Synthesis, characterization and application of pure and decorated with palladium mesoporous cobalt hydroxide hexagonal nanorings

Masih Darbandi, Ehsan Narimani, Diana Díaz-García, Santiago Gómez-Ruiz

PII: S0925-8388(20)32786-9

DOI: https://doi.org/10.1016/j.jallcom.2020.156422

Reference: JALCOM 156422

To appear in: *Journal of Alloys and Compounds*

Received Date: 3 June 2020

Revised Date: 14 July 2020

Accepted Date: 15 July 2020

Please cite this article as: M. Darbandi, E. Narimani, D. Díaz-García, S. Gómez-Ruiz, Synthesis, characterization and application of pure and decorated with palladium mesoporous cobalt hydroxide hexagonal nanorings, *Journal of Alloys and Compounds* (2020), doi: https://doi.org/10.1016/j.jallcom.2020.156422.

Synthesis, characterization and application of pure and decorated with palladium mesoporous cobalt hydroxide hexagonal nanorings

Masih Darbandi [1,]*, Ehsan Narimani [1], Diana Díaz-García [2] and Santiago Gómez-Ruiz [2,]*

[1] Nanomaterials research laboratory, Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

[2] COMET-NANO Group, Departamento de Biología y Geología, Física y Química Inorgánica, ESCET, Universidad Rey Juan Carlos, Calle Tulipán s/n, E-28933 Móstoles (Madrid), Spain

* Corresponding authors: Masih Darbandi email: Masih.Darbandi@gmx.de, masih.darbandi@tabrizu.ac.ir

Santiago Gómez-Ruiz email: santiago.gomez@urjc.es

Credit authors Statement:

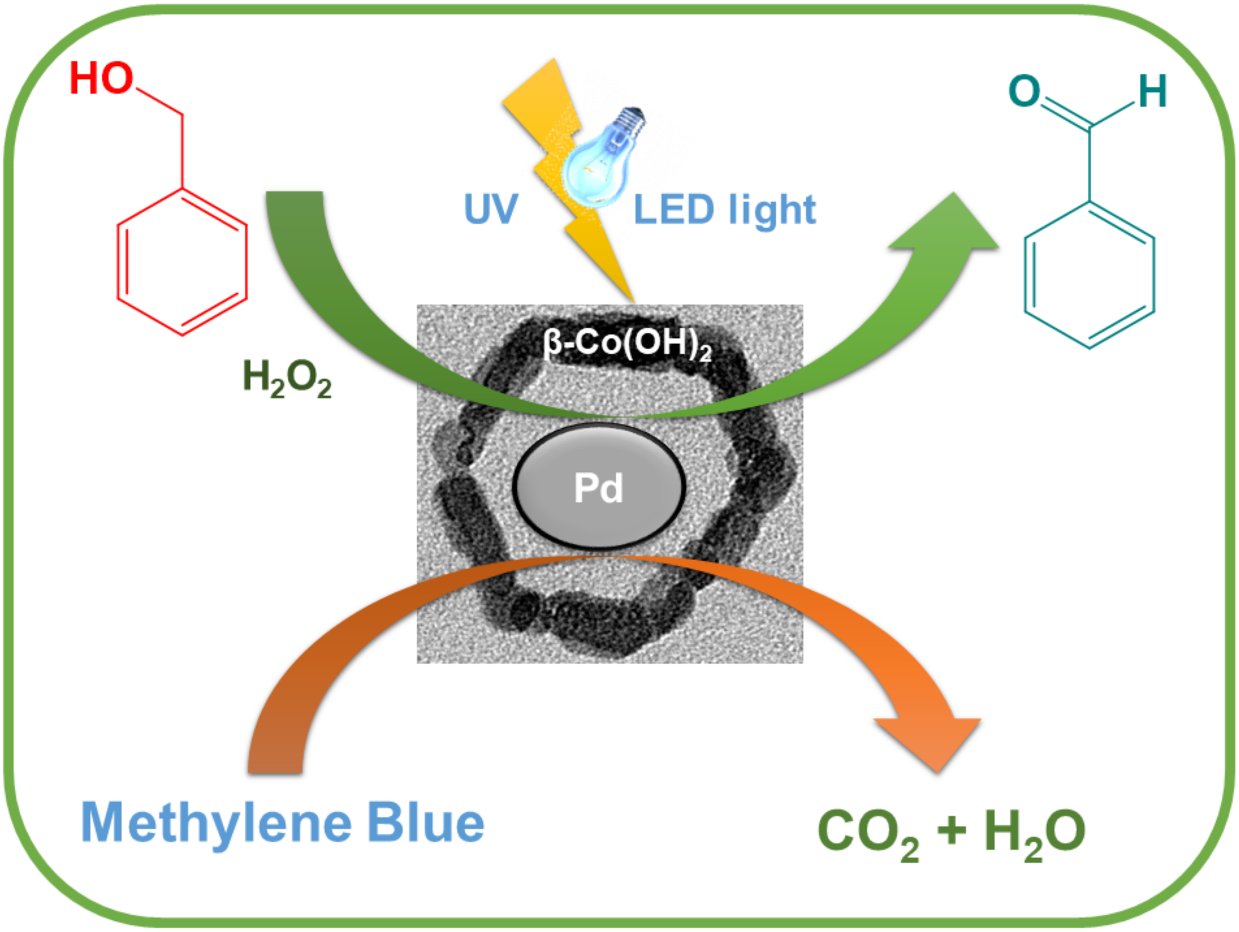
Masih Darbandi: Conceptualization, methodology, resources, supervision, writing - original draft and writing - review & editing

Ehsan Narimani: Methodology, investigation, visualization, writing - original draft.

Diana Díaz-García: Methodology, investigation, visualization, writing - original draft.

Santiago Gómez-Ruiz: Conceptualization, methodology, resources, supervision, writing - original draft and writing - review & editing.

All the authors have supervised and agreed with the final version of this manuscript.


HO
UV
LED light
O
H
H_2O_2
β-$Co(OH)_2$
Pd
Methylene Blue
$CO_2 + H_2O$

Synthesis, characterization and application of pure and decorated with palladium mesoporous cobalt hydroxide hexagonal nanorings

Masih Darbandi [1],*, Ehsan Narimani [1], Diana Díaz-García [2] and Santiago Gómez-Ruiz [2],*

[1] Nanomaterials research laboratory, Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

[2] COMET-NANO Group, Departamento de Biología y Geología, Física y Química Inorgánica, ESCET, Universidad Rey Juan Carlos, Calle Tulipán s/n, E-28933 Móstoles (Madrid), Spain

* Corresponding authors: Masih Darbandi email: Masih.Darbandi@gmx.de, masih.darbandi@tabrizu.ac.ir

Santiago Gómez-Ruiz email: santiago.gomez@urjc.es

ABSTRACT

For most of the catalytic reactions dealing with noble metals, a replacement of pure noble metals with hybrid noble metal-nanomaterials or nanocomposites is a well-stablished strategy for reducing the cost of the catalytic process. The application of this strategy is challenging and of interest for the scientific community. In this context, we report the design of Pd-anchored mesoporous cobalt hydroxide nanoring composites which, used as catalysts, can efficiently catalyze Suzuki C-C coupling reactions with excellent activity, versatility and selectivity due to the strong synergetic effect standing from its structure and composition. Hybrid systems based on mesoporous $Co(OH)_2$ nanoparticles and Pd are able to reach up to 88% conversion of iodobenzene and 37% yield of the biphenyl product at 24 h. Additionally, the photocatalytic performance of the hybrid system has been investigated in selective oxidation of benzylalcohol and organic dye degradation. This nanostructured material was able to selectively photo-oxidize benzyl alcohol to benzaldehyde under LED light with moderate catalytic activity (turnover numbers and and turnover frequencies were of 4.62 and 0.78 h^{-1} respectively with 95% selectivity). In addition, the studied hybrid system was able to degrade methylene blue in water with good performance via a photocatalytic reaction by irradiation with UV light and LED light (the kinetic constant for a first order degradation was $1.03 \cdot 10^{-4}$ s^{-1} and $1.24 \cdot 10^{-5}$ s^{-1}, respectively). Thus, our preliminary catalytic results show that these nanomaterials, based on $Co(OH)_2$ nanoparticles with low content of noble-metal, are promising candidates for their potential use in different industrial catalytic applications.

Keywords

Nanostructured materials; Composite materials; Chemical synthesis; Catalysis; Kinetics

1. Introduction

Systems based on noble metals (such as Pt, Pd, etc) are one of the most active materials with good catalytic performance and have extensively been used for different catalytic reactions ranging from organic processes such as C-C couplings, carbonylation or oxidation reactions[1–9] to inorganic processes such as water splitting [10,11].

The main problem regarding the use of noble metal-based catalysts is the high price and low abundance of some of the metals, which confines their applications. In order to solve the problems associated with the use of noble metals in some important reactions, in recent years a different strategy has been developed by depositing or by doping with noble metals into the structure of nanoparticles (NPs).

Although considerable efforts have been carried out to reduce the cost of fabrication and to improve the resistance to deactivation in oxidation reactions and the development of other non-noble-metal catalysts containing abundant elements has increased over the past decade [12–17], the support of noble metal on nanostructured materials is still the most widely used strategy in catalysis.

Nowadays, the loading of noble metal nanoparticles is carried out via two different methods: a) directly during the synthetic process of the supporting nanomaterial [18–21], b) by post-synthesis procedures on the surface of NPs or metal ions with a noble-metal precursor [4,22–29].

In this context, the presence of noble metals on porous nanomaterials acting as supporting systems can enhance the catalytic performance of the materials, by providing them with higher active surface, enhancing the catalytic interactions. Therefore, a high number of research groups have already reported studies on the support of noble-metal ions [30–34] or metal nanoparticles [31,35–39] onto high-surface nanomaterials for various applications.

An exhaustive study of the literature indicated that, to the best of our knowledge, there is not an established chemical method available to load noble-metals (especially Pd) on mesoporous $Co(OH)_2$ NPs. This encouraged us to study more in detail the potential functionalization with nobel metal ions or nanoparticles of this kind of nanostructured $Co(OH)_2$, as well as the potential synergistic effect of both metals.

Thus, this work reports an easy, efficient and cost effective two-step process for the synthesis of palladium-loaded $Co(OH)_2$ NPs. The first step is the controlled synthesis of mesoporous nanorings of $Co(OH)_2$ NPs with an hexagonal morphology and subsequently the functionalization with Pd ions on the surface of $Co(OH)_2$ NPs by the reduction reaction of an organometallic Pd(II) precursor at mild temperature.

The resultant nanohybrids were used for the catalytic study of Suzuki C-C coupling reactions and the catalytic results showed a good performance of the synthesized hybrid materials with high conversions at 110 ºC in the reactions of iodobenzene or bromobenzene and phenylboronic acid. In addition, the synthesized materials were tested as catalysts in the selective oxidation of aromatic alcohols to aldehydes, as this is a current challenge of the chemical industry. Furthermore, the synthesized materials have been tested in the photo-oxidation of benzyl alcohol as a model reaction, observing a good catalytic activity and selectivity in the formation of benzaldehyde. Finally, the synthesized nanohybrids were also used as photocatalyst in the decomposition of an organic dye such as methylene blue (MB) under LED and UV light irradiation, as a model of a water decontamination reaction (as MB is widely used as dye in cosmetics, food industries, pharmaceutical and polymeric process and is found in waste waters of those industries).

2. Experimental part

2.1. Preparation of $Co(OH)_2$ nanoparticles

Mesoporous hexagonal cobalt hydroxide NPs were prepared through a chemical precipitation method following similar procedures to those described by our group [13]. An amount of cobalt precursor ($CoCl_2$) was added in a three-necked flask and with vigorous stirring dissolved into pure H_2O at room temperature. In a subsequent step, a certain amount of NaOH solution was slowly poured into the above-mentioned solution with intense stirring, in which the pH was controlled and maintained around 9.0 and an aqueous solution of 30% H_2O_2 was quickly added to the solution.

After the completion of the precipitation reaction, the NPs were separated from the solution by centrifugation, and finally heated in an oven at 120 ^{o} C for about three hours.

2.1.1. Characterization

For the preparation of TEM samples, a drop of a suspension containing the final NPs was casted on a copper TEM grid coated with an amorphous C film. The TEM measurement was conducted using a Philips CM12 microscope working at 120 kV. The XRD experiments were carried out using a Philips, PW1730a (commercial θ-2θ X-ray diffractometer). The measurement was conducted at RT with the characteristic Kα X-ray lines of Cu.

2.2. Preparation of the hybrid materials $Co(OH)_2$-Pd-1

2.2.1. Synthesis of the Pd precursor

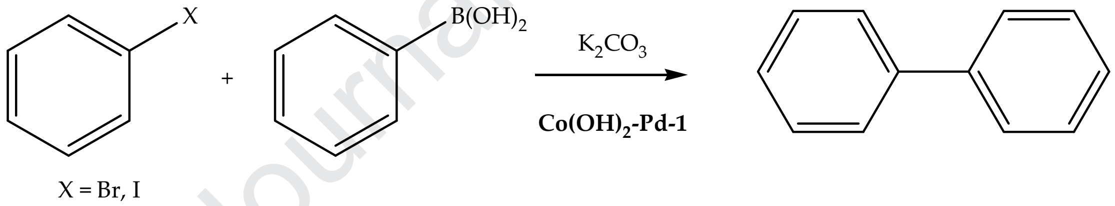
8.6 mmol (1.53 g) of $PdCl_2$ was dissolved in concentrated (35%) HCl (6 mL). The resultant mixture was diluted with 150 mL of ethanol and filtered through a filter paper. The filter paper and the brown residue were washed twice with 10 mL of ethanol. Subsequently, 20.4 mmol (2.5 mL) of 1,5-cyclooctadiene was added to the $PdCl_2$ solution with stirring. The color of this solution changed immediately from brown to orange and then a yellow-orange solid precipitated. The solution stirred for additional 20 minutes and filtered. The yellow-orange precipitated was washed with diethylether (3 · 10 mL). Finally, the product was dried overnight under vacuum to give about 16.2 mmol (2.29 g) of [$PdCl_2$(cod)] (yield: 96%).

2.2.2. Preparation of hybrid Pd-$Co(OH)_2$ systems

Functionalization of **$Co(OH)_2$** was carried out using the Pd precursor [$PdCl_2$(cod)] and **$Co(OH)_2$** following a general procedure described previously by our research group [40–43]. Briefly, 50 mg of **$Co(OH)_2$** and 4.2 mg of [$PdCl_2$(cod)] (to give a theoretical loading of Pd about 1% wt.) were added to a Schlenk tube and dried in vacuum for about one hour at RT. Subsequently, 50 mL of dimethylformamide (DMF) was added to this solution under an inert atmosphere. The mixture was then heated to 110 °C and stirred for three additional hours. The product was then separated by filtration and washed twice with 10 mL of DMF and 10 mL of diethylether. The hybrid product **$Co(OH)_2$-Pd-1** was dried under vacuum at RT for about 12 hours to remove the trace of solvents.

2.3. Studying the catalytic performance in Suzuki C-C coupling reactions

The catalytic studied was carried out on the reaction of phenylboronic acid and iodobenzene or bromobenzene. Two different temperatures 70 and 110 °C were tested and the reaction mixture was 95:5 DMF:water in the presence of K_2CO_3 as a base. The catalytic study was performed at different reaction times (6, 24 and 48 hours). The experiments were carried out under the same conditions in order to compare the results and facilitate a subsequent analysis. The reactions were conducted using bromo- or iodobenzene as limiting reagent and the molar ratio between the boronic acid and the halide was 1.2:1. Additionally, the molar ratio between the K_2CO_3 base and the halide was 2:1. The amount of catalyst in all cases was 20 mg. To achieve higher final catalytic performance all reactions were conducted using degassed solvents and under inert atmosphere [44].



Scheme 1. C-C coupling reaction catalyzed by **$Co(OH)_2$-Pd-1**

Briefly, a 0.02 M solution of 1-bromobenzene or 1-iodobenzene in a mixture of degassed solvents (DMF:H_2O 95:5) was added under N_2 atmosphere to a Schlenk tube. In a parallel step, another Schlenk flask was filled with 7.3 mg (0.060 mmol) phenylboronic acid, and K_2CO_3 (13.8 mg, 0.100 mmol) and Pd catalyst (20 mg of **$Co(OH)_2$-Pd-1**, 0.2 mg of Pd, $1.87 \cdot 10^{-3}$ mmol Pd, 3.7% mol Pd in the reaction). To remove adsorbed water from the solids and oxygen from the reaction atmosphere 3 times vacuum/N_2 cycles (10 min/1 min) were conducted.

Later, 0.05 mmol (2.5 mL) of the solution 0.02 M of 1-iodobenzene or 1-bromobenzene were transferred under nitrogen to the Schlenk flask containing the solid product. Subsequently, the solution heated to the desired temperature (110 or 70 °C) with a condenser. Solution was then stirred for 6, 24 and 48 hours. In the next step, the mixture was cooled to RT and filtered with a nylon filter (0.22 µm). Finally, the product was analyzed with a GC-FID instrument (Perkin-Elmer GC Clarus 580) using a Velocity® column (dimethylpolysiloxane, 30 m, 0.25 mm, 1.00 µm) and a temperature program (Fig. 1) with an injection temperature of 240 ºC and a detector temperature of 300 ºC.

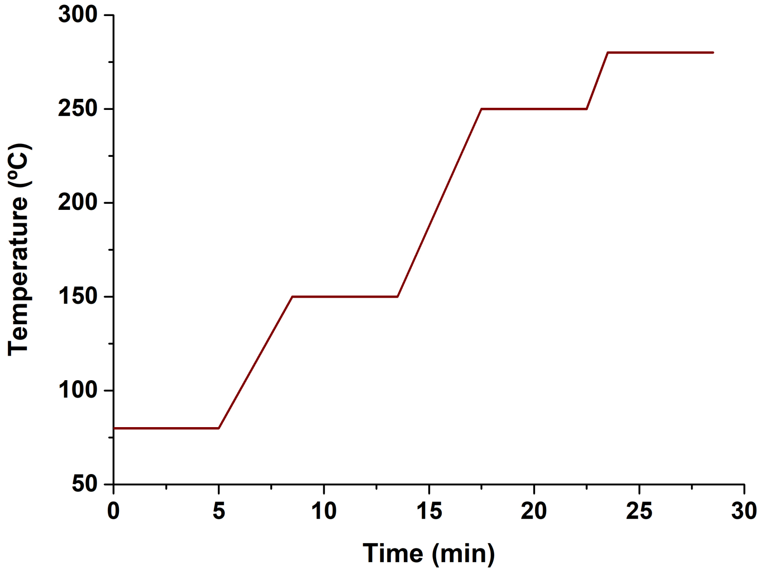


Fig. 1. Temperature program for GC quantification of catalytic and photocatalytic products

2.4. Photocatalytic study

2.4.1. Benzyl alcohol oxidation in the absence of light

Co(OH)$_2$ NPs were used as heterogeneous catalysts for the oxidation of benzyl alcohol in regular catalytic conditions (in the absence of light) and under LED or UV light, in order to clarify their photocatalytic and catalytic performance and its selectivity in the formation of benzaldehyde.

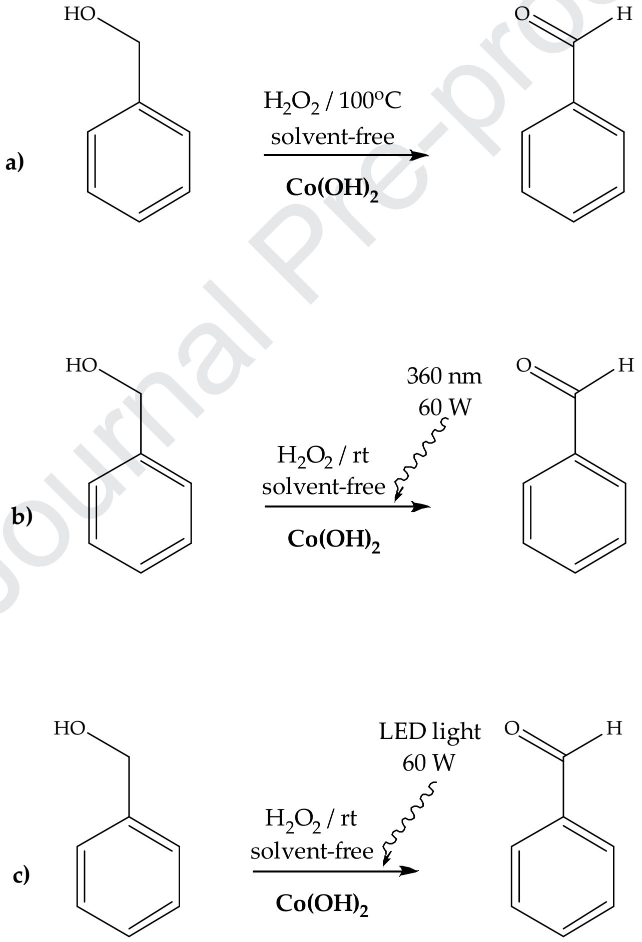
In a normal catalytic reaction, 48.1 mmol (5 mL) of benzyl alcohol, 19.6 mmol (2.00 mL) of H_2O_2 solution in H_2O 30 % (w/w) and 25 mg of catalyst were mixed under N_2 atmosphere in a Schlenk tube. The mixture was stirred at 110 ºC for 6 hours. Later, the reaction product was filtered with a nylon filter (0.45 µm) and the solid product was analysed by GC-FID (Perkin-Elmer GC Clarus 580) with a Velocity® column (dimethylpolysiloxane, 30 m, 0.25 mm, 1.00 µm) to estimate the conversion efficiency to benzaldehyde, using the temperature ramp of Fig. 1. The injection temperature was 240 ºC and the detector temperature was 300 ºC.

2.4.2. Benzyl alcohol photo-oxidation under UV light

The reaction was carried out using the same process described in 2.4.1 but at RT and using a UV lamp of 60 W and 360 nm (Scheme 2b)

2.4.3. Benzyl alcohol photo-oxidation under LED light

The reaction was carried out using the same process described in 2.4.1 but at RT and using a LED lamp of 60 W (6000 K) (Scheme 2c)



Scheme 2. Studied catalytic and photocatalytic oxidation of benzylalcohol to benzaldehyde

2.4.4. Methylene blue (MB) photodegradation under UV-light

MB photodegradation experiments were carried out under UV-light, 15 mg of the $Co(OH)_2$ NPs was added to 50 mL of a 0.02 mM MB solution. The reaction was carried out in a black box with a UV lamp (365 nm, 36W) as light source. Before irradiation, the studied suspensions containing the photocatalyst and MB were stirred for 1 h in the dark to reach the adsorption/desorption equilibrium. Subsequently, the suspensions were exposed to UV-light for a maximum of 3 hours. The decomposition of MB was monitored by measuring the absorbance (every 15 min) with a UV-spectrophotometer (Jena Analytik) at 660 nm wavelength (absorbance maximum of MB). The experiments were carried out in duplicate and the absorbance measured in triplicate.

2.4.5. Methylene blue photodegradation under LED light

MB photodegradation experiments were carried out using the same conditions described in the section 2.4.4 with a visible LED lamp (4.5 W, 6000 K, AS-Schwabe 42411) as the radiation source. The reaction time was 16 h and the experiments were conducted in duplicate and the absorbance measurement in triplicate.

3. Results and discussion

3.1. Physical characterization of NPs

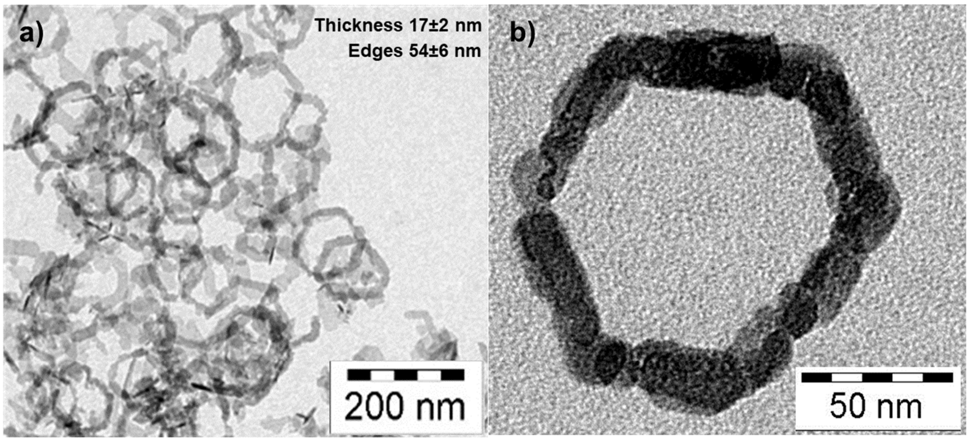


Fig. 2. a) TEM image of β-$Co(OH)_2$ NPs and b) detail of the hexagonal nanorings, including data of the thickness and edges.

A morphological analysis of the nanostructure of the synthesized $Co(OH)_2$ NPs was studied by TEM. As previously reported by our group [13] and observed in Fig. 2, the $Co(OH)_2$ NPs present an hexagonal nanoring morphology. In addition, a few rod-like NPs could also be observed in the TEM image, which means that some of the synthesized NPs stand on the side of the hexagonal nanorings.

Interlayer spacing of the as-synthesized NPs was also characterized (Fig. 2b inset) to confirm, as previously reported by our group, the presence of β form (not α) [13]. The measured interlayer lattice spacing was about 0.27 nm which fit well to crystal plane of (100) in β-$Co(OH)_2$ structure.

The crystalline structure and phase of the as-synthesized $Co(OH)_2$ NPs was also characterized by XRD (Fig. 3). Diffraction peaks were in agreement with those observed for β-$Co(OH)_2$ NPs (JCPDS file no. 30-443). There were no additional phases observed in the XRD pattern, indicating a high degree of purity of the obtained crystalline phase. The pattern of $Co(OH)_2$ NPs gave signals at 2θ 20, 39, 50, 65 and 92º assigned to Miller indices (001), (102), (002), (111) and (200), respectively.

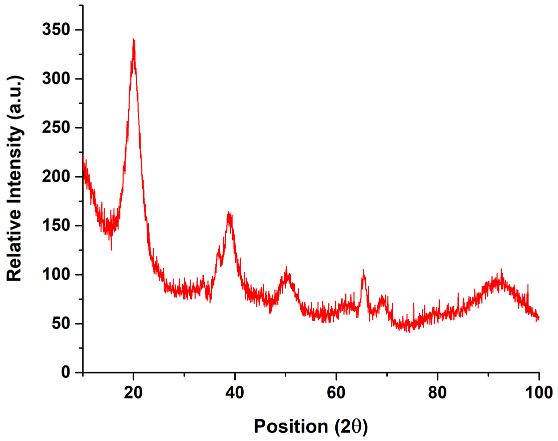


Fig. 3. Powder X-ray diffractogram of β- $Co(OH)_2$ NPs

The N_2 adsorption–desorption measurements (Fig. 4) gave a type IV isotherm (according to IUPAC classification) with a considerable hysteresis loop, which confirms the mesoporous nature of the studied NPs. The BET specific surface area of the NPs determined from the isotherm was ca. 215 m^2 g^{-1}. To estimate the pore size distribution of the sample a BJH approach was used, observing that the mean pore diameter of the NPs was ca. 4.8 nm, which is also in agreement with the nature of the prepared NPs as a mesoporous solid material [13].

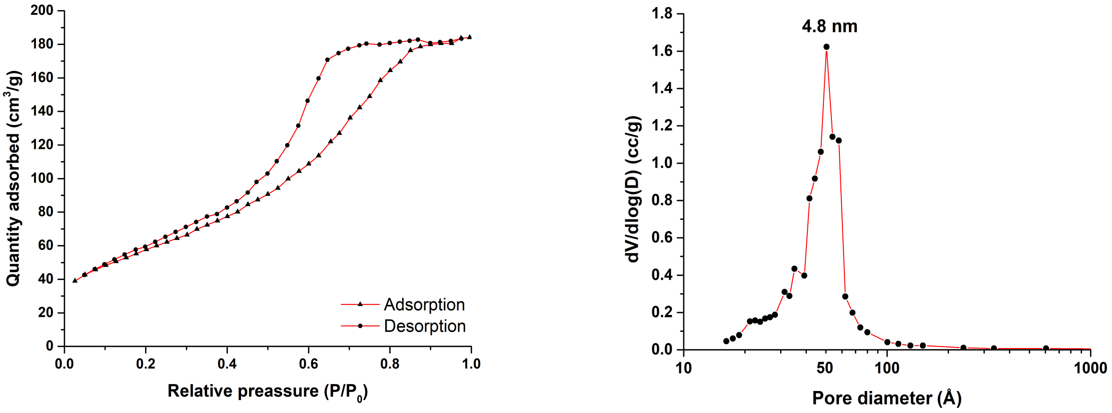


Fig. 4. Nitrogen adsorption–desorption isotherm of the mesoporous β-$Co(OH)_2$ nanorings in STP condition (left) and BJH pore-size distribution of the mesoporous β-$Co(OH)_2$ nanorings (right)

3.2. Preparation of $Co(OH)_2$-Pd-1

A hybrid material based on $Co(OH)_2$ and palladium was prepared by the reaction of the nanostructured **$Co(OH)_2$** with [$PdCl_2$(cod)] in DMF for 3 hours. This reaction allowed the formation of a hybrid material formed by supported Pd, obtained probably by the reduction of [$PdCl_2$(cod)], as described previously by our group for other support materials such as titanium oxide, silica or alumina or graphene oxide [40–43,45].

3.3. Catalytic study of $Co(OH)_2$-Pd-1 in Suzuki C-C coupling reactions

Noble metals (especially Pd) can effectively catalyse C-C cross-coupling reactions. In this context, Suzuki-Miyaura process is one of the most widely studied reaction for the synthesis of biphenyl products. To evaluate the catalytic performance of the hybrid catalyst, we used **$Co(OH)_2$-Pd-1** in two different Suzuki C-C coupling reactions, namely, 1-bromobenzene with phenylboronic acid and 1-iodobenzene with phenylboronic acid (Scheme 1). For this kind of reactions, we had already observed that the most interesting temperatures to explore were 70 and 110 ºC using K_2CO_3 as base and mixture of DMF/H_2O (95:5) as solvent [45]. In order to determine the evolution of the reaction kinetics, the conversion and yields were monitored at different reaction time intervals of 6, 24 and 48 hours.

Table 1. Halide conversions and Ph-Ph yields in C-C coupling reactions using 1-bromobenzene or 1-iodobenzene and phenylboronic acid catalyzed by **$Co(OH)_2$-Pd-1**.

Time (h)	T (ºC)	Halide conversion (molar %)	TON conversion	TOF conversion (h $^{-1}$)	Halide	Ph-Ph yield (molar %)

6		20	53	8.9		9.1
24	70	66	176	7.4	Br	21
48		70	187	3.9		23
6		21	56	9.4		8.3
24	110	71	189	7.9	Br	24
48		72	193	4.0		26
6		25	67	11		12
24	70	78	209	8.7	I	32
48		80	214	4.5		36
6		29	78	13		14
24	110	82	219	9.1	I	35
48		88	235	4.9		37

The obtained results of the C-C coupling reactions are given in Table 1 and Fig. 5. The catalytic study shows that the highest conversions were found at 110 ºC. In this context, the hybrid catalyst **$Co(OH)_2$-Pd-1** was able to reach up to 88% conversion of iodobenzene and 37% yield of the biphenyl product at 24 h, while the conversion and yield slightly decreased to 72% and 26% in the case of the use of bromobenzene. These results are comparable, if not somewhat better, than those obtained for other supported systems based on graphite, graphene oxide, or silica and Pd nanoparticles [4,40,45].

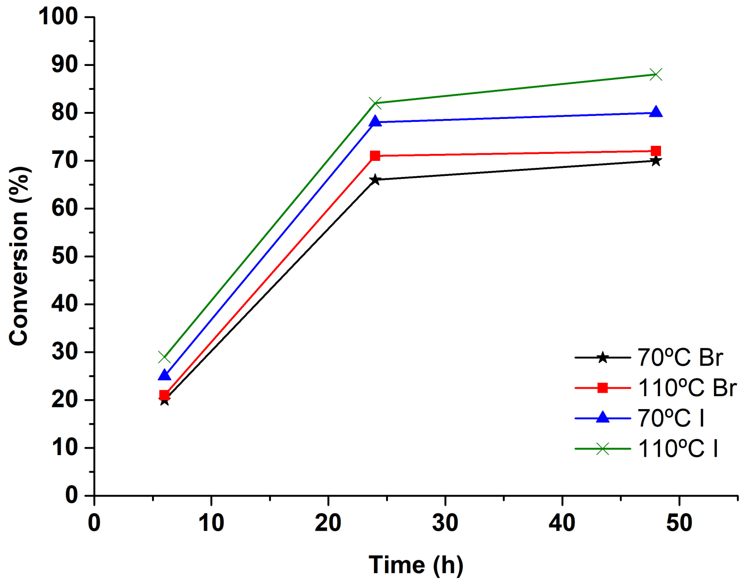


Fig. 5. Change of conversion with time in the reaction of 1-bromobenzene or 1-iodobenzene and phenylboronic acid catalyzed by **$Co(OH)_2$-Pd-1** at 70 °C or 110 °C.

3.4. Catalytic and photocatalytic study of $Co(OH)_2$-Pd-1 in benzyl alcohol oxidation

For the production of high valuable organic raw materials at industrial scale, the selective oxidation of alkylaromatics is a crucial point. The development of catalytic oxidation systems in the nanoscale range under mild synthesis conditions, is an attractive research field. Therefore, the interest in this field of research arises not only because of its importance in academic research but also because of its potential industrial application. For example, the selective oxidation of benzyl alcohol to benzaldehyde has remarkable importance in the food and cosmetic industry.

Thus, the catalytic study was focused on the selective oxidation of benzyl alcohol as a model process to investigate the catalytic performance of **$Co(OH)_2$-Pd-1** in oxidation reactions. The catalytic activity of **$Co(OH)_2$-Pd-1** in oxidation was studied with H_2O_2 as a green oxidant agent for the oxidation of benzyl alcohol. Normally, H_2O_2 is a greener oxidant than some other organic agents such as TBHP. Hydrogen peroxide is cheaper than most of the organic oxidants and its harmful environmental effect is much lower. Furthermore, the reactions were carried out in the absence of solvent, using the benzyl alcohol as the reaction medium. In addition, hydrogen peroxide was chosen as oxidant reagent because it is a better oxidant when using inorganic materials, due to its high mobility onto the materials surface.

At these conditions after 6 h at room temperature, the reaction using **$Co(OH)_2$-Pd-1** as catalyst did only give traces of benzaldehyde. The reaction temperature was, therefore, increased to 110 ºC in order to force the catalytic oxidation, however, only the formation of traces of benzaldehyde resulting from a very low conversion of benzyl alcohol, was again observed.

However, considering the interesting photocatalytic properties of $Co(OH)_2$ in water photo-oxidation [46], and that several nanostructured oxides functionalized with Pd are very active in catalytic oxidation of alcohols [47–49], we tested the photocatalytic benzyl alcohol oxidation by using $Co(OH)_2$-Pd-1 under UV and LED light (Table 2). The results show that, under UV light (360 nm) the selectivity towards benzaldehyde is higher than 99% but the conversion is not very high (TON of 0.81 and TOF of 0.13 h^{-1}). However, the photocatalytic activity increased when using LED light (with the same potency of 60 W, the TON is 4.62 and TOF 0.78 h^{-1}). Nevertheless, when using LED light, the selectivity towards benzaldehyde slightly decreases to 95%. This phenomenon may rely on a slightly different, less selective, mechanism of photo-oxidation which may be promoted by the use of different light sources and, therefore, different activation environment [50].

Table 2. Catalytic and photocatalytic results of the oxidation of benzyl alcohol in 6 hours of reaction with **$Co(OH)_2$-Pd-1** as catalyst.

T (^oC)	**Light source**	**TON (benzaldehyde)**	**TOF (benzaldehyde, h^{-1})**	**TON (benzyl benzoate)**	**TOF (benzyl benzoate, h^{-1})**	**Selectivity to benzaldehyde (%)**
rt	none	-	-	-	-	-
	UV	0.81	0.1	$3.4 \cdot 10^{-3}$	$5.7 \cdot 10^{-4}$	>99
	LED	4.6	0.8	0.28	0.1	95

3.5. Photocatalytic degradation of methylene blue with $Co(OH)_2$-Pd-1

Additionally, the photocatalytic activity of the synthesized NPs was investigated in organic dye decomposition. At this photodegradation experiment, MB was taken as a model of water contaminant. To reach the adsorption-desorption equilibrium, in a first step, the mixture of the solution of MB in water and **$Co(OH)_2$-Pd-1** was stirred in the dark for one hour. Later, the degradation was studied with a 36W UV lamp (365 nm) irradiation for 2 hours. Fig. 6 shows the results that confirm that the decomposition of MB rules with a first order kinetics. Therefore, the apparent rate constant for the decomposition (k, s^{-1}) was estimated from the regression curve of $\ln(C/C_0)$ *vs* the time of irradiation. The value of k for **$Co(OH)_2$-Pd-1** was $1.03 \cdot 10^{-4}\ s^{-1}$.

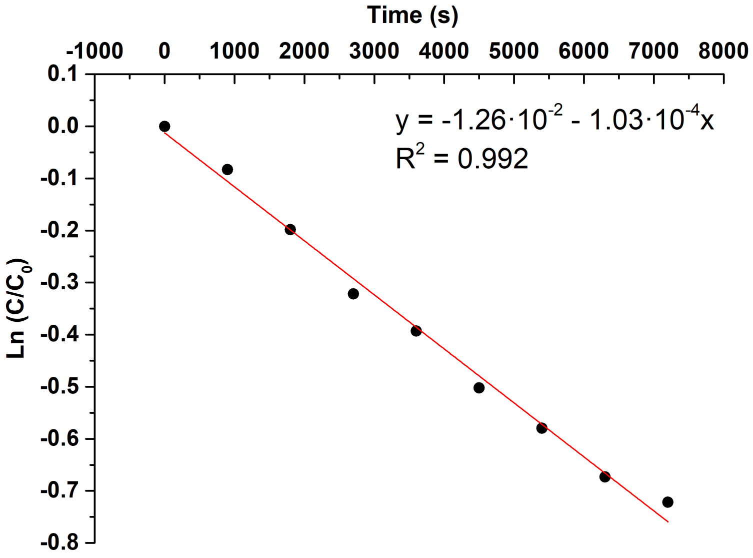


Fig. 6. Kinetic study of the MB degradation by **$Co(OH)_2$-Pd-1** during 2 h under UV light (36 W).

Finally, a photocatalytic degradation experiment using visible LED source (4.5 W) for 16 h was carried out (Fig. 7). The results show that the degradation of MB was slower than when using UV light, the kinetic constant (for a first order degradation) was calculated from the degradation curve and its value was 1.24×10^{-5} s^{-1}. In this case, the change of UV light to LED light did not lead to an increase of the photoactivity but to a considerable decrease. It is important to note that this experiment was designed for the same consumption of W·h (4.5 W for 16 hours) than in the case of UV light (36 W for 2 hours) in order to compare the final photoactivity. In this context, the differences in the photocatalytic degradation activity may probably be to the extension of time in the LED degradation, which increases the possibility the recombination of electron-hole pair, precluding the decomposition process and decreasing, therefore, the photocatalytic performance.

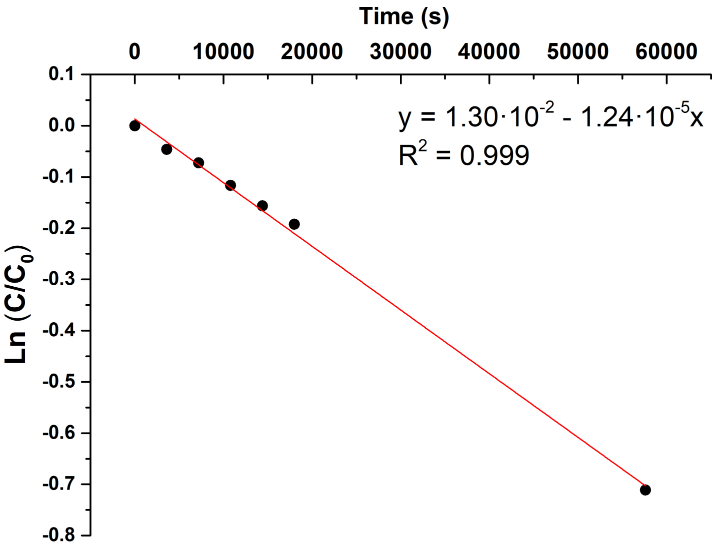


Fig. 7. Kinetic study of the MB degradation by $Co(OH)_2$ NPs during 16 h under LED light (4.5 W).

4. Conclusions

Herein we have provided a promising and facile strategy for the preparation and functionalization with a simple doping of the material with 1% Pd nanoparticles, of NPs with mesoporous structure of hexagonal nanorings for different catalytic reactions. In this study we have demonstrated the high versatility of the nanostructured system, which is able to selectively photooxidize benzyl alcohol to benzaldehyde under LED and UV lights and to degrade methylene blue in water via a photocatalytic reaction. This could be attributed to the unique mesoporous structure and the effect of the multiple active catalytic sites. In addition, the hybrid system catalyzed Suzuki cross-coupling reactions, confirming that these cobalt-based materials may be further explored in other catalytic and photocatalytic reactions for improving their potential applicability in other industrial processes. This study also confirmed that such mesoporous hexagonal nanorings of $Co(OH)_2$ may be helpful in the future treatment of environmental problems such as water purification or high value organic materials production. Future work of our group will now be focused on the use and determination of the optimal properties for the catalytic application of other systems based on other cheaper metals such as copper.

Acknowledgment

This work has been supported by the Center for International Scientific Studies & Collaboration (CISSC), Ministry of Science Research and Technology. S. G-R. and D.D-G. would also like to thank Ministerio de Ciencia, Innovación y Universidades of Spain (Grant no. RTI2018-094322-B-I00).

References

[1] S.K. Movahed, S. Miraghaee, M. Dabiri, AuPd alloy nanoparticles decorated graphitic carbon nitride as an excellent photocatalyst for the visible-light-enhanced Suzuki–Miyaura cross-coupling reaction, J. Alloys Compd. 819 (2020) 152994. https://doi.org/10.1016/j.jallcom.2019.152994.

[2] C. Zhu, J. Liu, M.-B. Li, J.-E. Bäckvall, Palladium-catalyzed oxidative dehydrogenative carbonylation reactions using carbon monoxide and mechanistic overviews, Chem. Soc. Rev. 49 (2020) 341–353. https://doi.org/10.1039/C9CS00397E.

[3] E. Fernández, M.A. Rivero-Crespo, I. Domínguez, P. Rubio-Marqués, J. Oliver-Meseguer, L. Liu, M. Cabrero-Antonino, R. Gavara, J.C. Hernández-Garrido, M. Boronat, A. Leyva-Pérez, A. Corma, Base-Controlled Heck, Suzuki, and Sonogashira Reactions Catalyzed by Ligand-Free Platinum or Palladium Single Atom and Sub-Nanometer Clusters, J. Am. Chem. Soc. 141 (2019) 1928–1940. https://doi.org/10.1021/jacs.8b07884.

[4] M. Díaz-Sánchez, D. Díaz-García, S. Prashar, S. Gómez-Ruiz, Palladium nanoparticles supported on silica, alumina or titania: greener alternatives for Suzuki–Miyaura and other C–C coupling reactions, Environ. Chem. Lett. 17 (2019) 1585–1602. https://doi.org/10.1007/s10311-019-00899-5.

[5] D. Elhamifar, A. Eram, R. Moshkelgosha, Ionic liquid and ethyl-based bifunctional ordered nanoporous organosilica supported palladium: An efficient catalyst for homo-coupling of phenylacetylenes, Micropor. Mesopor. Mat. 252 (2017) 173–178. https://doi.org/10.1016/j.micromeso.2017.06.024.

[6] T. Tabakova, L. Ilieva, P. Petrova, A.M. Venezia, G. Avdeev, R. Zanella, Y. Karakirova, Complete benzene oxidation over mono and bimetallic Au–Pd catalysts supported on Fe-modified ceria, Chem. Eng. J. 260 (2015) 133–141. https://doi.org/10.1016/j.cej.2014.08.099.

[7] I. Maluenda, O. Navarro, Recent Developments in the Suzuki-Miyaura Reaction: 2010–2014, Molecules. 20 (2015) 7528–7557. https://doi.org/10.3390/molecules20057528.

[8] F. Liu, S. Zuo, C. Wang, J. Li, F.-S. Xiao, C. Qi, Pd/transition metal oxides functionalized ZSM-5 single crystals with b-axis aligned mesopores: Efficient and long-lived catalysts for benzene combustion, Appl. Catal. B: Environm. 148–149 (2014) 106–113. https://doi.org/10.1016/j.apcatb.2013.10.054.

[9] C.C.C. Johansson-Seechurn, M.O. Kitching, T.J. Colacot, V. Snieckus, Palladium-Catalyzed Cross-Coupling: A Historical Contextual Perspective to the 2010 Nobel Prize, Angew. Chem. Int. Ed. 51 (2012) 5062–5085. https://doi.org/10.1002/anie.201107017.

[10] K. Jiang, B. Liu, M. Luo, S. Ning, M. Peng, Y. Zhao, Y.-R. Lu, T.-S. Chan, F.M.F. de Groot, Y. Tan, Single platinum atoms embedded in nanoporous cobalt selenide as electrocatalyst for accelerating hydrogen evolution reaction, Nature Commun. 10 (2019) 1743. https://doi.org/10.1038/s41467-019-09765-y.

[11] J. Wu, H. Yang, Platinum-Based Oxygen Reduction Electrocatalysts, Acc. Chem. Res. 46 (2013) 1848–1857. https://doi.org/10.1021/ar300359w.

[12] J. Wang, X. Yue, Y. Yang, S. Sirisomboonchai, P. Wang, X. Ma, A. Abudula, G. Guan, Earth-abundant transition-metal-based bifunctional catalysts for overall electrochemical water splitting: A review, J. Alloys Compd. 819 (2020) 153346. https://doi.org/10.1016/j.jallcom.2019.153346.

[13] M. Darbandi, B. Shaabani, A. Alizadeh, P. Yardani, E. Shahryari, M.G. Hosseini, Preparation and characterization of hexagonal mesoporous β-$Co(OH)_2$ nanorings, Micropor. Mesopor. Mater. 284 (2019) 421–426. https://doi.org/10.1016/j.micromeso.2019.04.048.

[14] X. Ji, Y. Chen, B. Paul, S. Vadivel, Photocatalytic oxidation of aromatic alcohols over silver supported on cobalt oxide nanostructured catalyst, J. Alloys Compd. 783 (2019) 583–592. https://doi.org/10.1016/j.jallcom.2018.12.307.

[15] W. Zhou, K. Huang, M. Cao, F. Sun, M. He, Z. Chen, Selective oxidation of toluene to benzaldehyde in liquid phase over CoAl oxides prepared from hydrotalcite-like precursors, Reac. Kinet. Mech. Cat. 115 (2015) 341–353. https://doi.org/10.1007/s11144-015-0833-4.

[16] F. Shi, Y. Li, Q. Zhang, H. Wang, Preparation of Core/Shell Structured Rutile/Anatase Photocatalyst via Vapor Phase Hydrolysis and its Photocatalytic Degradation of Phenol and Methylene Blue, J. Am. Ceram. Soc. 95 (2012) 1927–1932. https://doi.org/10.1111/j.1551-2916.2011.05069.x.

[17] U. Zavyalova, B. Nigrovski, K. Pollok, F. Langenhorst, B. Müller, P. Scholz, B. Ondruschka, Gel-combustion synthesis of nanocrystalline spinel catalysts for VOCs elimination, Appl. Catal. B: Environm. 83 (2008) 221–228. https://doi.org/10.1016/j.apcatb.2008.02.015.

[18] E. Niknam, F. Panahi, A. Khalafi□Nezhad, Immobilized Pd on a NHC functionalized metal–organic framework MIL-101(Cr): an efficient heterogeneous catalyst in Suzuki−Miyaura coupling reaction in water, Appl. Organomet. Chem. 34 (2020) e5470. https://doi.org/10.1002/aoc.5470.

[19] Y. Chai, W. Shang, W. Li, G. Wu, W. Dai, N. Guan, L. Li, Noble Metal Particles Confined in Zeolites: Synthesis, Characterization, and Applications, Adv. Sci. 6 (2019) 1900299. https://doi.org/10.1002/advs.201900299.

[20] D. Sánchez-Rodríguez, S. Yamaguchi, D. Ihara, H. Yamaura, H. Yahiro, Self-propagating high-temperature synthesis of highly dispersed noble metals on ceria powder: Application to Pd/CeO_2 catalyst, Ceram. Int. 43 (2017) 14533–14536. https://doi.org/10.1016/j.ceramint.2017.07.208.

[21] H. Bastami, E. Taheri□Nassaj, P.F. Smet, K. Korthout, D. Poelman, (Co, Nb, Sm)-Doped Tin Dioxide Varistor Ceramics Sintered Using Nanopowders Prepared by Coprecipitation Method, J. Am. Ceram. Soc. 94 (2011) 3249–3255. https://doi.org/10.1111/j.1551-2916.2011.04467.x.

[22] Z. Li, S. Ji, Y. Liu, X. Cao, S. Tian, Y. Chen, Z. Niu, Y. Li, Well-Defined Materials for Heterogeneous Catalysis: From Nanoparticles to Isolated Single-Atom Sites, Chem. Rev. 120 (2020) 623–682. https://doi.org/10.1021/acs.chemrev.9b00311.

[23] M.K. Samantaray, V. D'Elia, E. Pump, L. Falivene, M. Harb, S. Ould Chikh, L. Cavallo, J.-M. Basset, The Comparison between Single Atom Catalysis and Surface Organometallic Catalysis, Chem. Rev. 120 (2020) 734–813. https://doi.org/10.1021/acs.chemrev.9b00238.

[24] I. Favier, D. Pla, M. Gómez, Palladium Nanoparticles in Polyols: Synthesis, Catalytic Couplings, and Hydrogenations, Chem. Rev. 120 (2020) 1146–1183. https://doi.org/10.1021/acs.chemrev.9b00204.

[25] Y. Liu, X. Bai, S. Li, In-situ preparation of Pd nanoparticles in the pore channel of CMK-3 for Suzuki coupling reaction, Micropor. Mesopor. Mater. 260 (2018) 40–44. https://doi.org/10.1016/j.micromeso.2017.06.006.

[26] A.C. Ianculescu, C.A. Vasilescu, M. Crisan, M. Raileanu, B.S. Vasile, M. Calugaru, D. Crisan, N. Dragan, L. Curecheriu, L. Mitoseriu, Formation mechanism and characteristics of lanthanum-doped $BaTiO_3$ powders and ceramics prepared by the sol–gel process, Mater. Charact. 106 (2015) 195–207. https://doi.org/10.1016/j.matchar.2015.05.022.

[27] C. Xiang, Z. She, Y. Zou, J. Cheng, H. Chu, S. Qiu, H. Zhang, L. Sun, F. Xu, A room-temperature hydrogen sensor based on Pd nanoparticles doped TiO_2 nanotubes, Ceram. Int. 40 (2014) 16343–16348. https://doi.org/10.1016/j.ceramint.2014.07.073.

[28] M. Kashif, M.E. Ali, S.M.U. Ali, U. Hashim, Sol–gel synthesis of Pd doped ZnO nanorods for room temperature hydrogen sensing applications, Ceram. Int. 39 (2013) 6461–6466. https://doi.org/10.1016/j.ceramint.2013.01.075.

[29] A.P. Kumar, B.P. Kumar, A.B.V.K. Kumar, B.T. Huy, Y.-I. Lee, Preparation of palladium nanoparticles on alumina surface by chemical co-precipitation method and catalytic applications, Appl. Surf. Sci. 265 (2013) 500–509. https://doi.org/10.1016/j.apsusc.2012.11.035.

[30] R. Du, X. Jin, R. Hübner, X. Fan, Y. Hu, A. Eychmüller, Engineering Self-Supported Noble Metal Foams Toward Electrocatalysis and Beyond, Adv. Energy Mat. 10 (2020) 1901945. https://doi.org/10.1002/aenm.201901945.

[31] M.E. Shabestari, O. Martín, D. Díaz-García, S. Gómez-Ruiz, V.J. Gonzalez, J. Baselga, Facile and rapid decoration of graphene oxide with copper double salt, oxides and metallic copper as catalysts in oxidation and coupling reactions, Carbon. 161 (2020) 7–16. https://doi.org/10.1016/j.carbon.2020.01.015.

[32] B.J. Rani, M. Praveenkumar, S. Ravichandran, V. Ganesh, R.K. Guduru, G. Ravi, R. Yuvakkumar, Ultrafine M-doped TiO_2 (M = Fe, Ce, La) nanosphere photoanodes for photoelectrochemical water-splitting applications, Mater. Charact. 152 (2019) 188–203. https://doi.org/10.1016/j.matchar.2019.04.024.

[33] Y. Oumellal, K. Provost, C.M. Ghimbeu, A.M. de Yuso, C. Zlotea, Composition and size dependence of hydrogen interaction with carbon supported bulk-immiscible Pd–Rh nanoalloys, Nanotechnology. 27 (2016) 465401. https://doi.org/10.1088/0957-4484/27/46/465401.

[34] Y. Zhu, H. Su, Y. Chen, Z. Jin, J. Xu, D. Zhang, A Facile Synthesis of PdO-Decorated SnO_2 Nanocomposites with Open Porous Hierarchical Architectures for Gas Sensors, J. Am. Ceram. Soc. 99 (2016) 3770–3774. https://doi.org/10.1111/jace.14378.

[35] T.W. van Deelen, C. Hernández Mejía, K.P. de Jong, Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity, Nature Catal. 2 (2019) 955–970. https://doi.org/10.1038/s41929-019-0364-x.

[36] T. Hattori, A. Tsubone, Y. Sawama, Y. Monguchi, H. Sajiki, Palladium on Carbon-Catalyzed Suzuki-Miyaura Coupling Reaction Using an Efficient and Continuous Flow System, Catalysts. 5 (2015) 18–25. https://doi.org/10.3390/catal5010018.

[37] S. Yamamoto, H. Kinoshita, H. Hashimoto, Y. Nishina, Facile preparation of Pd nanoparticles supported on single-layer graphene oxide and application for the Suzuki–Miyaura cross-coupling reaction, Nanoscale. 6 (2014) 6501–6505. https://doi.org/10.1039/C4NR00715H.

[38] C.M.A. Parlett, D.W. Bruce, N.S. Hondow, M.A. Newton, A.F. Lee, K. Wilson, Mesoporous Silicas as Versatile Supports to Tune the Palladium-Catalyzed Selective Aerobic Oxidation of Allylic Alcohols, ChemCatChem. 5 (2013) 939–950. https://doi.org/10.1002/cctc.201200301.

[39] Y. Liu, J. Zhang, W. Hou, J.-J. Zhu, A Pd/SBA-15 composite: synthesis, characterization and protein biosensing, Nanotechnology. 19 (2008) 135707. https://doi.org/10.1088/0957-4484/19/13/135707.

[40] A. Balbín, F. Gaballo, J. Ceballos-Torres, S. Prashar, M. Fajardo, G.N. Kaluđerović, S. Gómez-Ruiz, Dual application of Pd nanoparticles supported on mesoporous silica SBA-15 and MSU-2: supported catalysts for C–C coupling reactions and cytotoxic agents against human cancer cell lines, RSC Adv. 4 (2014) 54775–54787. https://doi.org/10.1039/C4RA11759J.

[41] A.M.S. Hossain, A. Balbín, R.S. Erami, S. Prashar, M. Fajardo, S. Gómez-Ruiz, Synthesis and study of the catalytic applications in C–C coupling reactions of hybrid nanosystems based on alumina and palladium nanoparticles, Inorg. Chim. Acta. 455 (2017) 645–652. https://doi.org/10.1016/j.ica.2016.04.045.

[42] S. Lázaro-Navas, S. Prashar, M. Fajardo, S. Gómez-Ruiz, Visible light-driven photocatalytic degradation of the organic pollutant methylene blue with hybrid palladium–fluorine-doped titanium oxide nanoparticles, J. Nanopart. Res. 17 (2015) 94. https://doi.org/10.1007/s11051-015-2902-z.

[43] B. Rico-Oller, A. Boudjemaa, H. Bahruji, M. Kebir, S. Prashar, K. Bachari, M. Fajardo, S. Gómez-Ruiz, Photodegradation of organic pollutants in water and green hydrogen production via methanol photoreforming of doped titanium oxide nanoparticles, Sci. Total Environm. 563–564 (2016) 921–932. https://doi.org/10.1016/j.scitotenv.2015.10.101.

[44] M. Trilla, G. Borja, R. Pleixats, M.W.C. Man, C. Bied, J.J.E. Moreau, Recoverable Palladium Catalysts for Suzuki–Miyaura Cross- Coupling Reactions Based on Organic-Inorganic Hybrid Silica Materials Containing Imidazolium and Dihydroimidazolium Salts, Adv. Synth. Catal. 350 (2008) 2566–2574. https://doi.org/10.1002/adsc.200800455.

[45] R.S. Erami, D. Díaz-García, S. Prashar, A. Rodríguez-Diéguez, M. Fajardo, M. Amirnasr, S. Gómez-Ruiz, Suzuki-Miyaura C-C Coupling Reactions Catalyzed by Supported Pd Nanoparticles for the Preparation of Fluorinated Biphenyl Derivatives, Catalysts. 7 (2017) 76. https://doi.org/10.3390/catal7030076.

[46] G. Zhang, S. Zang, X. Wang, Layered $Co(OH)_2$ Deposited Polymeric Carbon Nitrides for Photocatalytic Water Oxidation, ACS Catal. 5 (2015) 941–947. https://doi.org/10.1021/cs502002u.

[47] J. Yang, K. Cao, M. Gong, B. Shan, R. Chen, Atomically decorating of MnO_x on palladium nanoparticles towards selective oxidation of benzyl alcohol with high yield, J. Catal. 386 (2020) 60–69. https://doi.org/10.1016/j.jcat.2020.03.029.

[48] S.M. Abdel-Fatah, M. Díaz-Sánchez, D. Díaz-García, S. Prashar, L.H. Abdel-Rahman, S. Gómez-Ruiz, Nanostructured Metal Oxides Prepared from Schiff Base Metal Complexes: Study of the Catalytic Activity in Selective Oxidation and C–C Coupling Reactions, J. Inorg. Organomet. Polym. Mat. 30 (2020) 1293–1305. https://doi.org/10.1007/s10904-019-01269-y.

[49] M. Du, G. Zeng, J. Huang, D. Sun, Q. Li, G. Wang, X. Li, Green Photocatalytic Oxidation of Benzyl Alcohol over Noble-Metal-Modified $H_2Ti_3O_7$ Nanowires, ACS Sustainable Chem. Eng. 7 (2019) 9717–9726. https://doi.org/10.1021/acssuschemeng.9b01817.

[50] R. Marotta, I. Di Somma, D. Spasiano, R. Andreozzi, V. Caprio, Selective oxidation of benzyl alcohol to benzaldehyde in water by TiO_2/Cu(II)/UV solar system, Chem. Eng. J. 172 (2011) 243–249. https://doi.org/10.1016/j.cej.2011.05.097.

- Pd-anchored mesoporous beta-cobalt hydroxide hexagonal nanorings have been synthesized.
- Catalytic activity for Suzuki C-C coupling reactions has been tested.
- Photocatalytic and photodegradation performance of the nanosystems have been investigated.
- Nanosystems were able to degrade organic dyes in water with good performance.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: