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ELECTRONIC SUPPLEMENTARY INFORMATION

Rhodium nanoparticles impregnated on TiO_2: Strong morphological effects on hydrogen production

Brunno L. Albuquerque,*[a] Gustavo Chacón [a], Michael Nazarkovsky [b] and Jairton Dupont [a]

a. LAMOCA – Laboratory of Molecular Catalysis, Institute of Chemistry – Universidade Federal do Rio Grande do Sul. Av. Bento Gonçalves, 9500 Porto Alegre 91501-970 RS (Brazil).
b. Pontifícia Universidade Católica de Rio de Janeiro, Rua Marquês de São Vicente, 225, Rio de Janeiro 22451-900 RJ (Brazil).

(*) Corresponding author: E-mail address: brunno.albuquerque@ufrgs.br

Summary

Additional Figures and Tables

Figure S1. a) 3D Drawing of the reactor used in the experiments, b) exploded view of the UV-LED reactor assembly and c) Digital photograph of the adapted Schlenk tube for the photocatalysis experiments.

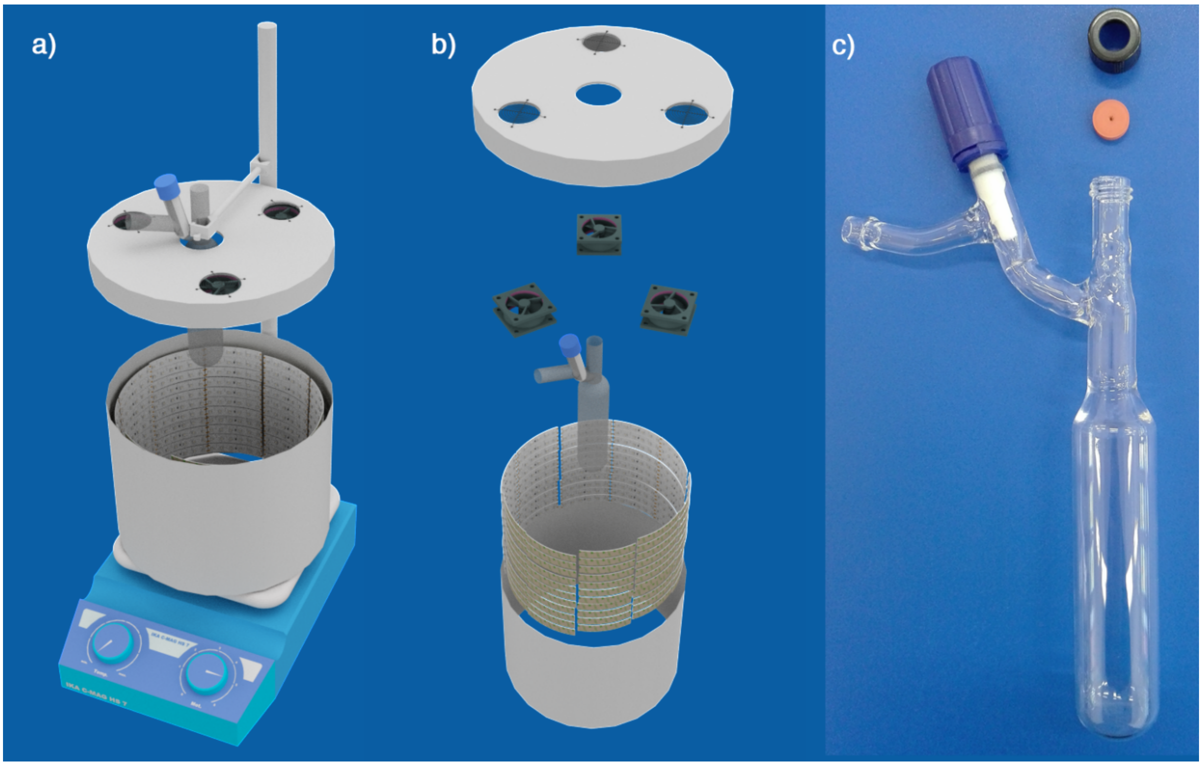


Figure S2. (a) The violin graphs plotted by frequency for Rh nanoparticles distributions in RhNP, RhNC and RhOh with the (b) bar plots for average size, standard deviation and interquartile ranges correlating with the nanoparticles shape.

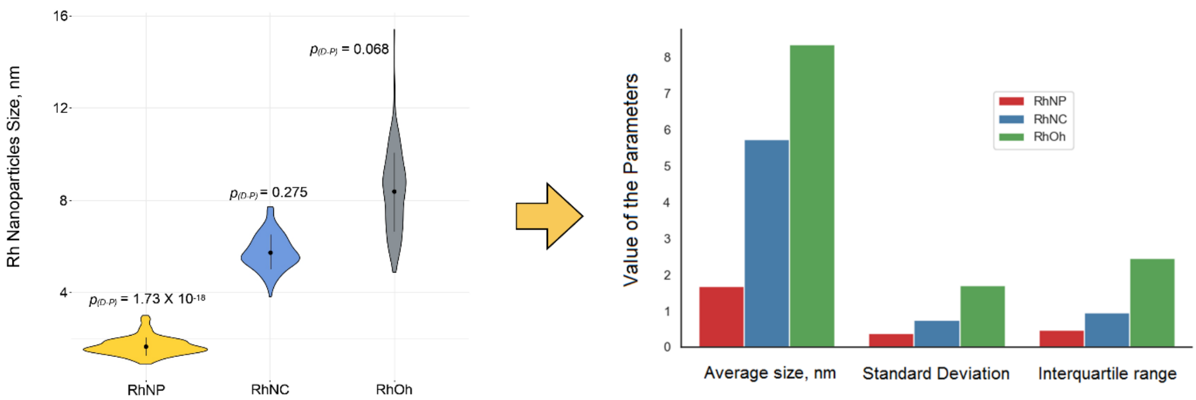


Figure S3. UV-vis DRS spectra of the of the Rh and IL impregnated TiO_2 photocatalysts. (a) absorption spectra of all catalysts and Tauc plots for (b) IL-impregnated TiO2, (c) RhNP, (d) RhNC, (e) RhOh, (f) RhOh with additional IL impregnation and (g) RhNC with increased concentration of rhodium nanocubes.

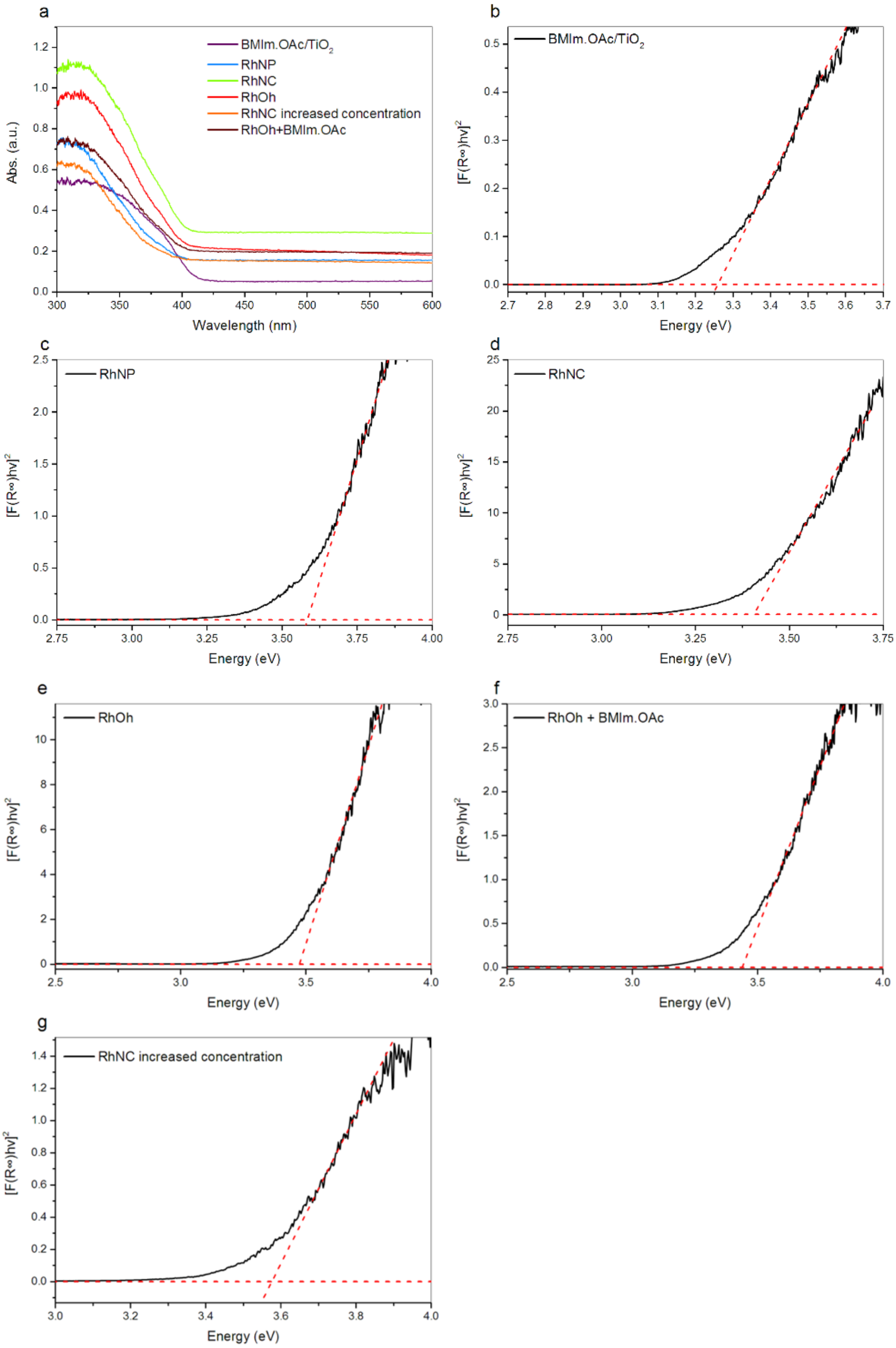


Figure S4. XPS Survey spectra of the as prepared a) RhNP, b) RhNC an c) RhOh.

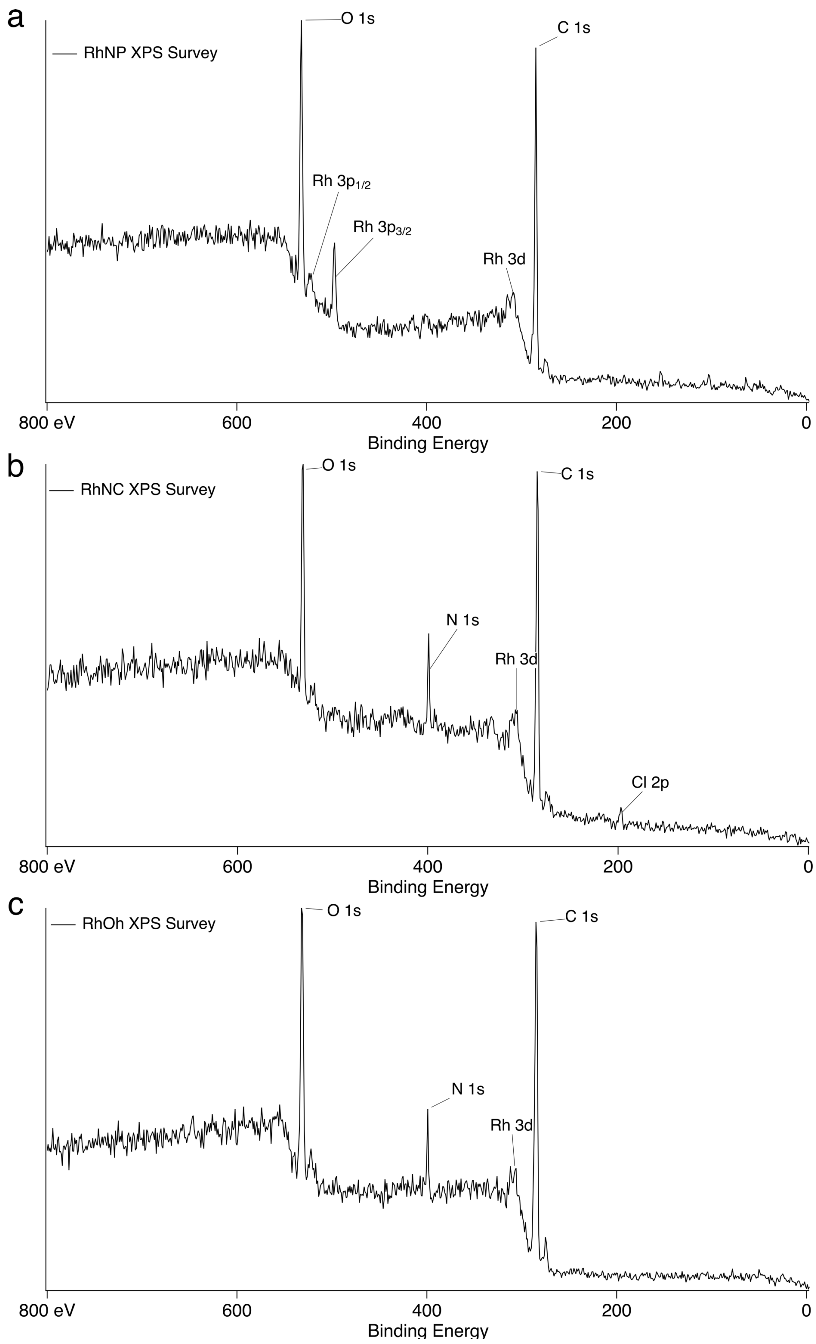


Figure S5. Frenkel-Halsey-Hill plots for (a) RhNP, (b) RhNC and (c) RhOh.

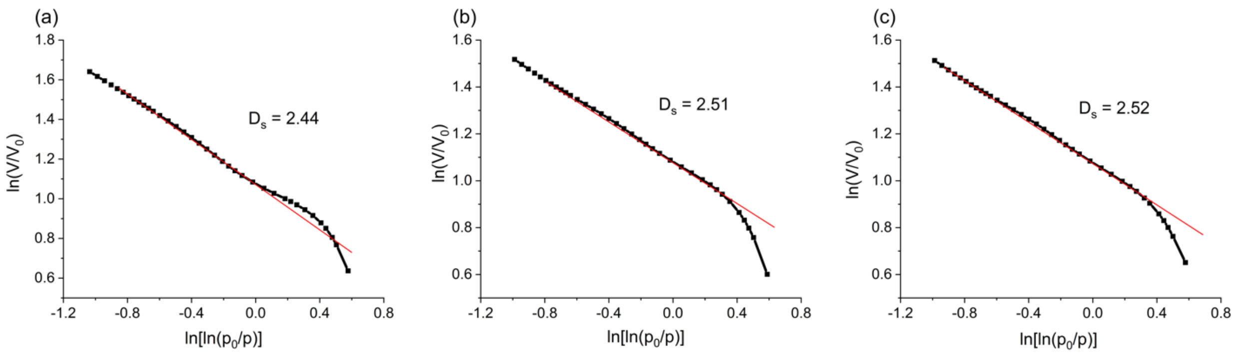


Table S1. Comparison of the Rh-based photocatalysts for H_2 production.

Catalyst	Concentration, g/L	Sacrificial reagent, %	Wavelength, nm	Rate of H_2 produced, µmol/h[a]	Reference
RhNP	1.0	MeOH (10%)	365 (LED)	49.7	this work
RhNP	1.0	MeOH (10%)	400 (LED)	11.1	this work
RhNC	1.0	MeOH (10%)	365 (LED)	17.4	this work
RhNC	1.0	MeOH (10%)	400 (LED)	14.0	this work
Rh(PVP)/C_3N_4-4.1	0.25	MeOH (10%)	> 400	1.5	1
Rh/g-C_3N_4	1.0	TEA (10%)	> 400	1.6	2
Rh/Cr_2O_3@ GaN:ZnO	0.375	H_2SO_4 (pH 4.5)	> 400	600	3
Rh/Cr_2O_3/GaN:ZnO	0.375	None	> 400	426	4
Rh(0.03)-doped $KCa_2Nb_3O_{10}$	0.033	MeOH (10%)	300	385	5
Rh:$BaTiO_3$	1.0	MeOH (10%)	> 420	30.8	6
MoOy/RhCrOx/STO:Al	1.0	MeOH (10%)	300 ~ 500	1700	7

Obs. [a] The data were calculated in disregard of the catalyst loading to facilitate the comparison.

Figure S6. RhNC amount impregnated in TiO_2 influence in the H_2 production (the connecting lines are a guide for the eyes).

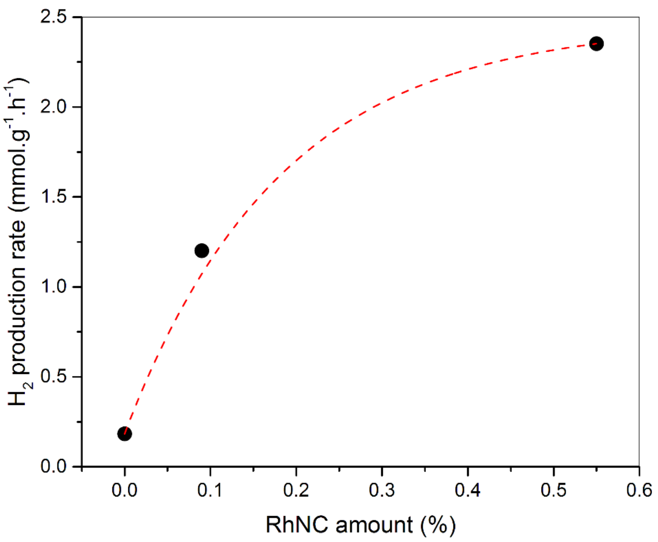


Figure S7. Comparison of photon source, full spectrum vs monochromatic, in the kinetics of H_2 photocatalytic production.

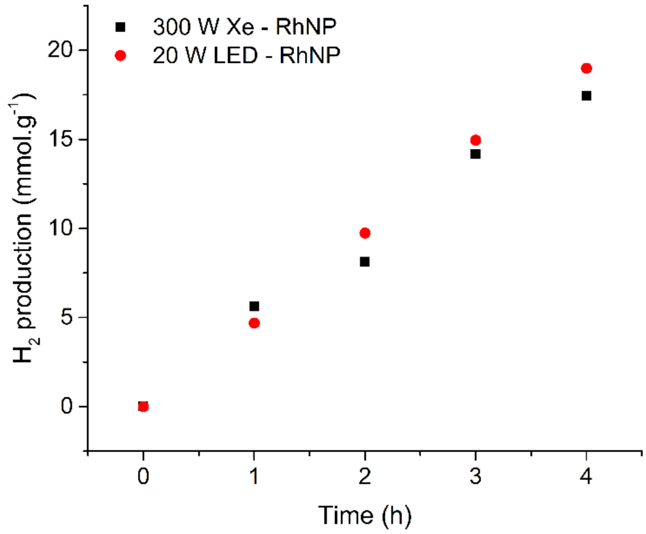


Figure S8. Conventional TEM analysis of after/before catalytic cycle attesting the stability of the Rh nanoparticles by exposing to UV light (a) TiO_2-supported hNP and (b) unsupported.

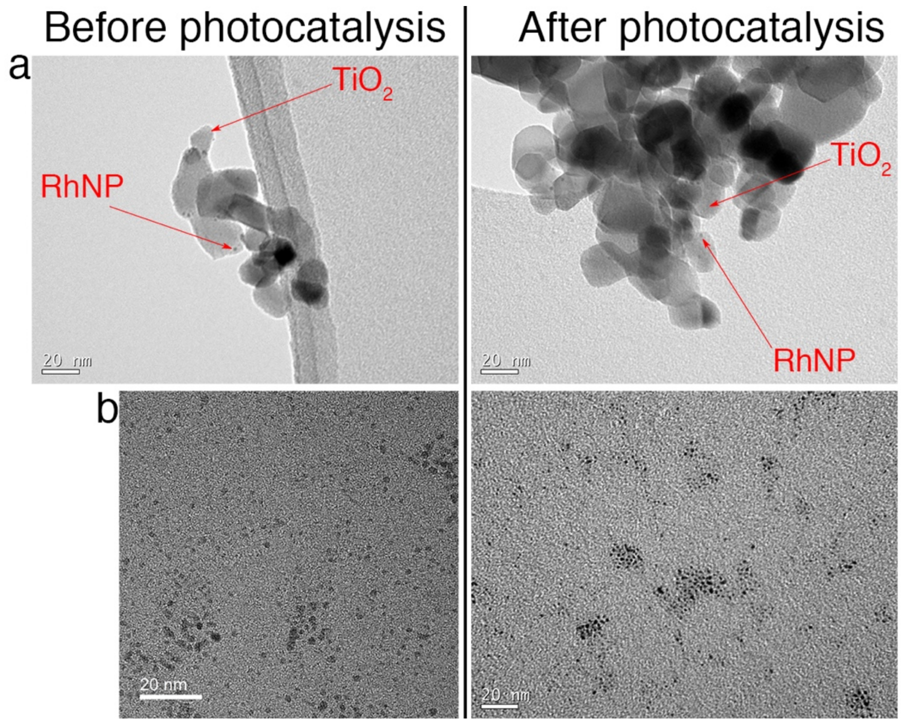


Figure S9. TGA analysis of RhOh after and before impregnation with BMIm.OAc.

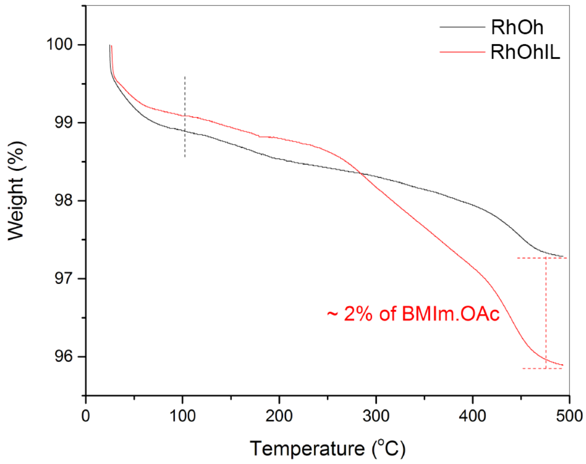
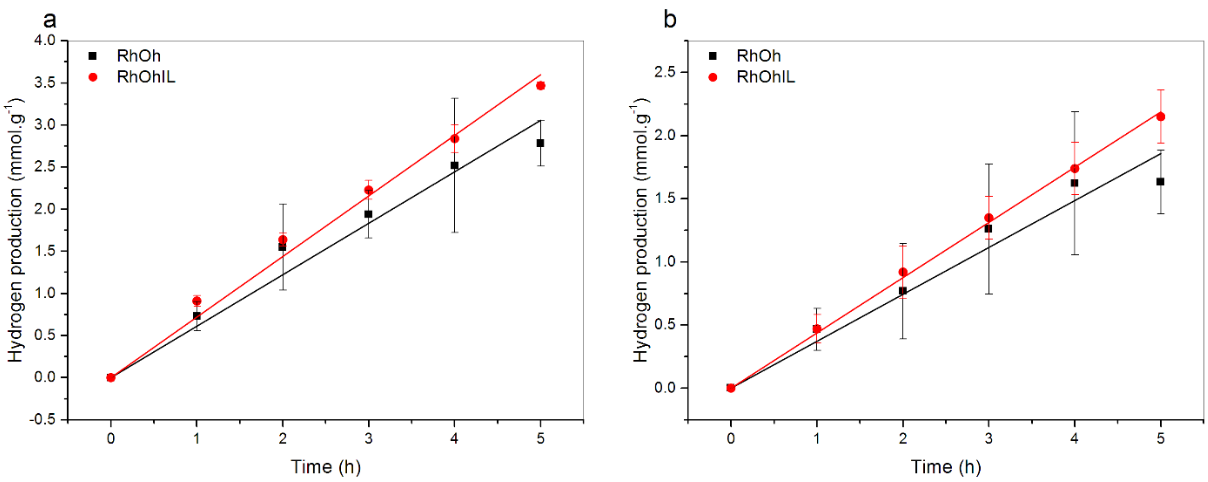


Figure S10. H_2 production with RhOh before and after BMIm.OAc impregnation at (a) 365 nm irradiation and (b) 400 nm irradiation.



Nanoparticle Surface Area Estimation

The surface area estimation of the catalysts used in this work was calculated based on previous works on colloidal nanoparticles using the magic number approach and the Platonic solids as a representation of the nanoparticle's shapes.[8] An Excel spreadsheet was constructed in order to aid the calculation based on the nanoparticles size, morphology and amount impregnated in the support. For colloidal nanoparticles it was estimated from the volume of the reaction.

Firstly, the volume of the nanoparticles is calculated by equations 1, 2 and 3 for each morphology of the nanoparticles synthesized in this work. The volume in cubic centimetre is then converted from cubic nanometres by dividing by 10^{21}.

Sphere (cuboctahedron)	Cube	Octahedra
$V = \frac{4\pi}{3}(R_{NP})^3$ (1)	$V = (R_{NP})^3$ (2)	$V = \frac{(R_{NP})^3}{3\sqrt{2}}$ (3)

The mass of a single nanoparticle is obtained by dividing the volume of the nanoparticle for the density of rhodium (12.41 g/cm^3). The number of nanoparticles in the reaction can be estimated by the mass of impregnated metal in TiO_2 as determined by FAAS divided by the mass of a single particle. The results are summarized in table 4 below.

Table S2. Number of particles determined by amount of impregnated Rh nanoparticles and the size as determined by TEM analysis.

Catalyst	N_{NP} *(x10^{12})* particles
RhNP	79.2
RhNC	4.13
RhOh	3.17

Therefore, the surface area of the nanoparticles is approximated by the area of platonic solids regarding each shape synthesized in this work:

Sphere (cuboctahedron)	Cube	Octahedra
$S_T = 4\pi(R_{NP})^2 N_{NP}$ (4)	$S_T = 6{R_{NP}}^2 N_{NP}$ (5)	$S_T = 2\sqrt{3}(R_{NP})^2 N_{NP}$ (6)

The normalization of activity per surface area is done by dividing the rate of production of H_2 per hour (μmol.h^{-1}) by the surface area calculated in this method.

Bibliographic References

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