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Cite this: DOI: 10.1039/c0xx00000x

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Paper

L-lysine-assisted fabrication of Pd_xPt_{1-x}/Ni(OH)₂ (0 ≤ x ≤ 1) hybrids with composition-dependent catalytic properties

Jiangman Zhen,^{a,b} Dapeng Liu,^{*a} Xiao Wang,^a Junqi Li,^{a,b} Fan Wang,^{a,b} Yinghui Wang^a and Hongjie Zhang^{*a}

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

A fast and facile self-assembly method has been developed to deposit 3-5 nm sized Pd_xPt_{1-x} (0 ≤ x ≤ 1) nanoparticles (NPs) on Ni(OH)₂ nanosheets. The biomolecule L-lysine has been used here as the linker to hybridize Pd_xPt_{1-x} NPs and Ni(OH)₂ nanosheets together. The catalytic properties of the obtained Pd_xPt_{1-x}/Ni(OH)₂ hybrids were evaluated by employing the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH₄ as a model reaction. The results reveal that the stability, activity and recyclability of Pd_xPt_{1-x} NPs have been remarkably enhanced after supported on Ni(OH)₂ nanosheets. Moreover, the influence of the compositions of noble metals has been studied in depth on the catalytic properties and Pd_{0.5}Pt_{0.5}/Ni(OH)₂ hybrids show the optimal catalytic property.

Introduction

In the past decades, noble metal bimetallic alloy NPs consisting of two distinct metals such as Pd and Pt are attractive for a wide variety of catalytic and electrocatalytic applications.¹⁻⁶ As they can exhibit not only a combination of the properties associated with both metals but also enhancement or synergy due to strong coupling between them.¹⁻³ Generally speaking, the catalytic properties of noble metal bimetallic alloy NPs highly depend on their particle sizes, because the smaller sized particles own more surface atoms and thus might be more active in those surface related reactions. However, smaller NPs are apt to aggregate due to high surface energy, and hence the heavy loss of catalytic active centers results in serious catalytic deterioration and even

inactivation. Besides, smaller catalyst NPs are very difficult to be recycled from the reaction media.⁷ In consideration of the above-mentioned problems as well as the high cost and limited supply, noble metal bimetallic alloy NPs usually need to be loaded on supports with large surface areas, good chemical and mechanical stability.⁸⁻¹²

According to previous reports, Ni(OH)₂ nanosheets can be synthesized by a facile hydrothermal process,¹³ and such obtained sheet-like nanostructures have large surface areas and good chemical and mechanical stability that are suitable for loading noble metal alloy NPs. More importantly, Ni(OH)₂ can also show excellent synergistic effects with other catalytic active components. For instance, Ni(OH)₂ plays a key role in stabilizing the interface against dehydration of Pt/FeNi(OH)_x catalyst, which is much important for the highly efficiency for carbon monoxide (CO) oxidation.¹⁴ Besides, the presence of Ni(OH)₂/NiOOH improves the catalytic activity and stability of MnO₂ catalyst for oxygen reduction reaction by assisting the charge transfer to oxygen and stabilizing the Mn^{III}/Mn^{VI} species.^{15,16} So it seems a good choice to load noble metal alloy NPs on Ni(OH)₂ nanosheets for the optimization of both the catalytic stability and activity.

In recent years, two main methods have been widely used for the synthesis of noble metal NPs/support hybrids: in situ growth and self-assembly process.¹⁷⁻²⁵ In situ growth is relatively simple but often results in poor control over the size and morphology of noble metal NPs. Comparatively, self-assembly process could well control the sizes and shapes of both of noble metal NPs and

[a] J. M. Zhen, Dr. D. P. Liu, Dr. X. Wang, J. Q. Li, F. Wang, Dr. Y. H. Wang, and Prof. H. J. Zhang

State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, Jilin, China.
Fax: (+86-431-85698041.
E-mail: liudp@ciac.ac.cn; hongjie@ciac.ac.cn.

[b] J. M. Zhen, J. Q. Li, F. Wang, Graduate School of the Chinese Academy of Sciences Beijing 100039 (P.R. China)

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supports.²⁰⁻²³ Our group have realized the self-assembly of two different kinds of NPs by the aid of electrostatic interactions.²⁴⁻²⁶

In this paper, we have successfully synthesized Pd_xPt_{1-x}/Ni(OH)₂ hybrids via a simple self-assembly process by mixing L-lysine modified Ni(OH)₂ nanosheets and PVP stabilized Pd_xPt_{1-x} NPs. Due to the similar crystal cell parameters, minor lattice mismatch of only 0.77 % and good miscibility between Pd and Pt, Pd_xPt_{1-x} alloy NPs have been obtained with varied compositions. It is hence feasible to optimize the catalytic properties of Pd_xPt_{1-x}/Ni(OH)₂ hybrids by simply varying Pd/Pt molar ratios. As an important chemical intermediate for synthesizing analgesic and antipyretic drugs, photographic developers as well as corrosion inhibitors, 4-AP can be produced by catalytic hydrogenation of 4-NP using noble metal (e.g. Pt, and Pd) catalysts. Here we evaluated the catalytic properties of the as-obtained Pd_xPt_{1-x}/Ni(OH)₂ hybrids systematically to find out the influence of the compositions of noble metals by employing the reduction of 4-NP to 4-AP by NaBH₄ as a model reaction. In addition, the effects of the Ni(OH)₂ on the stability, activity and recyclability of Pd_xPt_{1-x} NPs have been also investigated.

Experimental Section

Characterization.

The X-ray diffraction patterns of the samples were collected on a Rigaku-D/max 2500 V X-ray diffractometer with Cu-K radiation ($\lambda = 1.5418 \text{ \AA}$), with an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopic (TEM) images and energy dispersive X-ray spectra (EDX) were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted by applying an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al K X-ray radiation as the X-ray source for excitation. Decreases in the concentrations of 4-NP were analyzed by UV-vis-NIR (Purkinje General, TU-1900) spectrophotometer. The FT-IR spectrum was obtained using a Magna-IR 750 spectrometer in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Synthesis of Pd_xPt_{1-x} NPs.

For preparation of Pd_{0.5}Pt_{0.5} NPs, 0.5 mL of K₂PtCl₄ (20 mM) aqueous solution and 0.5 mL of K₂PdCl₄ (20 mM) aqueous solution were mixed with 10 mL of water and 1 mL of PVP (0.1 M) aqueous solution together. Then 0.5 mL of NaBH₄ (0.1 M) aqueous solution was added to the mixed solution followed by stirring for 20 min. The obtained solution was Pd_{0.5}Pt_{0.5} NPs dispersed solution, which was prepared for the production of Pd_{0.5}Pt_{0.5}/Ni(OH)₂ hybrids. For preparation of other Pd_xPt_{1-x} NPs, the conditions and procedures were the same except that different amounts of K₂PtCl₄ and K₂PdCl₄ were added. 1 mL of K₂PtCl₄ (20 mM) aqueous solution was used for preparation of Pt NPs; 0.7 mL of K₂PtCl₄ (20 mM) aqueous solution and 0.3 mL of K₂PdCl₄ (20 mM) aqueous solution were used for preparation of Pd_{0.3}Pt_{0.7} NPs; 0.3 mL of K₂PtCl₄ (20 mM) aqueous solution and 0.7 mL of K₂PdCl₄ (20 mM) aqueous solution were used for

preparation of Pd_{0.7}Pt_{0.3} NPs; 1 mL of K₂PdCl₄ (20 mM) aqueous solution was used for preparation of Pd NPs.

Synthesis of Ni(OH)₂ nanosheets.

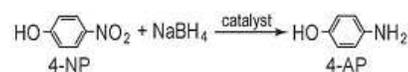
1 mmol Ni(CH₃COO)₂ and 1 mmol L-lysine were added into 10 mL of water. 1 mL of NaOH (2 M) aqueous solution was added into the above mentioned solution. Then the solution was transferred into a 15 mL Teflon-lined stainless steel autoclave, followed by heating at 120 °C for a period of 10 h in an electric oven. Afterwards the autoclave was cooled naturally to room temperature. The final products were purified by centrifugation and then redispersed in 20 mL of water. Then the Ni(OH)₂ dispersed solution was divided equally into five parts for the preparation of Pd_xPt_{1-x}/Ni(OH)₂ hybrids.

Synthesis of Pd_xPt_{1-x}/Ni(OH)₂ hybrids.

10 mL of water was added into the above mentioned Ni(OH)₂ dispersed solution. Then the as-obtained Pd_xPt_{1-x} NPs dispersed solution was added to the Ni(OH)₂ dispersed solution drop by drop with stirring. 20 min later, Pd_xPt_{1-x}/Ni(OH)₂ hybrids were obtained by centrifugation and washed with water for three times.

Catalytic tests.

Aqueous solution of 4-NP (0.01 M) and NaBH₄ (1 M) were freshly prepared. 30 μL of 4-NP solution and 30 μL of NaBH₄ solution were added to a quartz cuvette containing 2 mL of water. Then, 20 μL of Pd_xPt_{1-x}-Ni(OH)₂ catalyst (10 mM) was injected into the cuvette to start the reaction. Since the spectrophotometer has a function to display instant absorbance of a fixed absorption peak such as 400 nm, so we tuned the UV/Vis spectrophotometer, and then the intensity of the absorption peak at 400 nm was monitored easily as a function of time. After each round of reaction, another 30 μL of 4-NP (0.01 M) and 30 μL of NaBH₄ (1 M) were added to the reaction solution. This step was repeated ten times to study the stability of the catalysts. The reduction 4-NP by NaBH₄ can be briefly expressed as follows:



Results and Discussion

According to the previous report, strong coordination was observed between carboxyl groups and metal hydroxides, and also amino groups were able to coordinate noble metals.²⁷ Notice that in this strategy bio-molecular L-lysine, which has two kinds of functional groups (-NH₂ and -COOH), is chosen as linker to assist the aqueous synthetic process. Since negative charges are uniformly distributed on the PVP-stabilized noble metal NPs surfaces,⁹ while the carboxyl groups of L-lysine are apt to coordinate with metal hydroxide support left positive charges of amino groups uniformly distributed on the surfaces of the supports, the connection between noble metal NPs and supports should be easily realized via electrostatic interactions. Consequently, L-lysine can help Pd_xPt_{1-x} NPs deposit on Ni(OH)₂ nanosheets. The synthesis process has been described in Fig. 1 that PVP stabilized Pd_xPt_{1-x} NPs and L-lysine modified Ni(OH)₂

nanosheets were synthesized respectively. Then $\text{Pd}_x\text{Pt}_{1-x}/\text{Ni}(\text{OH})_2$ hybrids were obtained by self-assembly. The samples with different Pd/Pt feeding molar ratios are named as $\text{Pd}/\text{Ni}(\text{OH})_2$, $\text{Pd}_{0.7}\text{Pt}_{0.3}/\text{Ni}(\text{OH})_2$, $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$, $\text{Pd}_{0.3}\text{Pt}_{0.7}/\text{Ni}(\text{OH})_2$ and $\text{Pt}/\text{Ni}(\text{OH})_2$ respectively.

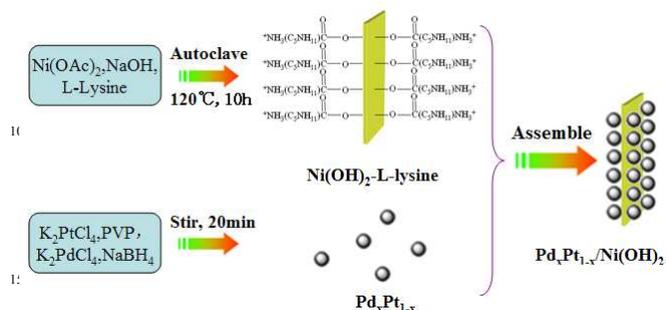


Fig. 1 Schematic process for preparation of $\text{Pd}_x\text{Pt}_{1-x}/\text{Ni}(\text{OH})_2$ hybrids.

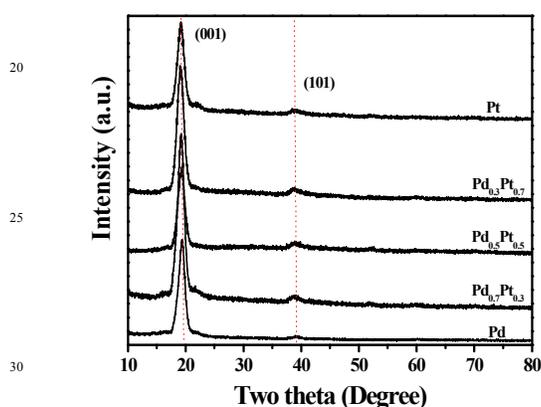


Fig. 2 XRD patterns of $\text{Pd}_x\text{Pt}_{1-x}/\text{Ni}(\text{OH})_2$ hybrids. Sample 1 to 5.

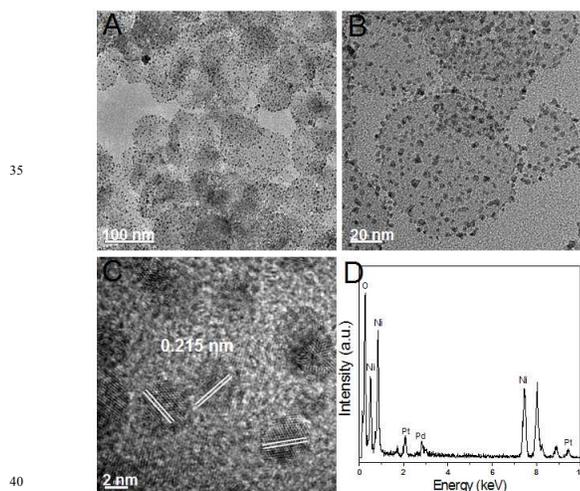


Fig. 3 (A, B) TEM images; (C) HRTEM image; and (D) EDX analysis of $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$.

FTIR spectroscopy in Fig. S1 identifies the successful grafting of bio-molecular L-lysine onto $\text{Ni}(\text{OH})_2$ nanosheets according to the appearance of typical peaks of L-lysine at 2923 cm^{-1} , 2855 cm^{-1} and around 2354 cm^{-1} . The XRD patterns of the as-obtained samples are shown in Fig. 2. The peaks at $2\theta = 19.4^\circ$ and 38.8° can be indexed into single phase $\beta\text{-Ni}(\text{OH})_2$ (001)

and (101) reflections, respectively (JCPDS No. 14-0117). However, no peaks related to noble metals were detected in all of the samples. The absence of noble metals signals might be attributed to their small sizes.^{28,29} In the following text, TEM, EDX and XPS analyses would be employed to verify the existence of noble metals in the samples.

The morphologies of the samples were characterized by TEM (Fig. 3, S2, S3, S4 and S5). Take $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$ as an example, it is clearly seen that $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs with an average diameter around 4 nm are evenly distributed onto the surface of $\text{Ni}(\text{OH})_2$ nanosheets. No scattered NPs are found outside the $\text{Ni}(\text{OH})_2$ nanosheets. The lattice fringes for those NPs are measured with the interplanar distance as 0.215 nm, which corresponds well to the (111) characteristic planes of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs. Furthermore, the selective EDX spectrum (Fig. 3D) firmly identifies the existence of Pd and Pt in $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$. Comparing the TEM images of the five samples, it is found that they show similar morphologies. 3-5 nm sized $\text{Pd}_x\text{Pt}_{1-x}$ NPs are well dispersed on the surface of $\text{Ni}(\text{OH})_2$ nanosheets. Moreover, the EDX data confirm the existence of Pd and Pt in the other four samples. XPS spectra were also conducted to further characterize the samples (Fig. 4, S6, S7, S8 and S9). The presence of Pd and Pt peaks suggests the existence of metallic Pd and Pt in the samples, which are in good agreement with HRTEM and EDS analysis.

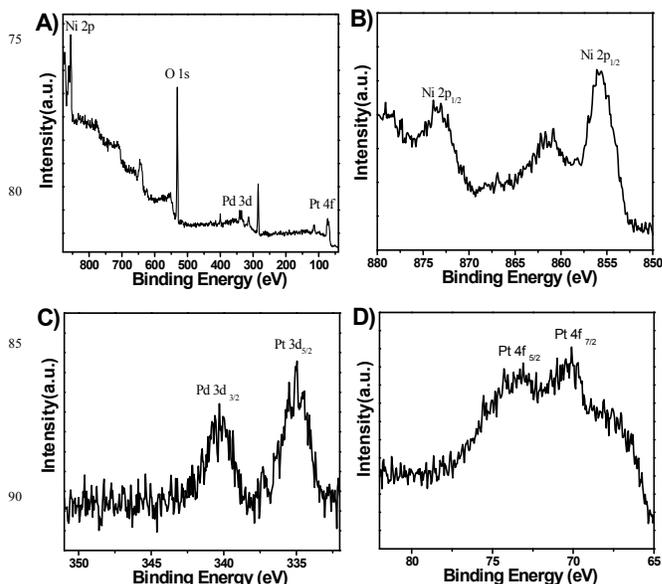


Fig. 4 XPS analysis of $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$. Sample 3.

The reduction of 4-NP to 4-AP by NaBH_4 was chosen as a model reaction to evaluate the catalytic properties of the as-obtained $\text{Pd}_x\text{Pt}_{1-x}/\text{Ni}(\text{OH})_2$ hybrids. The original absorption peak of 4-NP was centered at 317 nm and shifted to 400 nm immediately upon the addition of freshly prepared NaBH_4 solution due to the formation of 4-nitrophenolate ions. When adding $\text{Ni}(\text{OH})_2$ nanosheets, the reduction of 4-NP by NaBH_4 could not proceed. Whereas the absorption peak at 400 nm started to decrease when the reduction proceeded upon the addition of $\text{Pd}_x\text{Pt}_{1-x}/\text{Ni}(\text{OH})_2$ hybrids and then disappeared in a short time. Since NaBH_4 was in large excess to 4-NP, its concentration could

be considered as a constant during the reaction period. So the reduction rate can be evaluated by the pseudo-first-order kinetics with respect to 4-NP. Fig. 5A shows $\ln(C/C_0)$ versus reaction time t , where C/C_0 was obtained from the relative intensity ratio of the absorbance (A/A_0) at 400 nm. As all of these plots followed first-order reaction kinetics very well, the rate constant k can be calculated from the rate equation $\ln(C/C_0) = kt$ (Table 1). The catalytic activity of the five samples follows such a sequence: Pd/Ni(OH)₂ > Pd_{0.7}Pt_{0.3}/Ni(OH)₂ > Pd_{0.5}Pt_{0.5}/Ni(OH)₂ > Pd_{0.3}Pt_{0.7}/Ni(OH)₂ > Pt/Ni(OH)₂. Pd/Ni(OH)₂ is much more active than Pt/Ni(OH)₂, while Pd_xPt_{1-x}/Ni(OH)₂ hybrids ($x = 0.3, 0.5$ and 0.7) exhibit intermediate activities. As the ratio of Pt increased, a clear trend of decreased activity was observed. The catalytic activity strongly depends on the compositions of noble metals. It can be seen that the catalytic activities of Pd_xPt_{1-x}/Ni(OH)₂ hybrids ($x = 0.3, 0.5$ and 0.7) were enhanced by forming Pd_xPt_{1-x} alloy compared to Pt/Ni(OH)₂. This enhancement might be due to the formation of bimetallic arrangements of surface atoms (coexistence of surface Pd and Pt sites) or modification of the electronic structure of surface Pt atoms through alloying with Pd atoms.^{1,2} The electronegativity difference between Pd (2.20) and Pt (2.28) metals induced electron transfer from Pd to Pt resulting in the creation of electron rich and electron poor regions on the bimetallic surface.³⁰ The existence of these regions on metallic surfaces facilitates electronic communication between adsorbed reactant molecules, which could enhance the adsorption capability of alloy NPs.³¹

Hence alloying of Pd and Pt would cause higher uptake and increased electron transfer between substrate molecules resulting in high catalytic activity of alloy NPs. When the Pd/Pt ratio is higher, such electron transfer effect might be stronger, so Pd_{1-x}Pt_x/Ni(OH)₂ hybrids show higher activities with a larger Pd content. As previously reported,³² the reduction of 4-NP involves several intermediate steps, including the production of hydrogen radicals from borohydrite and adsorbed water as well as the addition of protons to the 4-NP and the simultaneous removal of its oxygen. The Pd_xPt_{1-x}/Ni(OH)₂ hybrids with a larger Pd content are yet more effective because of palladium's hydrogen absorption capacity, which is important for the reduction of 4-NP.³²⁻³⁴ Furthermore, the turnover frequency (TOF), defined as moles of the reactant (4-NP) converted by per mole of active metal in catalyst per hour was also calculated (Table 1). Clearly, the values of our samples are all higher than RGO@Pd@C, Au-Pt DW nanotubes and AuNPs/silica NTs catalysts in previous reports (see Table 2).

Table 1. Comparison of rate constant k , TOF and conversion for 4-NP reduction with Pd_xPt_{1-x}/Ni(OH)₂ catalysts

Catalyst	k (s ⁻¹)	TOF of the first cycle (h ⁻¹)	Conversion of the tenth cycle (%)
Pd/Ni(OH) ₂	0.065	1529	44.02
Pd _{0.7} Pt _{0.3} /Ni(OH) ₂	0.055	1338	62.55
Pd _{0.5} Pt _{0.5} /Ni(OH) ₂	0.043	1060	81.91
Pd _{0.3} Pt _{0.7} /Ni(OH) ₂	0.032	766	55.42
Pt/Ni(OH) ₂	0.031	688	48.2

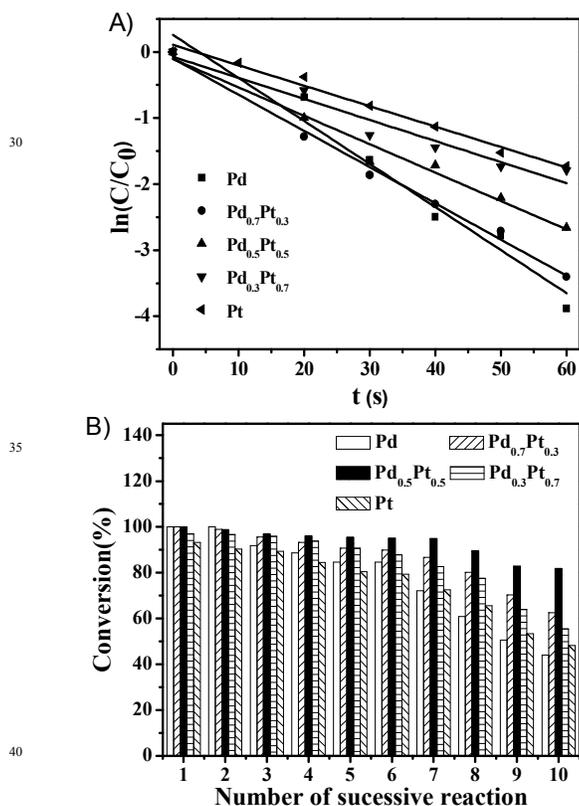


Fig. 5 A) $\ln(C/C_0)$ versus t for the reduction of 4-NP catalyzed by Pd_xPt_{1-x}/Ni(OH)₂ catalysts Sample 1 to 5. B) conversion in successive reaction cycles of Pd_xPt_{1-x}/Ni(OH)₂ catalysts.

Successive catalytic reduction reactions were performed to evaluate the stabilities of the Pd_xPt_{1-x}/Ni(OH)₂ hybrids. Fig. 5B shows the conversion efficiencies of the five samples for the same reaction time (90 s) over ten cycles. In order to avoid the loss of the catalysts caused by the separation process, the cycling test have been proceeded in situ. The conversions of 4-NP at the tenth cycle are showed in the last column in table 1. It suggests that the stability of the samples varies with the compositions of noble metals. Pd_{0.5}Pt_{0.5}/Ni(OH)₂ hybrids, which show the best stability, still retained 82 % conversion after ten cycles. Based on the results and discussions above, it is confirmed that the activity and stability of the as-obtained Pd_xPt_{1-x}/Ni(OH)₂ hybrids are strongly dependent on the compositions of noble metals. Among the as-synthesized hybrids, Pd_{0.5}Pt_{0.5}/Ni(OH)₂ hybrids exhibit the best catalytic stability. This high stability can be partly attributed to the resistance of the alloys to dissolution.³⁸ DFT calculations have shown that for PdPt clusters, alloys with more uniformly mixed atoms are more stable thermodynamically than mixtures where the metals are segregated.³⁹ Despite it is not clear to us yet why the Pd_{0.5}Pt_{0.5} composition shows better catalytic stability than the others, it is supposed that there might be more uniformly mixed PdPt clusters in Pd_{0.5}Pt_{0.5}/Ni(OH)₂ hybrids. As shown in Fig. S10, after ten cycling tests of catalytic 4-NP reduction, Pd_{0.5}Pt_{0.5}/Ni(OH)₂ still well kept the original morphology, suggesting its good stability as catalyst for 4-NP reduction.

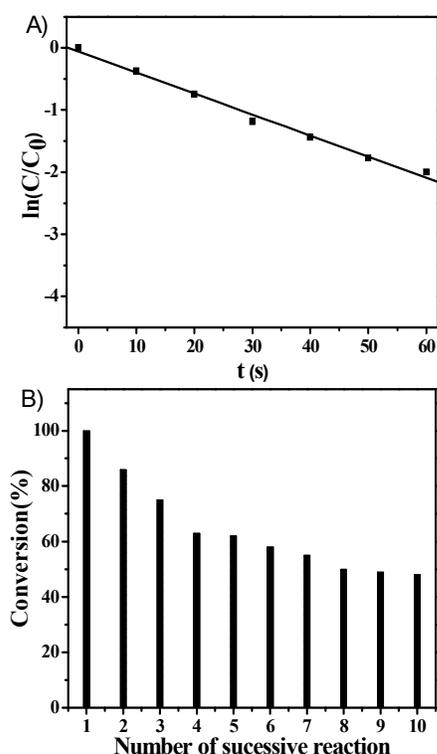


Fig. 6 A) $\ln(C_t/C_0)$ versus t for the reduction of 4-NP catalyzed by $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs. B) conversion in successive reaction cycles of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs.

However, until now it is still inconclusive whether loading $\text{Pd}_x\text{Pt}_{1-x}$ NPs on $\text{Ni}(\text{OH})_2$ supports could improve the catalytic properties of $\text{Pd}_x\text{Pt}_{1-x}$ catalysts or not, so comparative studies have been performed towards the following sample of PVP stabilized $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs. The catalytic results are shown in Fig. 6. The rate constant k is calculated to be 0.034 s^{-1} , which is lower than $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$ (0.043 s^{-1}). The tenth cycle of the conversion at 90 s is 48 %, which is also much lower than $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$ (82 %). Both the catalytic activity and stability of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ have been enhanced by loading on $\text{Ni}(\text{OH})_2$ nanosheets. Such enhancement of catalytic property might be ascribed to the following reasons.¹⁴⁻¹⁶ Firstly, $\text{Ni}(\text{OH})_2$ supports can effectively inhibit the aggregation of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs, and render $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$ with high catalytic stability due to excellent mechanical stability of $\text{Ni}(\text{OH})_2$. On the other hand, $\text{Ni}(\text{OH})_2$ might be beneficial to enhancing the catalytic activity of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ toward 4-NP reduction. As previously reported, the electron transfer is important for the above mentioned intermediate steps for 4-NP reduction.³⁵ While transition metal atoms could exist in several valence states, such as $\text{Ni}(\text{OH})_2/\text{NiOOH}$, and thus to assist the charge transfer during the 4-NP reduction process, leading to increased catalytic activity of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs.^{15,16} And it is found that $\text{Ni}(\text{OH})_2$ species could remarkably promote the dissociation of adsorbed water molecules and the proton transport of some materials.^{14,40,41} In other words, $\text{Ni}(\text{OH})_2$ could promote the intermediate steps of 4-NP reduction, resulting in a much higher catalytic activity of $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$ hybrids than $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs. Besides, $\text{Ni}(\text{OH})_2$ could be beneficial to improving the recyclability of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ catalysts. As seen in Fig. S11 S40, the colloids of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs in water are very

stable even after centrifugation at 12,000 rpm for 3 min. However after loaded on $\text{Ni}(\text{OH})_2$ nanosheets, the as-obtained $\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$ could be easily removed from water by centrifugation at a much lower speed of 8,000 rpm. The supernatant was colorless, confirming that most of the $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs had been loaded on $\text{Ni}(\text{OH})_2$ nanosheets. The fast and facile separation from the reaction condition (water) of the catalysts have been realized. Based on the above results, it can be figured out that the catalytic stability, activity and recyclability of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs have been remarkably optimized by loading on $\text{Ni}(\text{OH})_2$ supports.

Table 2. Comparison for the reduction of 4-NP with different catalysts.

Catalyst	Mole of noble metals (mmol)	Amount of 4-NP (mmol)	Conversion time (min)	TOF (h^{-1})	Reference
$\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{Ni}(\text{OH})_2$	2×10^{-5}	3×10^{-4}	0.85	1060	this work
RGO@Pd@C	1.4×10^{-4}	3×10^{-4}	0.5	274	35
Au-Pt DW nanotubes	1×10^{-5}	7.2×10^{-4}	14	680	36
AuNPs/silica NTs	1×10^{-3}	3.6×10^{-3}	1.2	185	37

Conclusions

In summary, we have demonstrated a facile self-assembly method to deposit 3-5 nm sized $\text{Pd}_x\text{Pt}_{1-x}$ NPs on $\text{Ni}(\text{OH})_2$ nanosheets. L-lysine plays a key role as connector to hybridize noble metal NPs and $\text{Ni}(\text{OH})_2$ nanosheets together. The catalytic properties of $\text{Pd}_x\text{Pt}_{1-x}/\text{Ni}(\text{OH})_2$ hybrids for the reduction of 4-NP to 4-AP by NaBH_4 have been investigated. Based on the results, it is confirmed that the catalytic activity and stability of the hybrids strongly depend on the compositions of noble metals. Among the as-synthesized hybrids, $\text{Pt}_{0.5}\text{Pd}_{0.5}/\text{Ni}(\text{OH})_2$ hybrids exhibit the best catalytic property. By loading on $\text{Ni}(\text{OH})_2$ supports, the catalytic stability, activity and recycling rate of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ NPs have been remarkably optimized. It is anticipated that this kind of bimetallic/supports hybrid nanocatalysts will be of great potential for applications. As well as an efficient support, $\text{Ni}(\text{OH})_2$ could be used to load other small catalyst NPs, which could be looking forward to show excellent catalytic performance.

Acknowledgements ((optional))

This work was supported by the financial aid from the National Natural Science Foundation of China (Grant Nos. 91122030, 5127224, 21210001, 21221061 and 21401186), and the MOST of China (Grant No. 2014CB643802).

References

- A. X. Yin, X. Q. Min, Y. W. Zhang and C. H. Yan, *J. Am. Chem. Soc.*, 2011, **133**, 3816.
- H. Zhang, M. S. Jin, H. Y. Liu, J. G. Wang, M. J. Kim, D. R. Yang, Z. X. Xie, J. Y. Liu and Y. N. Xia, *ACS Nano*, 2011, **5**, 8212.
- X. Q. Huang, Y. J. Li, H. L. Zhou, X. F. Duan and Y. Huang, *Nano Lett.*, 2012, **12**, 4265.

- 4 T. L. Tan, L. L. Wang, D. D. Johnson and K. Bai, *Nano Lett.*, 2012, **12**, 4875.
- 5 Y. Liu, M. F. Chi, V. Mazumder, K. L. More, S. Soled, J. D. Henao and S. H. Sun, *Chem. Mater.*, 2011, **23**, 4199.
- 6 J. B. Wu, L. Qi, H. J. You, A. Gross, J. Li and H. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 11880.
- 7 N. N. Tutar, A. Ristic, G. Mali, M. Mazaj, I. Arcon, D. Arcon, V. Kaucic and N. Z. Logar, *Chem. Eur. J.*, 2010, **16**, 5783.
- 8 X. Wang, D. P. Liu, S. Y. Song, and H. J. Zhang, *J. Am. Chem. Soc.*, 2013, **135**, 15864.
- 9 X. Wang, D. P. Liu, S. Y. Song and H. J. Zhang, *Chem. Commun.*, 2012, **48**, 10207.
- 10 G. X. Chen, H. Y. Yang, B. H. Wu, Y. P. Zheng and N. F. Zheng, *Dalton Trans.*, 2013, **42**, 12699.
- 12 X. M. Sun and Y. D. Li, *Angew. Chem. Int. Ed.*, 2004, **43**, 597.
- 13 Z. H. Liang, Y. J. Zhu and X. L. Hu, *J. Phys. Chem. B*, 2004, **108**, 3488.
- 14 G. X. Chen, Y. Zhao, G. Fu, P. N. Duchesne, L. Gu, Y. P. Zheng, X. F. Weng, M. S. Chen, P. Zhang, C. W. Pao, J. F. Lee and N. F. Zheng, *Science*, 2014, **344**, 495.
- 15 I. Roche, E. Chamet, M. Chatenet and J. Vondrak, *J. Phys. Chem. C*, 2007, **111**, 1434.
- 16 P. Bezdicka, T. Grygar, B. Klapste and J. Vondrak, *Electrochimica Acta*, 1999, **45**, 913.
- 17 X. Wang, X. Y. Li, D. P. Liu, S. Y. Song and H. J. Zhang, *Chem. Commun.*, 2012, **48**, 2885.
- 18 K. Isozaki, Y. Haga, K. Ogata, T. Naota and H. Takaya, *Dalton Trans.*, 2013, **42**, 15953.
- 19 G. C. Xi, J. H. Ye, Q. Ma, N. Su, H. Bai and C. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 6508.
- 20 W. Gao, A. Pei, X. M. Feng, C. Hennessy and J. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 998.
- 21 F. Dong, Q. Y. Li, Y. Zhou, Y. J. Sun, H. D. Zhang and Z. B. Wu, *Dalton Trans.*, 2014, **43**, 9468.
- 22 K. Bakhtmutsky, N. L. Wieder, M. Cargnello, B. Galloway, P. Fornasiero and R. J. Gorte, *ChemSusChem*, 2012, **5**, 140.
- 23 M. Cargnello, N. L. Wieder, T. Montini, R. J. Gorte and P. Fornasiero, *J. Am. Chem. Soc.*, 2010, **132**, 1402.
- 24 X. Y. Li, X. Wang, S. Y. Song, D. P. Liu and H. J. Zhang, *Chem. Eur. J.*, 2012, **18**, 7601.
- 25 X. Wang, D. P. Liu, S. Y. Song and H. J. Zhang, *Chem. Eur. J.*, 2013, **19**, 5169.
- 26 J. M. Zhen, X. Wang, D. P. Liu, S. Y. Song, Z. Wang, Y. H. Wang, J. Q. Li, F. Wang and H. J. Zhang, *Chem. Eur. J.*, 2014, **20**, 4469.
- 27 S. Guo, S. Dong and E. Wang, *J. Phys. Chem. C*, 2008, **112**, 2389.
- 28 C. Z. Zhu, L. Han, P. Hu and S. J. Dong, *Nanoscale*, 2012, **4**, 1641.
- 29 F. B. Su, Z. Q. Tian, C. K. Poh, Z. Wang, S. H. Lim, Z. L. Liu and J. Y. Lin, *Chem. Mater.*, 2010, **22**, 832.
- 30 D. S. Wang, Q. Peng and Y. D. Li, *Nano Res*, 2010, **3**, 574.
- 31 G. T. Fu, L. F. Ding, Y. Chen, J. Lin, Y. W. Tang and T. H. Lu, *CrystEngComm*, 2014, **16**, 1606.
- 32 J. F. Huang, S. Vongehr, S. C. Tang, H. M. Lu and X. K. Meng, *J. Phys. Chem. C*, 2010, **114**, 15005.
- 33 S. Kishore, J. A. Nelson, J.H. Adair and P. C. Eklund, *J. Alloys Compd.*, 2005, **389**, 234.
- 34 S. Harish, J. Mathiyarasu, K. L. N. Phani and V. Yegnaraman, *Catal. Lett.*, 2009, **128**, 197.
- 35 Z. Y. Zhang, F. Xiao, J. B. Xi, T. Sun, S. Xiao, H. R. Wang, S. Wang and Y. Q. Liu, Encapsulating Pd Nanoparticles in Double-Shelled Graphene@Carbon Hollow Spheres for Excellent Chemical Catalytic Property, *Scientific Reports*, DOI: 10.1038/srep04053.
- 36 L. Chen, L. Kuai, X. Yu, W. Z. Li and B. Y. Geng, *Chem. Eur. J.*, 2013, **19**, 11753.
- 37 Z. Y. Zhang, C. L. Shao, P. Zou, P. Zhang, M. Y. Zhang, J. B. Mu, Z. C. Guo, X. H. Li, C. H. Wang and Y. C. Liu, *Chem. Commun.*, 2011, **47**, 3906.
- 38 D. A. Slanac, L. Li, A. Mayoral, M. J. Yacaman, A. Manthiram, K. J. Stevenson, Keith. P. Johnston, *Electrochimica Acta*, 2012, **64**, 35.
- 39 S. R. Calvo, P. B. Balbuena, *Surf. Sci.*, 2007, **61**, 165.
- 40 R. Subbaraman, D. Tripkovic, D. Strmcnik, K. C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic and N. M. Markovic, *Science*, 2011, **334**, 1256.
- 41 M. A. Henderson, *Surf. Sci. Rep.*, 2002, **46**, 1.

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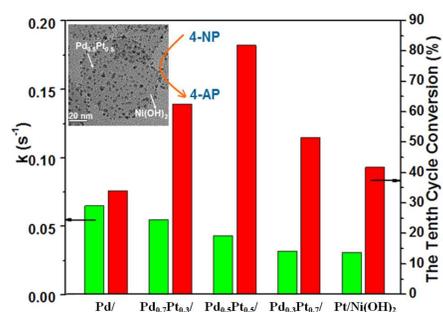
TABLE OF CONTENTS (TOC)

L-lysine-assisted fabrication of Pd_xPt_{1-x}/Ni(OH)₂ (0 ≤ x ≤ 1) hybrids with composition-dependent catalytic properties

Jiangman Zhen,^{a,b} Dapeng Liu,^{*a} Xiao Wang,^a Junqi Li,^{a,b}
Fan Wang,^{a,b} Yinghui Wang^a and Hongjie Zhang^{*a}

^aState Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, China.

^bSchool of the Chinese Academy of Sciences, Beijing 100039 (China)



Pd_xPt_{1-x}/Ni(OH)₂ hybrids with composition-dependent catalytic properties were produced by a facile self-assembly process with biomolecule L-lysine as the linker.

Hongjie Zhang, <http://lab.datatang.com/2007DA173041/AreaIndex.aspx?ItemID=68553>