in the aqueous phase, if possible at all. Although useful methods have been developed for this purpose,<sup>[10]</sup> these modifications might inevitably lead to issues such as low yield and particle agglomeration. On the other hand, with a typical loading method conducted in a non-aqueous solution, common supports such as oxides are usually not well dispersible due to their hydrophilic hydroxyl surfaces. Finding a solvent with suitable dispersibility for both oxides and the non-polar ligand-stabilized NCs is crucial to obtain well-distributed NCs. In addition, minimizing residual surface ligands by washing NCs with anti-solvents while avoiding destabilization can be very subtle for successful NCs deposition. Finding the appropriate conditions to deposit hydrophobic colloidal NCs on common oxide surfaces has therefore proven to be challenging, and a generalized and straightforward solution has not been found yet.

Stucky and co-worker investigated the complex interactions between colloidal Au NCs, oxide supports, and organic solvents.<sup>[11]</sup> An aprotic, slightly polar solvent such as chloroform was used as a good solvent for dispersing oxide materials while maintaining NCs stability and allowing uniform deposition. The weak dipole/induced-dipole or charge/induceddipole interactions between the oxides and NCs were claimed to drive deposition. Recently, de Jong and co-workers demonstrated adsorption of iron/iron oxide NCs on carbon nanotube supports at 200 °C in octadecene showing that diffusion and dynamic adsorption and desorption of NCs were important factors to uniformly deposit large loadings of NCs (2–30 wt.%) on a porous support.<sup>[12]</sup> The authors also hypothesized a mechanism where the carbon nanotube

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surface acts as a surface ligand to bind NCs and providing a driving force for lowering the NCs surface energy. While these studies partially solve the issues of NC adsorption in specific NC-support combinations, there is a lack of quantitative measurements and a more detailed analysis of the adsorption behavior. In this contribution, we report a generalized method for the adsorption of a variety of hydrophobic, ligand-stabilized colloidal NCs on oxide surfaces at high weight loadings through the understanding of surface modification and binding configuration. Primary amines are introduced on oxide support surfaces through condensation of an organosilane (Scheme 1 a) or using 3-amino-1,2-pro-



**Scheme 1.** Surface functionalization of amino groups on oxide supports using a) (3-aminopropyl)trimethoxysilane (APTS) or b) 3-amino-1,2-propanediol (APD). Proposed adsorption behavior of NCs on c) bare oxide and d) amine-functionalized oxide supports.

panediol (Scheme 1b). A strong affinity of the amino group to the ligand-stabilized NCs was observed even in the presence of a polar protic solvent, thus allowing strong adsorption of the NCs to the oxide surface. The chemical interactions between solvent, oxide surface, and NCs were elucidated in a quantifiable way using adsorption isotherms. The functionalized amino groups might partially exchange the surface ligands attached on the NCs at the adsorption interfaces leading to a stronger binding strength than that of bare oxide surfaces (Scheme 1 d).<sup>[13]</sup> In addition, the thermally removable diol modification is proven to be an important alternative to the organosilane modification which guarantees the preparation of a single-layer homogeneous supported NC catalyst with a wide range of tunable NC weight loadings without changing the surface property of the oxide supports deriving from the residual silica layer. The catalysts made by the presented method optimize the distribution of NCs on oxide supports even at weight loadings as high as 10 wt.%, displaying much higher catalytic activity than those prepared by conventional impregnation methods that lead to sintered metallic phases.

### **Results and Discussion**

The uniform dispersion and deposition of colloidal NCs on an oxide support was initially studied using previously reported approaches. All the NCs synthesized in this work (Figure S1) were stabilized by long chain alkyl surfactants such as oleylamine and oleic acid. To obtain homogeneously distributed NCs, a 10% by volume ethanol/toluene mixture was selected as the solvent for NC adsorption. This mixture was selected to obtain a compromise between dissolving the hydrophobic NCs in toluene, and dispersing the oxide support using ethanol to increase the mixture polarity. Comparing with using pure toluene, the 10% ethanol/toluene mixture shows more well-distributed NCs adsorption on oxide surfaces (Figure S3). In fact, when using the Hansen solubility parameter to compare this mixture with chloroform, their parameters are very close (including the components of dispersion, polarity, and hydrogen bonding). Chloroform has been demonstrated to be a good solvent for depositing dodecanethiol-stabilized Au NCs on oxides.<sup>[11]</sup> An initial study was performed by measuring the actual NC loading using monodisperse, 5.7 nm Pt NCs (Figure S1b) on selected oxide supports (y-Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>,) and reporting it as a function of targeted NC loading (Figure 1 a–c). While  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> fully adsorbed Pt NCs up to at least 15 wt. % loading (Figure 1 a),  $TiO_2$  and  $SiO_2$  showed much lower adsorption ability (Figure 1 b,c). As Stucky and co-worker pointed out, ethanol could interfere with the adsorption of NCs due to hydrogen bonding between alcohol and hydroxyl groups on oxides that is stronger than the interaction between NCs and oxide surface.<sup>[11]</sup> Among different supports, the available surface area and density of hydroxyl groups might cause differences in adsorption capacity. We hypothesized that chemical interactions between NC ligands and support oxides were not optimal for NC adsorption. Therefore, we decided to introduce functional groups on the surface of the oxide materials to strengthen the interaction with the NCs and allow deposition. The oxide supports were chemically modified with amino groups (see FTIR spectra in Figure S4) using an organosilane ((3-aminopropyl)trimethoxysilane, or APTS) as shown in Scheme 1a. The NC adsorption amounts were greatly improved after APTS modification for all the oxide supports (Figure 1 d-f), indicating the formation of stronger interactions between NCs and amine-functionalized surfaces. The functionalized APTS either can possibly disrupt the hydrogen bonding between the protic solvent and oxides, or the attractive interactions between functionalized amines and NCs appear to be even stronger than the hydrogen bonding because all APTS-modified supports could adsorb at least up to 15 wt.% metal NCs even in the presence of ethanol. It is noted that the adsorbed NCs on the APTS-modifed supports could still desorb from the oxide surfaces once the nanocomposites are redispersed in pure ethanol, indicating that the attractive force between the amine-functionalized oxides and NCs could be mainly due to dipole/induced-dipole or charge/induced-dipole interactions. It has been reported that a small amine-containing molecule (dimethylamine) exchanges the surface ligands in oleylamine- or polyvinylpyrrolidonestabilized metal NCs even if the binding strength of amino



**Figure 1.** Loading amount of Pt NC (5.7 nm) on bare (a, b, c) and APTS-functionalized (d, e, f)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, respectively, in 10 vol.% ethanol/toluene mixture with added 0.01 vol.% of 1-oleylamine (circles: bare oxides; squares: APTS-functionalized oxides). The insets in (g, h, i) show the pictures of vials containing the supernatant and NC-oxide supports following centrifugation.

groups to the NCs surface is similar.<sup>[13]</sup> Therefore, we considered the possibility of ligand-exchange at the interfaces between the NCs and amine-functionalized supports, which could in part contribute to the enhanced binding affinity and adsorption capacity, as depicted in Scheme 1 d. Through optimization of the dispersity and adsorption capability of the oxide supports by using a suitable solvent (10% ethanol/ toluene) and a simple surface functionalization (amino groups), respectively, a monolayer of adsorbed NCs on supports without obvious agglomeration even at the highest loading point shown in Figure 1 d–f was achieved (Figure S5).

Excess surfactant derived from the NC synthesis that was not properly removed during purification may also represent an important factor in determining the NC adsorption and the reproducibility of the process. Figure 1 g–i shows the adsorption of purified NCs in the ethanol/toluene mixture with intentionally added 0.01 vol. % of 1-oleylamine, which is used as the capping ligand for the Pt NCs. The adsorption capacity of the bare oxides was heavily influenced by this low concentration of free surfactant in solution. The loading amount was lowered to less than 2.0 wt. % on any support, including alumina, in the presence of oleylamine. One possible explanation is that the amino group of oleylamine molecules could physically adsorb on the oxide through hydrogen bonding with the surface hydroxyl groups, leading to the formation of a monolayer that varies the surface properties and leads to repulsive interactions with the NC capping ligands (Scheme 1 c). In fact, it was observed that the oxides are more dispersible in non-polar solvents when oleylamine was introduced, indirectly confirming that oleylamine binds to the surface. It is important to note that if NCs are not thoroughly purified after synthesis, any residual surfactant in the NC solution could then cause challenges in adsorbing NCs onto oxide supports. Despite the presence of extra surfactant, when the oxide surface is functionalized with amino groups from APTS, the NCs still fully adsorbed on the oxide surface within the tested loading range (Figure 1 g-i). This result suggests that surface functionalization impedes oleylamine from binding to the oxide surface, and the NCs therefore have stronger attractive interactions that allow their deposition (Scheme 1d). Since the excess oleylamine could still block particle deposition at high concentrations, this observation further suggests that it is not the interaction between organic groups on the support and organic ligands on the surface of the particles that drive the deposition, but instead dipole/induced-dipole or charge/induced-dipole interactions.

The data in Figure 1 demonstrates that the functionalization of oxide support surfaces with amino groups is therefore a successful strategy to directly adsorb large and controlled loadings of hydrophobic ligand-stabilized colloidal NCs from solution. It is noted that APTS-functionalization is a very common strategy used to prepare supported NCs in aqueous solution as well,<sup>[14]</sup> but the driving force is often based on electrostatic interaction which is different from the presented method as discussed above. However, in both cases surface modification using an organosilane such as APTS eventually leaves a silicon layer on the surface which cannot be removed with thermal treatments, thus changing the chemical properties of the support which are often crucial in some applications such as catalysis.<sup>[14a,15]</sup> To minimize the influence of surface modification, we therefore investigated support functionalization strategies with amine-containing molecules that can be removed through thermal treatments following deposition. 3-amino-1,2-propanediol (APD) which could possibly condense on oxide hydroxyl groups as shown in

Scheme 1b and two more molecules (Figure 2a) including 1,3-propanediamine (PDA) and N-(2-aminoethyl)-1,3-propanediamine (AEPA) were tested for the functionalization of TiO<sub>2</sub> in ethanol. After adsorption and drying, the functionalized supports were subjected to temperature-programmed oxidation to quantify the amount of bonded amine-containing molecules using  $CO_2$  formation as a proxy (Figure 2b). While diamine (PDA)- and triamine (AEPA)-modified TiO<sub>2</sub> showed much less of the CO<sub>2</sub> production (0.33 and 0.42 mmol  $g^{-1}$ , respectively) compared to that of APTS-modified TiO<sub>2</sub>  $(0.70 \text{ mmol g}^{-1})$ , the aminodiol (APD)-modified TiO<sub>2</sub> (0.71 mmolg<sup>-1</sup>) produced a similar amount of CO<sub>2</sub> as estimated from the integrated areas. The binding strength of 3-amino-1,2-propanediol to the oxide surface was clearly stronger than other physisorbed amines. Indeed, catechol compounds such as dopamine have been demonstrated to strongly bind to oxide surfaces in aqueous solution.<sup>[16]</sup> We chose the diol molecule instead of catechol compound to avoid possible polymerization byproducts (for example with dopamine<sup>[16b]</sup>).

Adsorption isotherms of Pt NCs on the amine-functionalized TiO<sub>2</sub> supports were then measured and plotted in Figure 2c. APTS-TiO<sub>2</sub> and APD-TiO<sub>2</sub> adsorbed a much larger amount of NCs, up to three times higher compared to the other samples, indicating that the density of amino groups is essential to the loading of NCs. It is possible that the slightly lower adsorption capacity of APD-TiO<sub>2</sub> than that of APTS- $TiO_2$  is due to the partial re-dissolution of adsorbed APD. Figure 2d shows the time-evolution of the NC adsorption behavior on the amine-modified TiO<sub>2</sub> targeting 5.0 wt.% loading of Pt NCs. APTS-TiO2 showed very fast NC uptake, reaching almost 100% adsorption in 5 minutes. APD-modified  $TiO_2$  only needed 60 minutes to achieve >95% adsorption whereas the samples of non-covalently modified  $TiO_2$  needed much longer time to reach equilibrium. These results highlight the importance of both the anchored amino group density and the bonding strength of the aminecontaining molecules on oxide support because the residual



*Figure 2.* a) The structures of the four amine-containing molecules for surface functionalization. b) Temperature-programmed oxidation of the amines molecules modified onto  $TiO_2$  and c) adsorption isotherms and d) time-course adsorption amount of Pt NC (5.7 nm) on the amine-functionalized  $TiO_2$  supports targeted at 5.0 wt.%.

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surfactants and protic ethanol could possibly disrupt the physisorbed amines and hinder NC adsorption.

To evaluate the adsorption ability of amine-modified supports more comprehensively and accurately, adsorption isotherms for various metal NCs (Au, Pt, and Pd) capped with oleylamine or oleic acid were measured for three representative samples, namely APTS-TiO<sub>2</sub>, APD-TiO<sub>2</sub>, and bare TiO<sub>2</sub>. The data (Figure S6) were normalized in terms of surface coverage, which was calculated as the ratio between the total projected area of the adsorbed NCs over the available surface area of the support calculated by N2 physisorption (see Figure S7 for detailed calculations). Since all supports have a similar specific surface area (Table S2), the difference in adsorption capability is attributed to the surface functionalization. Interestingly, similar adsorption isotherms were measured for the three tested noble metal NC samples (Figure 3 a-c). Considering the inhomogeneity of adsorption sites and adsorption processes, the Langmuir-Freundlich model was adopted to fit the isotherms. According to the fitted isotherms (Figure 3, solid curves) and extracted fitting parameters (Table S3), APTS- and APD-modified TiO<sub>2</sub> present a thermodynamically stronger affinity to NCs and higher saturation surface coverage than that of bare TiO<sub>2</sub> (70.1%, 49.2% and 34.9%, respectively). Especially in the ranges where NCs fully adsorbed at a target loading amount (dashed lines), APTS-TiO<sub>2</sub> and APD-TiO<sub>2</sub> guarantee around 4-fold and 2-fold increase of the loading range, respectively, compared with bare TiO<sub>2</sub> (Figure 3a-c), suggesting that the functionalization process with amines is indeed advantageous to improve NC deposition. In general, NC surface coverage is independent of oxide support specific surface area. For example, APTS-modified SiO<sub>2</sub> spheres (Figure S8), with a lower available surface area ( $18 \text{ m}^2 \text{g}^{-1}$ ), achieved an overall lower weight loading of Pd NC (  $\approx\!15.1~\text{wt.}\,\%$  ) compared to APTS-modified TiO<sub>2</sub>, but a similar maximum surface coverage ( $\approx 58\%$ ) is fitted with the same isotherm shown in Figure 3a. Increasing the number of amino groups on the surface increases surface coverage as well because more binding sites are used for NC adsorption. We demonstrate this hypothesis by creating a thin mesoporous silica layer on SiO<sub>2</sub> spheres (Figure S9) such that the APTS binding site for each individual NC is higher, leading to increased surface coverages up to  $\approx 90$ %. The surface coverage of NCs on the SiO<sub>2</sub> spheres modified with mesoporous layers clearly surpassed that on the bare SiO<sub>2</sub> spheres (Figure S9), indicating once again the crucial role played by the amino groups as surface ligands to immobilize NCs (Scheme 1 d). Figure 4a–d and Figure S10 show examples of NC adsorption using APTS-modified oxide supports including Pt NCs on amorphous SiO<sub>2</sub> gel and various sizes of Pd NCs on SiO<sub>2</sub> spheres with mesoporous layers. Even at a high surface coverage, monolayer deposition of NCs without agglomeration was realized by using the amine-functionalized oxides.

The APD modification is a very general method to achieve high NC loading and it is not limited to titania but it can also be used for many other oxide supports. Systematic deposition of a variety of NCs (Figure S1) using APDmodified oxides in 10% ethanol/toluene mixture was demonstrated using different loadings of NCs, different NC sizes, different metals, and different oxide supports (Figure 4). Importantly, in all cases, complete deposition was observed, as proven by the colorless supernatant following NC deposition (inset of each panel in Figure 4). Materials which have the same NC size but varying loading amount could be easily obtained by varying the initial NC concentration. This result is difficult to achieve using conventional impregnationcalcination methods especially at high weight loading. Figure S11 shows TEM images of Au (10 wt. %)/TiO<sub>2</sub> prepared by using a deposition-precipitation method and an incipient wetness impregnation method where non-uniform deposition and very large Au NCs were observed.<sup>[17]</sup> However, firstly, in a tested loading range of Au NCs from low (1.0 wt.%) to high (10.0 wt. %), homogeneous distribution of NCs on APDmodified  $TiO_2$  was obtained without clustering (Figure 4e-h), which is an important requirement for improved material properties such as maximized surface area of active sites. While the adsorption conditions remained the same, the supernatants were obviously colored when bare TiO<sub>2</sub> was used (insets of Figure 4e-h). The APD-functionalized oxides could indeed benefit from higher adsorption affinity in preparing supported NCs (Figure 3 and Table S3). Secondly, Figure 4i-l shows a series of Pd NCs successfully deposited on



*Figure 3.* Adsorption isotherms for Au NCs (4.5 nm, squares), Pt NCs (5.7 nm, circles), and Pd NCs (6.0 nm, triangles) on a) APTS-TiO<sub>2</sub>, b) APD-TiO<sub>2</sub>, and c) bare TiO<sub>2</sub> in 10 vol.% ethanol/toluene based on surface coverage. The solid lines are isotherms fitted using the Langmuir-Freundlich model. The dashed lines indicate the surface coverage at which the target NCs loading were fully adsorbed.

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## **Research Articles**





*Figure 4.* TEM images of supported NCs. (a–d) extra-high coverage of NC adsorbed on APTS-functionalized supports. a) Pt NC (5.7 nm)/SiO<sub>2</sub> gel, and b) Pd NC (3.8 nm), c) Pd NC (6.0 nm), and d) Pd NC (8.3 nm) on SiO<sub>2</sub> sphere coated with an APTS-modified mesoporous silica layer. e– x) NCs adsorbed on APD-functionalized supports. e) Au NC (4.5 nm, 1.0 wt.%)/TiO<sub>2</sub>, f) Au NC (4.5 nm, 2.5 wt.%)/TiO<sub>2</sub>, g) Au NC (4.5 nm, 5.0 wt.%)/TiO<sub>2</sub>, h) Au NC (4.5 nm, 10.0 wt.%)/TiO<sub>2</sub>, i) Pd NC (3.8 nm, 2.0 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, j) Pd NC (6.0 nm, 2.0 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, k) Pd NC (8.3 nm, 2.0 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, j) Pd NC (6.0 nm, 2.0 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, k) Pd NC (8.3 nm, 2.0 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, j) Pd NC (6.0 nm, 2.0 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, k) Pd NC (8.3 nm, 2.0 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, j) Pd NC (6.0 nm, 2.0 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, gel, o) Ru NC (3.0 nm, 1.5 wt.%)/SiO<sub>2</sub> gel, p) Ag NC (5.2 nm, 2.0 wt.%)/SiO<sub>2</sub> gel, q) Pd NC (6.0 nm, 4.5 wt.%)/CeO<sub>2</sub>, r) Pd NC (6.0 nm, 4.5 wt.%)/TiO<sub>2</sub>, s) Pd NC (6.0 nm, 4.5 wt.%)/NiO, t) Pd NC (6.0 nm, 4.5 wt.%)/γ-Al<sub>2</sub>O<sub>3</sub>, u) Pd NC (6.0 nm, 4.5 wt.%)/β-zeolite, v) Pd NC (6.0 nm, 4.5 wt.%)/SiO<sub>2</sub> gel, w) Pd NC (6.0 nm, 4.5 wt.%)/V<sub>2</sub>O<sub>5</sub>, and x) Pd NC (6.0 nm, 4.5 wt.%)/CuO. Insets: pictures of centrifuged vials after adsorption of NC on the amine-functionalized supports. The insets of (e)–(h) include both the APD-modified TiO<sub>2</sub> (left) and bare TiO<sub>2</sub> (right).

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APD-modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (2.0 wt. %) with varying particle sizes ranging between 3.8 and 13.7 nm. Other metal NCs with desired sizes and weight loading including Ni, Pt, Ru, and Ag deposited on APD-modified amorphous SiO<sub>2</sub> are shown in Figure 4m–p. Finally, the deposition of 4.5 wt. % Pd NCs was demonstrated on various kinds of commonly used oxides with APD-modification including semiconducting, insulating, reducible and non-reducible oxides and zeolites (Figure 4q-x). Therefore, we show that this method can disperse particles of different sizes, compositions, loadings, and surface ligands onto several oxide supports functionalized with amino group (Table S4). This robust NC deposition approach relies on (1) the suitable solvent mixture (10 vol.% ethanol/toluene) in which oxides achieve good dispersibility without destabilizing the NCs; (2) strong binding of APD to oxide surfaces during NC adsorption; and (3) strong affinity of amino groups on the oxide surface for metal NCs. Furthermore, the method is applicable to NCs with different ligand coatings.<sup>[18]</sup>

The use of APD rather than silanes for surface modification is key to avoiding surface contamination of oxide supports. This element is required in several applications and particularly crucial in the preparation of heterogeneous catalysts, where metal-support interactions determine catalyst performance.<sup>[15b, 19]</sup> Several catalysts made from bare, APTSmodified, and APD-modified oxides were tested for three different reactions (CO oxidation, Figure 5a; methane catalytic combustion, Figure 5b; and hydrogen production from glycerol photoreforming, Figure 5c) where metal-support interactions are crucial to determine catalytic activity and where silica-based supports are poorly active. The functionalized ligands are removed after NC deposition using a thermal treatment at 450 °C for 30 minutes (Figure S4). In CO oxidation (Figure 5 a), support functionalized by APTS or APD only barely influenced the catalytic activity of deposited Pd NCs, suggesting that in both cases the functional groups do not hinder catalytic activity. However, in catalytic methane combustion, even a thin layer of Si from APTS drastically decreases the activity of the deposited Pd NCs as shown by the drastic increase in the light-off temperature by nearly 200 °C, indicating that the interface between metal and oxide support is very crucial (Figure 5b). The APD modification does not change the support properties because the organics are completely removed by a thermal treatment, and thus the light-off curves of an APD-functionalized catalyst overlapped with the one where the bare support was used for deposition. In photocatalysis, silica residue from thermally treated, APTS-modified oxides results in an insulating layer which decreases the electron transfer rate between titania and metal NCs, leading to decreased hydrogen production rate for this sample (Figure 5c). Again, with the APD-modified  $TiO_2$ , the hydrogen production rate was very similar to that of bare TiO<sub>2</sub>. Therefore, APD modification allows to obtain a uniform and high loading of metal NCs on many oxide supports without compromising the properties and catalytic performance of the final materials. In addition, the thermal stability of the high weight loading catalysts prepared by this general approach was evaluated on supported Au NCs (6.0 nm, 10.0 wt. %)/APD-TiO<sub>2</sub> by analyzing the particle size distribution after treatments at 450 °C in air between 0.5 and 24 h (Figure S12). Although the particle size inevitably increased (6.8 nm), the Au catalyst showed good thermal stability up to 24 h considering the low Tamman temperature of Au  $(\approx 400 \,^{\circ}\text{C}).$ 

The performance of catalysts made with a high weight loading of colloidal NCs on oxide supports were further studied to demonstrate the advantage of this method compared to conventional impregnation approaches. In conventional impregnation, high weight loadings unavoidable lead to large supported particles and polydisperse size distributions. As a proof of concept, the relationship between NCs distribution and catalytic conversion as a function of temperature at a high weight loading was demonstrated on Pd(10 wt. %)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for methane catalytic combustion prepared by the APD-assisted approach and three other methods (Figure 6). In a first sample, Pd NCs were deposited on alumina in the absence of ethanol and using pure hexanes; the catalyst showed clustered Pd NCs due to the poor dispersity of oxide support (Figure 6b and Figure S13a-c). In a second sample, the NCs were deposited in an ethanol/ toluene mixture to increase alumina dispersion, but the low adsorption capacity of bare y-Al<sub>2</sub>O<sub>3</sub> could not allow full uptake of 10 wt.% of Pd NCs and thus the Pd NCs were deposited by evaporation of the solution. This option also resulted in agglomeration of Pd NCs (Figure 6c and Figure S13d-f). These two catalysts showed poor catalytic activity with full conversion of methane achieved at



*Figure 5.* Catalytic activities of NCs on bare (circles), APTS-functionalized (squares), and APD-functionalized (triangles) oxide supports. a) Pd (6.0 nm, 0.5 wt.%)/CeO<sub>2</sub> for CO oxidation, b) Pd (3.0 nm, 2.0 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for methane catalytic combustion, and c) Pt (2.4 nm, 1.0 wt.%)/TiO<sub>2</sub> for hydrogen production from glycerol photoreforming.

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*Figure 6.* a) Catalytic conversion as a function of temperature and (b)–(e) the corresponding TEM images of several Pd(10 wt.%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for methane catalytic combustion. The catalysts were prepared by adsorption of pre-synthesized Pd NCs (8.3 nm) in hexanes with bare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (b, squares), in 10 vol.% ethanol/toluene mixture with bare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> assisted by evaporation (c, circles), in 10 vol.% ethanol/toluene mixture with bare  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> fabricated by a conventional impregnation method (e, rhombuses).

 $\approx 500$  °C for the hexanes-prepared sample, and not even reaching full conversion in the case of the sample prepared from toluene/ethanol. On the contrary, the catalyst prepared using the APD-functionalized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in ethanol/toluene mixture showed Pd NCs that were uniformly distributed on the support surface without obvious agglomeration after removing the organic ligands (Figure 6d and Figure S13g-i). This catalyst demonstrated outstanding performance with full conversion of methane achieved at  $\approx 425$  °C under the conditions of our tests that include steam in the feed. The catalyst obtained by the APD-assisted approach also showed much superior performance compared with a catalyst prepared by a conventional impregnation method from Pd<sup>II</sup> salt (Figure 6e and Figure S13j-l). Despite the presence of Pd particles of similar size to the APD sample, at this high weight loading the conventional impregnation method again inevitably produced sintered and large Pd particles (inset of Figure 6e). As a result, its activity was not favorable and the catalyst did not reach full methane conversion by 500°C. Kinetic studies further exhibited a similar turnover frequency among these catalysts indicating that the difference in catalytic performance was mainly caused by the difference in metal surface area (Figure S14). This result underlines that it is important to control the NCs distribution on oxide supports and that the performance of the catalyst at a high metal loading was successfully optimized through controlling the interfacial chemistry between NCs and oxide supports. After 1 h of catalytic reaction at 400 °C, the catalyst prepared by the APD-functionalized support still showed uniformly distributed NCs without obvious sintering (Figure S15c), while sintered and large particles were observed in other catalysts (Figure S15a, b, d). The developed APD-functionalized strategy for the adsorption of hydrophobic ligandstabilized NCs is a reliable approach for the preparation of supported catalysts with a wide loading range and high stability and activity.

#### Conclusion

In summary, we demonstrated a general and robust method for the deposition of hydrophobic ligand-stabilized colloidal NCs on oxide support materials. Through functionalization with a primary amine, we showed that amino groups on the oxide surface are able to strongly bind metal NCs, leading to uniform monolayer deposition at high weight loadings. Adsorption isotherms clearly quantify the important role played by amino groups in the monolayer deposition of metal NCs on oxides. The development of removable modification of oxide supports with 3-amino-1,2-propanediol (APD) guarantees NC adsorption up to very high weight loadings (10 wt.%) without affecting the oxide support properties after a thermal treatment. The tunable loading and homogeneously distributed NCs on oxide supports are excellent materials in heterogeneous catalysis, showing no degradation of catalytic properties after functionalization and thus opening the opportunity to extend the use of colloidal NCs in heterogeneous catalysts.

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## **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** adsorption · heterogeneous catalysis · nanocrystals · oxide supports · surface functionalization

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