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Sharp Volcano-Type Synergy and Visible Light Acceleration in H₂ Release upon B₂(OH)₄ Hydrolysis Catalyzed by Au-Rh@Click-Dendrimer Nanozymes

Qiuxia Zhao, Naixin Kang, Marta Martinez Moro, Eduardo Guisasola Cal, Sergio Moya, Emerson Coy, Lionel Salmon, Xiang Liu, Didier Astruc

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12 Lionel Salmon, Xiang Liu, Didier Astruc,*
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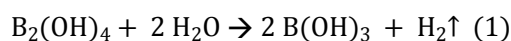
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17 **Abstract**
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19 Hydrogen (H₂) formation from hydrogen-rich precursors is a hot topic, whereby carbon-
20 free energy perspectives, mechanistic features and synthetic applications are actively
21 searched. Here, we report oxygen atom uptake from water under ambient conditions
22 producing H₂ in the presence of alloyed Au-Rh nanoparticle (NP) catalysts encapsulated
23 in a “click” dendrimer. These systems are named nanozymes (NZs), because their function
24 and mechanism resemble that of hydrogenase enzymes. The Au-Rh NZs with variable
25 proportions of Au and Rh exhibit positive sharp volcano-type synergy and visible-light
26 induced acceleration. The best synergy in the dark is disclosed in Au₄Rh₁, achieving a
27 turnover frequency (TOF_s) of 5100 mol_{H₂} mol_{cata}⁻¹ min⁻¹ in dark, 3.4 times higher than
28 related Au NZ and 8.9 times higher than the related Rh NZ at 25 ± 1 °C. The catalytic
29 activity of Au-Rh for H₂ evolution is enhanced by visible-light irradiation due to the Au
30 plasmon, so that the synergistic effect in the dark and the visible-light induced rate
31 enhancement cumulate for Au₄Rh₁, allowing complete B₂(OH)₄ hydrolysis in 39 sec at 25
32 ± 1°C (TOF_s = 6000 mol_{H₂} mol_{cata}⁻¹ min⁻¹). Upon increasing the Rh content, Au-Rh
33 provides less synergy in the dark, whereas the light enhancement of the reaction rate
34 increases, reaching a maximum for Au₁Rh₂. Experiments using D₂O, including kinetic
35 isotope effect determination, suggest that the rate-determining step of the reaction involves
36 concerted O-H bond cleavage of water and support the proposed catalytic reaction
37 mechanism.
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40 **Keywords:** hydrogen production; B₂(OH)₄ hydrolysis; plasmonic rate enhancement;
41 volcano-synergy effect; visible-light acceleration; gold; rhodium
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1. Introduction

We report oxygen atom uptake from H₂O producing H₂ upon reaction with B₂(OH)₄ catalyzed under ambient condition by bimetallic Au-Rh nano-particles (NPs) encapsulated in a “click”-dendrimer. These nano catalysts of metallo-macromolecular type play the role of “nanozymes” (NZs), a general term currently utilized for artificial nanomaterials with catalytic activities resembling those of enzymes.¹ In the present case, we will show some resemblance of these nanocatalysts² with hydrogenase that catalyze the formation of H₂ from water protons, including mechanistic results.^{3,4} B₂(OH)₄, a useful borylation agent, sometimes used in hydrogenation reactions,⁵⁻⁸ is potentially usable for H₂ generation upon hydrolysis according to equation (1):



Transfer hydrogenation⁹ of unsaturated hydrocarbon using catalytic B₂(OH)₄ hydrolysis was pioneered in 2016 by Stokes and his group who reported that this reaction could be used for hydrogenation and deuteration of a variety of alkenes and alkynes and showed that both hydrogen atoms of water were transferred to the unsaturated substrates.⁵ A catalytic mechanism was suggested without H₂ formation involving the intermediacy of a Pd-H species in which the unsaturated hydrocarbon inserted to end up with its hydrogenation. It has also been shown that H₂ formation proceeded upon Pd-catalyzed hydrolysis of B₂(OH)₄.⁹ For comparison, ammonia borane (AB) hydrolysis is a well-known classic method of H₂ generation in which one of the generated H₂ atoms (the “hydridic” one) is provided by hydrogen-rich AB and the other one (the “acidic” one) from water.¹⁰ On the other hand, B₂(OH)₄ only contains acidic hydrogen atoms, and apparently both hydrogen atoms of produced H₂ seem to come from water (*vide infra*), thus none would come from B₂(OH)₄. Consequently, B₂(OH)₄ is not a hydrogen storage material, contrary to AB and derivatives. By the way, the fact that water behaves as a hydrogen storage source upon utilizing B₂(OH)₄ hydrolysis offers a D₂ production method from D₂O, applicable for the deuteration of unsaturated compounds of extensive utility in mechanism studies,¹¹ and analytical chemistry.^{12,13}

B₂(OH)₄ is stable in water at room temperature, and thus a catalyst is required for its hydrolysis to H₂ according to equation (1). Formation of H₂ would be of interest given the considerable application in its production as a long-term sustainable energy supply.¹⁴⁻¹⁹

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3 Given the absence of reasonably practical loop to recycle $B_2(OH)_4$ from the reaction
4 product $B(OH)_3$, however, reaction (1) can rather be considered as a test reaction and a
5 useful and fast way to produce H_2 or D_2 on the laboratory scale under ambient conditions.
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7 Bimetallic NPs, constituted of two distinct metal elements, often show an enhanced
8 chemical performance compared to those of their monometallic counterparts.²⁰ The
9 presence of a second metal indeed usually provokes a modification of the electronic state
10 of each metal in the NP and consequently modifies the catalytic activity of the bimetallic
11 nanocatalysts. Besides, the second metal induces a geometric effect often reducing the
12 number of multiple adsorption sites by partially blocking the surface or facilitating access
13 to more active sites owing to specific atomic arrangement.²¹ This frequently positive
14 synergistic effect has received much attention in optical, catalytic, and photocatalytic
15 applications.²⁰

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17 Photocatalysis is regarded as a prominent approach utilizing the endless and diffuse
18 solar energy.²² Recently, the plasmonic metal NPs (PMNPs)²³ have drawn much attention
19 owing to their surface plasmonic resonant (SPR) effect that is utilized for plasmonic
20 photocatalytic hydrogen evolution. Light excitation provokes hot charge transfer to the
21 nearby substrate for a few tenths of fs, which reduces the activation energy of the reaction
22 of the adsorbed substrate.²⁴ Therefore, PMNP morphology, size and structure control the
23 efficiency of the photocatalytic system.^{25,26}

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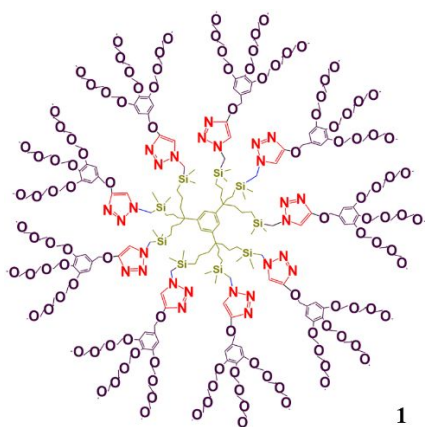


Figure 1. "Click" dendrimer 1.

Dendrimer-RNA NPs are known to provide protective immunity against several lethal viruses,²⁷ and polyamidoamine (PAMAM) dendrimers encapsulating NPs have functioned as catalysts.^{28,29} Dendrimers of "click" type are known as effective nanocatalyst encapsulating supports for a variety of reactions.³⁰ They contain intradendritic 1,2,3-triazolyl groups resulting from "click" reactions. They are therefore called "click" dendrimers (Figure 1), because they result from the Cu(I)-catalyzed Huisgen 1,3-dipolar azide-alkyne cycloaddition (CuAAC, the most known so-called "click" reaction³¹) of the terminal azido groups of dendrimer cores with dendrons containing an alkyne group at their focal points. These "click" dendrimers, such as **1**, are of micellar type, due to their hydrophobic interior and the presence of hydrophilic triethylene glycol (TEG) terminal groups. They are dendritic amphiphilic unimolecular micelles allowing coordination, to their intradendritic triazole groups, of transition-metal ions and, more mildly, NPs.³¹ These intradendritically coordinated metal cations and NPs are stabilized by protection, due to the bulk of the "click" dendrimer periphery. Therefore, here, "click"-dendrimer-encapsulated, mono-metallic and bimetallic transition metal NPs including Au have been prepared, tested and compared towards H₂ evolution upon B₂(OH)₄ hydrolysis under both dark and visible-light illumination conditions. Several gold-containing bimetallic nano-catalytic systems, Au_x-Rh_y have been selected and examined with various metal ratios, allowing to determine the optimized metal ratios in the dark, light-induced acceleration, and combined effects. From these results, the benefits of bimetallic synergy and visible light illumination are analyzed and discussed. Finally, hydrolysis experiments using D₂O instead of H₂O including determination of the kinetic isotope effect (KIE) are carried out in order to contribute to a mechanistic proposal concerning the AuRh NZ-catalyzed B₂(OH)₄ hydrolysis.

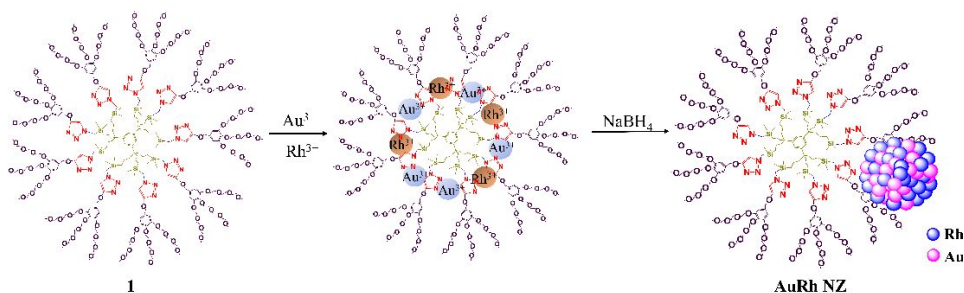
2. Experimental Section

2.1. Materials

The precursors used for the click-dendrimer-encapsulated NP preparations, RhCl_3 , $\text{KAuCl}_4 \cdot x\text{H}_2\text{O}$, NaBH_4 and $\text{B}_2(\text{OH})_4$ were purchased from Sigma-Aldrich and are analytical grade. All flasks were washed with aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$) before usage to avoid the presence of metal residues. Milli-Q water ($18.2 \text{ M}\Omega$, Thermo Fischer Scientific Inc., USA) was used in the process of NP fabrication and catalytic reactions.

2.2. Synthesis of the “click” dendrimer-encapsulated Au-Rh NZs

The “click” dendrimer (Figure 1 and S1) containing nine 1,2,3-triazole ligands on the tethers and 27 water-solubilizing triethylene glycol termini was fabricated via a method previously reported.³² Taking advantage of the presence of nitrogen-rich 1,2,3-triazoles along the “click” dendrimer tethers, Rh (III) and Au (III) were coordinated to the intra-dendritic 1,2,3-triazoles upon blending together their precursor metal derivatives with the dendrimer under N_2 . Then, the Au-Rh NPs were generated upon addition of a freshly-prepared solution of the reductant NaBH_4 to the dendrimer-metal (III) assembly (Scheme 1).³³ The composition of Au and Rh in the bimetallic NPs is termed as Au_xRh_y , where x and y indicate the molar ratio of Au and Rh, for example Au_4Rh_1 for an Au-Rh NZ containing 80% mol Au and 20% mol Rh. Various Au_xRh_y NPs were prepared upon varying the proportions x/y of the metal precursors from 0.5 to 6.



Scheme 1. Synthesis of various Au-Rh NZs supported by the “click” dendrimer **1**.

2.3. Au-Rh NZ characterizations

The overall characterizations of the Au-Rh @click-dendrimer NZs were carried

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3 out using NMR and UV-vis. spectroscopies, transmission electron microscopy (TEM),
4 high-resolution TEM (HRTEM), Energy-Dispersive X-ray Spectroscopy (EDS), X-ray
5 Photoelectron Spectroscopy (XPS) and chromatography-mass spectrometry (GC-MS).
6 Bruker AC 300 MHz was used for the NMR spectra with all chemical shifts in parts per
7 million (δ , ppm) referring to TMS at room temperature. UV- vis. spectra were recorded
8 using a Perkin-Elmer Lambda 19 UV-vis. spectrometer. TEM images were recorded on
9 TEM JEOL JEM 1400 (120 kV) - 2100F. HRTEM images were recorded by Jéol JEM-
10 ARM200f -200 kV with a probe corrector, which was also equipped with a STEM HAADF
11 system (Scanning Transmission Electron Microscopy Hight Angle Annular Dark Field)
12 and energy-dispersive X-ray Spectroscopy (EDS) analysis system. XPS experiments were
13 performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source
14 (magnesium $K\alpha$ line of 1253.6 eV energy and 252 W)
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25 **2.4. Catalytic reactions**

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27 The catalytic hydrolysis of $B_2(OH)_4$ was carried out at 25 ± 1 °C. In a typical experiment,
28 0.1 % mmol Au-Rh NZ dissolved in 4 ml deionized water was placed in a 50-ml round
29 bottom flask with two outlets. Then, $B_2(OH)_4$ (1mmol, 90 mg) dissolved in 5 ml deionized
30 water was added under vigorous stirring. The measurement of the produced H_2 gas was
31 conducted in a typical water-filled gas burette. A 7-W visible LED lamp (Sunshine
32 Lighting Limited, France) with a light intensity of 1540 lx was used for the light irradiation.
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38 The temperature of the reaction was measured using an electronic thermometer.
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3. Results and discussions

3.1. Au-Rh NZ characterizations

The microstructure and size distribution of the metal NPs were investigated by TEM and high-resolution TEM (HRTEM). The as-prepared mono- and bimetallic NPs are homogeneously dispersed with a narrow small size distribution (Figure 2 and S2-S14). For Au₄Rh₁ NPs, a very fine diameter size distribution of 1.5 ± 0.4 nm is observed (Figure S4). This good confinement of the NPs is attributed to the stabilization effect of the intradendritic triazole ligands that coordinate to the gold and rhodium atoms. The intradendritic NPs make these nano-assemblies resemble metalloenzymes in their sizes, inner

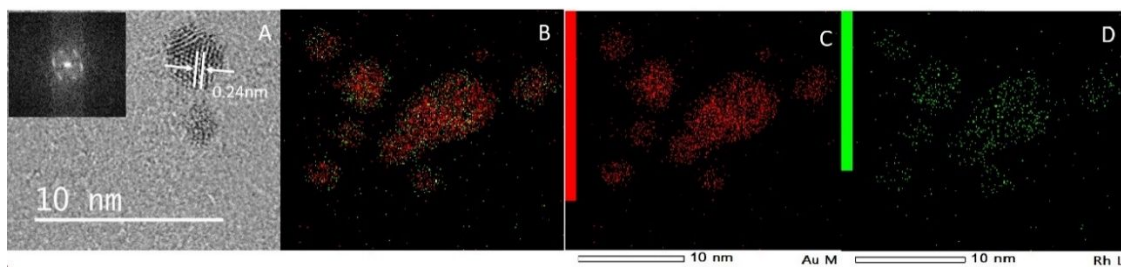


Figure 2. Transmission Electron Microscopy for Au₄Rh₁ NZs. HRTEM images; inset: corresponding Fast-Fourier transform (FFT) pattern (A). EDX elemental mapping images of the overlapped Au and Rh (B), and Au mapping (C) and Rh mapping (D)

catalytic site localization, transition-metal catalysts and hydrogenase-like function (*vide infra*, mechanistic section).^{3, 28} Figure 2A exhibits clear lattice fringes with a space of 0.24 nm, which confirms the crystallinity of the Au₄Rh₁ NPs. A diffraction pattern with six-fold rotational symmetry in the inset fast-Fourier transform pattern evidences the (111) facets of Au and Rh.³⁴ The element mapping of Au and Rh by EDS) (Figure 2B, 2C, 2D) shows the alloy structure of the Au₄Rh₁ NZ. The Au element is more concentrated in the core of the NPs, which is also evidenced by the distribution of Au and Rh along the cross-section (Figure S9).

In order to investigate the surface electronic structure, XPS was recorded for the dendritic and the Au-Rh alloy NZ parts. As shown in Figure 3, comparing to the binding energy of pure AuNPs (87.38 eV and 83.70 eV) and pure RhNPs (312.63 eV and 307.96 eV), the alloyed Au₄Rh₁NZs exhibits a small upshift of 0.14 and 0.16 eV for Au⁰ and a large upshift of 2.02 and 2.25 eV for Rh⁰. The XPS data show that the Au atoms are not

much perturbed upon alloying, whereas the Rh 3d orbitals are shifted to higher energy upon alloying Rh with Au, which means that the Rh atoms undergo some decrease of electron density in the Au-Rh alloy upon atom redistribution.^{35,36}

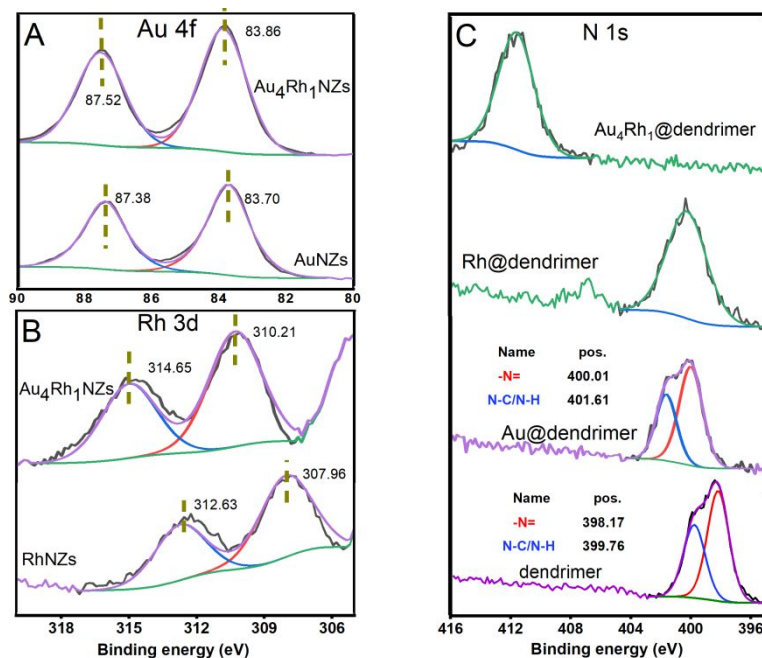


Figure 3. XPS patterns of the Au 4f (A), Rh 3d (B) for AuNZs, RhNZs, Au₄Rh₁NZs and N 1s for dendrimer, RhNPs@dendrimer, AuNPs@dendrimer and Au₄Rh₁NPs @dendrimer.

Let us now examine the shifts occurring for the dendritic triazole N 1s band upon dendrimer coordination to the alloyed metal atoms. The N 1s region of the dendrimer has two components centered at 398.17 and 399.76 eV that are assigned to -N=C- and -N-C/N-H of the triazole ligand in the dendrimer (Figure 3).^{37,38} After loading the metal NPs in the dendrimer, the N 1s bands shift towards higher binding energies, exhibiting peaks at 400.01 eV and 401.61 eV for the monometallic AuNPs, 400.27 eV for the monometallic RhNPs and 411.56 eV for the Au₄Rh₁NPs, which discloses significant electronic interactions between the NPs and the triazole ligand. The significance of the higher binding energy values in the NZ compared to the dendrimer alone is a decreased electron density on the dendritic N atoms upon coordination to the metals due to the N ligand electronic donation to these metal atoms.

Let us now consider the reduction by NaBH₄ of the two intra-dendritically coordinated metal cations to metal (0) NPs. Au³⁺ has a higher reduction potential than Rh³⁺ and, based on this consideration only, the Marcus theory region for exergonic electron transfer would

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3 dictate faster Au NP formation compared to Rh NP formation.³⁹ The coordination of
4 chlorides and heteroatom ligands of the dendrimer, including in particular triazoles,
5 changes the reduction potentials of the metal cations, however. Then, another factor that
6 affects the relative rates of formation of the two NPs is the nucleation kinetics. Altogether,
7 there is still a preference for the faster Au NP formation compared to the Rh NP formation,
8 and the result may then be either formation of an Au@Rh core-shell NP or an alloy with
9 an Au-enriched core. For instance, a related case was reported by Tsang's group with
10 Ag@Pd NPs that catalyzed H₂ production from formic acid.⁴⁰ From EDX data obtained
11 through the cross-section line element mapping (Figure S9 and S10), it is concluded that
12 the alloy structure preferably contains Rh atoms located at the periphery of these bimetallic
13 NPs and preferably Au atoms at the center. When the Au proportion is dominant, however,
14 the introduction of a small amount of Rh is envisioned to tune the electron distribution of
15 Au and Rh and generate defect sites at the surface of the Au-Rh NPs.³⁴
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26 **3.2. Volcano-type synergistic effects in Au-Rh nanozymes for B₂(OH)₄** 27 **hydrolysis** 28

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30 A series of “click” dendrimer-supported Au_xRh_y NPs with diverse Au and Rh
31 proportions (Rh mole content varying from 0 to 100%) were applied as NZs for the
32 hydrolysis of B₂(OH)₄ at 25 ± 1 °C. The time profile plots of H₂ evolution and TOF_s values
33 of Au-Rh nanozyme-catalyzed B₂(OH)₄ hydrolysis are presented in Figure 4. The catalytic
34 performance of H₂ evolution is determined by the reaction time at 10% B₂(OH)₄ conversion.
35 Thus, the TOF_s value here is defined as mole of generated H₂ divided by the total number
36 of surface atoms over the time span of 10% B₂(OH)₄ conversion.⁴¹ When 1 mmol B₂(OH)₄
37 is consumed, 1 equiv. H₂ is produced in B₂(OH)₄ hydrolysis (Equation (1)). The
38 monometallic Au and Rh NZs are valuable catalysts providing TOF_s values of 1500 and
39 570 mol_{H₂} mol_{cata}⁻¹ min⁻¹ (Table 1), respectively, which indicates that the Au NZ is more
40 active than Rh NZ. This result is opposite to those reported for NPs supported by graphene
41 quantum dots (GQDs) reported by Jang *et al.*, demonstrating a dramatic effect of the support
42 on the nanocatalysts.⁹ However, a dramatic rise of the TOF_s value was observed when Rh
43 was introduced to form Au-Rh NZs. As shown in Figure 4B, the alloyed Au-Rh NZs
44 displayed an enhanced catalytic activity compared to the monometallic counterparts, with
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a TOF_s value of $3700 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cata}}^{-1} \text{ min}^{-1}$ for Au_6Rh_1 , $5100 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cata}}^{-1} \text{ min}^{-1}$ for Au_4Rh_1 , $3200 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cata}}^{-1} \text{ min}^{-1}$ for Au_2Rh_1 , and $1900 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cata}}^{-1} \text{ min}^{-1}$ for Au_1Rh_2 , respectively (Table 1).

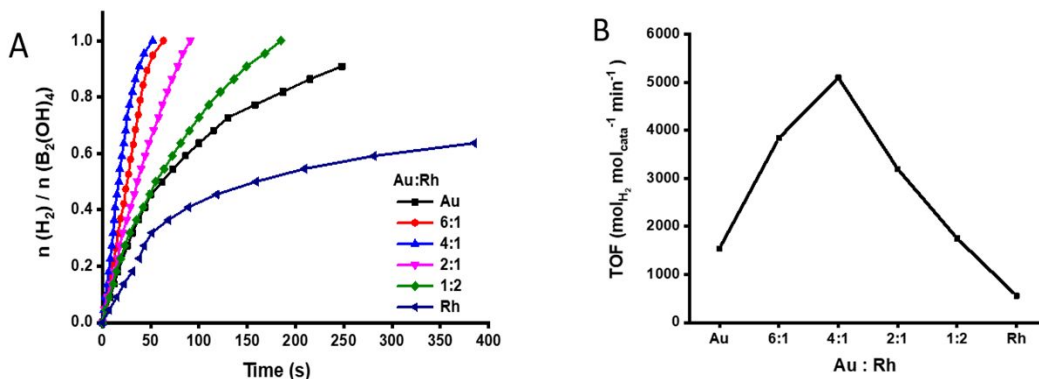


Figure 4. (A) Time profile plots of H_2 evolution and (B) TOF_s value of $\text{B}_2(\text{OH})_4$ hydrolysis catalyzed by 0.1 mol % Au-Rh NZs with different Au/Rh molar ratios in the dark at $25 \pm 1 \text{ }^\circ\text{C}$

Among all the NZs, Au_4Rh_1 NZ exhibited the highest enhancement with a 3.4-time higher TOF_s value compared to pristine Au NZ under the same conditions. All these results reveal an impressive volcano-type synergistic effect between the Au and Rh components. To verify the bimetallic synergy between Au and Rh, a mixture of 80% monometallic Au NZ and 20% monometallic Rh NZ was conducted for $\text{B}_2(\text{OH})_4$ hydrolysis, and the result (Figure S 17A) indicates that there is no additional efficiency upon physically blending these two monometallic NZs. Besides, the recyclability of the best Au_4Rh_1 NZ shows completion of quantitative hydrolysis during 4 cycles in dark, requiring progressively increased reaction time along these cycles, however (Figure 5A). There is slightly reduced efficiency of this NZ catalyst upon recycling. Catalytic AuRh NZ efficiency is demonstrated upon $\text{B}_2(\text{OH})_4$ hydrolysis in the absence of catalyst (Figure S20) at 25°C , 50°C and 90°C , which indicates that catalysis at 25°C even with Au_1Rh_2 NZ that shows the least synergy is faster than $\text{B}_2(\text{OH})_4$ hydrolysis alone at 90°C . It is known that the substrate adsorption and product desorption step impact the efficiency of the catalyst.^{34,42} When Au alloys with Rh, tuning the Au and Rh composition, Au_4Rh_1 NZ and Au_1Rh_2 NZ exhibit different Rh exposures of NP surfaces (Figure 2, Figure S8), which results in a diversity of active sites, and thus different catalytic performances. Additionally, electronic effects also

Table 1 TOF values of Au-Rh NZ catalysts with various molar ratios under dark and light conditions at 25 ± 1 °C unless noted otherwise.

catalyst	Au ₁ Rh ₀	Au ₆ Rh ₁	Au ₄ Rh ₁	Au ₂ Rh ₁	Au ₁ Rh ₂	Au ₁ Rh ₂	Au ₀ Rh ₁
						28±1 °C	
Time(s)-dark	248±5	63±2	52±2	91±2	185±2	153±2	385±8
TOF _i -dark	410±30	1200±80	1800±180	820±40	530±20	2000±200	132±4
TOF _s -dark	1500±100	3700±300	5100±400	3200±300	1900±300	5700±400	570±70
Time (s)-light	237±5	52±2	39±2	69±2	131±2	-	379±8
TOF _i -light	410±40	1300±150	2100±400	1100±100	735±50	-	134±4
TOF _s -light	1500±500	4000±300	6000±400	4300±300	2600±500	-	580±70
R _{atom} (nm)	0.135	0.135	0.135	0.135	0.135	-	0.135
R _L /R _D	1.0	1.1	1.2	1.3	1.4	-	1.0
Size(nm)	2.0±0.4	1.7±0.2	1.5±0.4	2.1 ±0.5	1.9±0.2	-	2.3±0.2

TOF_i = mol_{H₂} produced / [mol_{cat_i} × reaction time (min)], where mol_{cat_i} is the mole of the total atoms of the catalyst, calculated at 10% conversion of B₂(OH)₄ hydrolysis.

TOF_s = mol_{H₂} produced / [mol_{cat_s} × reaction time], where mol_{cat_s} the turnover mole of the surface atoms of the catalyst, calculated at 10% conversion of B₂(OH)₄ hydrolysis.

The unit of TOF_i and TOF_s is mol_{H₂} mol_{cat}⁻¹ min⁻¹. R_{atom} is the radius of the atom. N_s and N are the numbers of surface atoms and total atoms of the catalyst, respectively. R_L/R_D is the light enhancement rate.

impact the catalytic B₂(OH)₄ hydrolysis as indicated by the XPS data (Figure 3) involving Au and Rh in the alloyed Au₄Rh₁ NZs that exhibit an upshift of binding energy compared to the monometallic Au and Rh NZs.⁴²

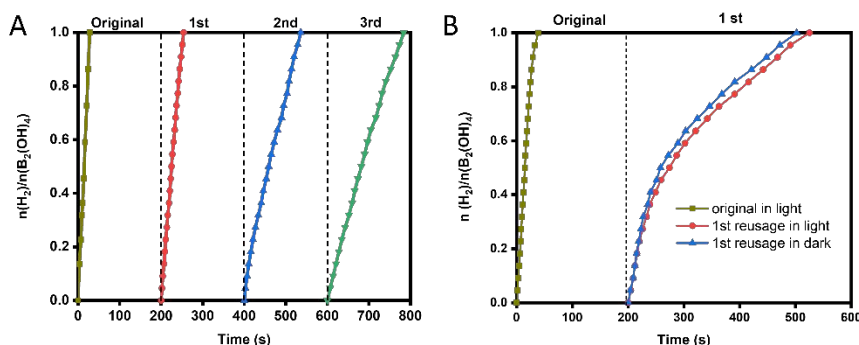


Figure 5. (A) Time plots of H₂ evolution for B₂(OH)₄ hydrolysis catalyzed by 1 mol % Au₄Rh₁NZ in the original, and 1st, 2nd and 3rd recycling tests in dark. (B) Time plots of H₂ evolution from B₂(OH)₄ hydrolysis catalyzed by 0.1 mol % Au₄Rh₁NZs under light (original) including 1st recycling under light and dark conditions. After photocatalysis, reused Au₄Rh₁NZs shows a TOF in dark or light of 1300 ± 200 mol_{H₂} mol_{cat}⁻¹ min⁻¹)

3.3. Photocatalytic $B_2(OH)_4$ hydrolysis by the Au-Rh NZs

In order to explore the photocatalytic activity of the Au-Rh NZs, a low-power white-light LED was used to irradiate the reaction medium. Such a low-intensity light should avoid the participation of a significant photothermal effect (*vide infra*). As shown in Figure 6 and S16, the alloyed Au-Rh NZ clearly exhibits light-accelerated H_2 production, whereas the catalytic activities of the monometallic Au NZ and Rh NZ do not show any observable light-induced enhancement (Figure S 19). Besides, the Au_4Rh_1 NZ possess the highest TOF_s value in both dark and light conditions, as a result of the cumulative effect of synergy in the dark and light-induced enhancement. In order to further investigate the efficiency of light irradiation, the light-enhancement rate (R_L / R_D) is introduced here, defined by simply dividing the TOF_s value of the catalyst under visible light (R_L) by that enhancement. The R_L / R_D value is 1.2 for the most effective nanocatalyst, Au_4Rh_1 NZ. Under dark conditions (R_D).⁴³

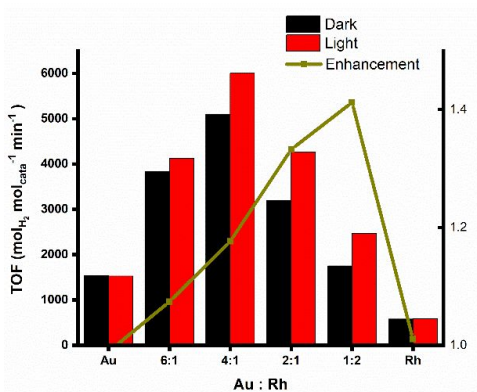


Figure 6. TOF_s value and enhancement rate (R_L/R_D) of $B_2(OH)_4$ hydrolysis photocatalyzed by 0.1 mol % Au-Rh NPs with various Au/Rh molar ratios at $25 \pm 1^\circ C$.

Many efforts have been devoted to the explanations of the photocatalysis mechanisms in the literature. For plasmonic metal NPs of Au and Ag, the surface plasmon resonance (SPR) effect is supposed to be the main factor responsible for the photocatalytic activity.^{22, 24-26} Besides, it has been suggested that the photothermal effect is also involved in the light enhancement.⁴⁴ As the Au_1Rh_2 NZ exhibited the highest light-induced enhancement (Figure 6 and Table 1), it was selected for photocatalytic investigations. In

order to search any photothermal effect, the temperature of the Au_1Rh_2 NZ catalyst was monitored during the light irradiation period. Specifically, the temperature change was recorded by a thermometer that was inserted in a sealed vial containing 4 ml catalyst under light illumination. The results (Figure S 17B) indicate that there is only 1.6 °C temperature increase during 10 minutes of visible-light illumination, which shows only modest heat generation under such light irradiation under these conditions. Aiming at this clarification, the catalytic reaction was carried out, when the reaction vial was covered by tin foil, but

still exposed to light illumination. In this case, the catalytic system was still influenced by the light-induced heating, but there was no visible-light available for SPR-related acceleration. The results shown in Figure S 18A reveal that there is no significant catalytic efficiency variation between dark and tin foil-covered situations. Although there is heat release under light irradiation, the heating scale is negligible, because the catalytic reaction finishes within 3 min for Au₁Rh₂ NZs, which can only cause ~0.5 °C temperature increase under this light irradiation (Figure S 17B). The time plot in Figure S16D shows that H₂ generation in dark at 28 °C is less efficient than that in light at 25 °C. Besides, the temperature change of the catalytic reaction in light underwent almost the same route as that under dark conditions (Figure S 18B). All these results reveal that the photothermal effect is only an extremely minor component, if any, of the reason for the light-induced acceleration.

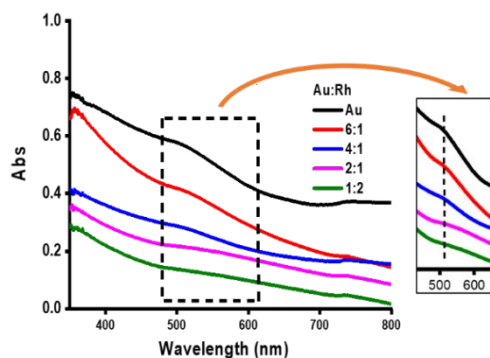


Figure 7. UV-vis. spectra of Au and Au-Rh NZs

On the other hand, the intrinsic plasmonic property of the prepared Au-Rh NPs is shown in Figure 7. Au NZ and Au-Rh NZ show a wide plasmon band around 500-540 nm, and the Au plasmonic absorption weakens as the percentage of Rh increases. This is ascribed to the shielding of the plasmon excitation of Au by Rh in the outer surface of the NP.^{45,46} Previous studies have demonstrated that the integration of a

plasmonic metal, such as Cu, Au, or Ag, and a catalytically active noble metal (e.g., Rh, Ru, Pd, or Pt) in a bimetallic system could be attributed to photocatalytic chemical transformations.²⁶ For instance, Ye et al reported a Rh-Au- SrTiO₃ photocatalyst for the synthesis of syngas using the CO₂ and H₂O under visible-light illumination.⁴⁷

In the presence of light, the coherent electron oscillation of plasmonic Au nonradiative dephase results in the generation of hot electron carriers owing to the SPR effect.²⁴ Subsequently, giving a lower work function of Au (4.45 eV) than that of Rh (5.0 eV),⁴⁸ the active hot electrons resulting from the SPR of Au are driven to migrate to Rh sites. This equilibrates the Fermi level of a Au/Rh alloy within a few fs, causing an electron transfer from Au to Rh. The resulting enrichment of the Rh site favors oxidative addition cleavage

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3 of a water O-H bond that is involved in the rate-determining step (*vide infra*). Therefore,
4 the catalytic efficiency of $B_2(OH)_4$ hydrolysis is enhanced under light illumination.⁴³
5 Besides, the recyclability of Au_1Rh_2 NZ after photocatalysis is investigated. As shown in
6 Figure 5B, after photocatalysis, reused Au_4Rh_1 NZs shows a TOF in dark and light of 1300
7 $\pm 200 \text{ mol}_{H_2} \text{ mol}_{cat}^{-1} \text{ min}^{-1}$). There is almost no light-induced enhancement after photocatalysis
8 for Au_1Rh_2 NZs, probably indicating an atomic rearrangement of Au and Rh in the alloy,⁴⁹
9 which need further investigation.

10
11 In order to verify the role of the SPR in photocatalysis, lights with wavelengths of 520
12 nm and 450 nm were employed to conduct catalytic $B_2(OH)_4$ hydrolysis. Photon fluxes at
13 different wavelength are calculated here for the analysis of photons on photocatalysis.⁵⁰
14 The result shown in Figure S24 indicates that 520 nm, which is near the SPR peak of Au/Rh
15 NZs, is more efficient than 450 nm irradiation as indicated by the TOF_s comparison. On
16 the other hand, photon flux, calculated following a standard ferrioxalate actinometry,⁵¹
17 reveals that 450 nm irradiation ($2.92 \times 10^{-9} \text{ einsteins} \cdot \text{s}^{-1}$) possesses a higher photon flux than
18 520 nm ($2.34 \times 10^{-9} \text{ einsteins} \cdot \text{s}^{-1}$). This result indicates that irradiation by more photons does
19 not necessarily lead to an increased efficiency, because it is selectively the light
20 corresponding to the surface plasmon band of Au/Rh NZs that provides enhanced catalytic
21 efficiency.⁵²

22
23 In conclusion, Au_4Rh_1 NZ is the best nanocatalyst for this reaction both in the dark and
24 under light illumination while Au_1Rh_2 NZs exhibit the highest light enhancement rate
25 among a series of Au-Rh NZs. This result indicates the great significance of the metal
26 proportions in an alloy and also demonstrates that Au is beneficial to this catalytic reaction
27 in two cumulative ways: volcano-type synergy in dark and plasmonic effect under light
28 illumination.

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3.4. Kinetic study

In order to gain in-depth understanding of $B_2(OH)_4$ hydrolysis catalyzed by the Au-Rh NZs, the kinetics with Au_4Rh_1 NZ, the best catalyst in term of TOF_s , was investigated for catalytic H_2 generation under various catalysts, $B_2(OH)_4$ concentration and temperatures.

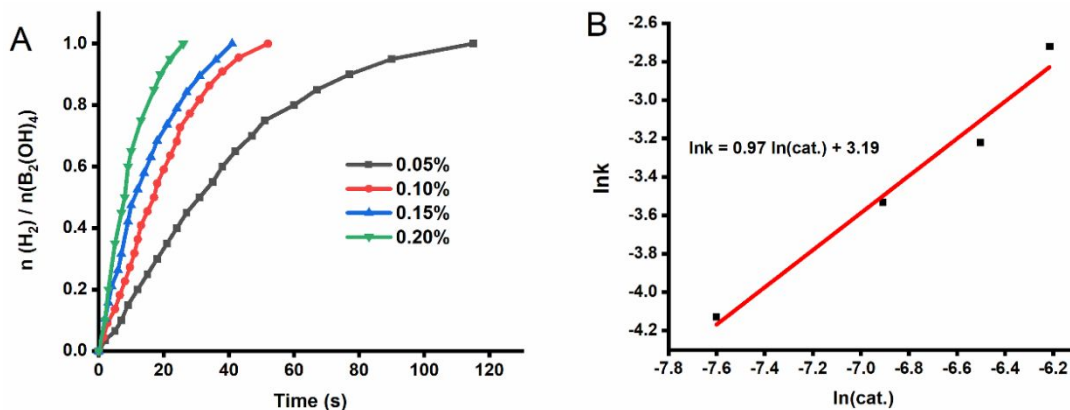


Figure 8. (A) Time plots of H₂ generation in the hydrolysis of B₂(OH)₄ catalyzed by various concentration of Au₄Rh₁ NZ catalyst in dark. (B) Plot of H₂ evolution rate vs. catalyst concentration ($R^2 = 0.96$).

Figure 8A shows the time plot of H₂ generation catalyzed by 0.05 mol %-0.2 mol % Au₄Rh₁ NZ at 25 ± 1 °C. The hydrogen evolution exhibited a linear increase with respect to reaction time in the initial period. Based on the slope of the fitted linear portions of the plots, all the reaction rate constants (k) were calculated, providing the plot of the logarithm of H₂ evolution vs. Au₄Rh₁ NZ concentration in Figure 8B. The slope of the logarithmic plot was 0.97, indicating that the B₂(OH)₄ hydrolysis reaction is first order with respect to the catalyst concentration.¹⁰

The time plot of H₂ evolution at different concentrations of B₂(OH)₄ is shown in Figure 9A. The slope of the logarithmic plot of H₂ evolution vs. B₂(OH)₄ amount in Figure 9B is 0.107, demonstrating that H₂ generation closely follows zero-order kinetics in B₂(OH)₄ amount.

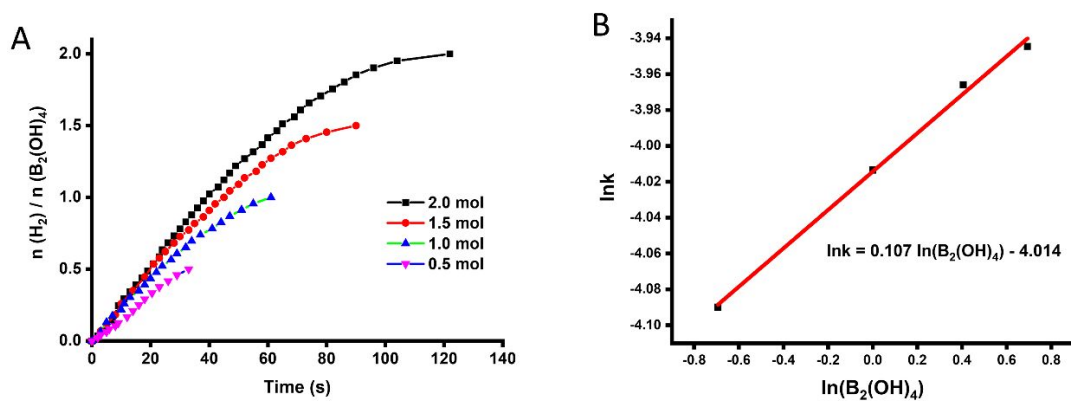


Figure 9. (A) Time plots of H₂ generation catalyzed by 0.1 mol % Au₄Rh₁ NZs with various B₂(OH)₄ amounts in the dark. (B) Plot of H₂ evolution rate vs. B₂(OH)₄ amount ($R^2 = 0.99$).

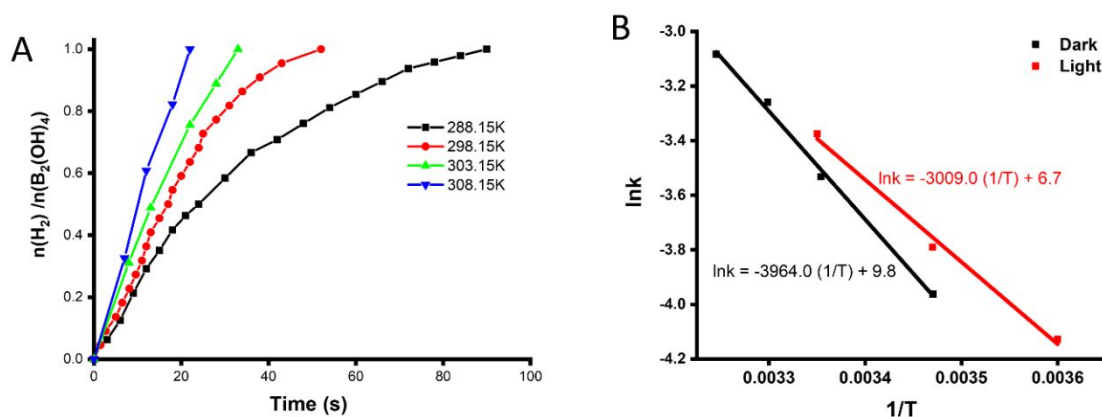


Figure 10. (A) Time plots of H₂ generation in the hydrolysis of B₂(OH)₄ catalyzed by 0.1 mol % Au₄Rh₁ NZs at various temperatures in the dark. (B) Arrhenius plots in the dark ($R^2 = 0.99$) and light ($R^2 = 0.98$) according to H₂ generation vs. time at different temperatures.

The time dependence of H₂ evolution catalyzed by 0.1 mol % Au₄Rh₁ NZ at different temperatures is illustrated in Figure 10A. As the reaction rate constant k is related to the activation energy (E_a) by the Arrhenius equation,³³ the Arrhenius plots of $\ln k$ vs. $1/T$ (Figure 10B) is depicted in accordance with the fitted linear parts of the plots in Figure 10A. The activation energy (E_a) is calculated to be 32.9 ± 1.4 kJ/mol in the dark and 25.0 ± 2.0 kJ/mol with visible light irradiation according to the Arrhenius equation (Equation S1). The reduced activation energy in light illumination may also be an indicator of the SPR-induced catalytic enhancement of H₂ evolution.

3.5. Mechanistic study

In order to confirm the hydrogen source of the produced H₂ gas, D₂O was used instead of H₂O as solvent in the hydrolysis of B₂(OH)₄ catalyzed by Au₄Rh₁. As shown in Figure 11, the catalysis in mixture dissolved in D₂O exhibits a lower slope in the time plot of H₂ generation, exhibiting a $k_{\text{H}}/k_{\text{D}}$ value of 2.52 in dark. This result indicates a kinetic isotope effect (KIE)¹¹ showing that the cleavage of an O-H bond in water is involved in the rate-determining step of the B₂(OH)₄ hydrolysis process. The low KIE value is the result of a concerted process involving the O-H oxidative addition. Besides, the $k_{\text{H}}/k_{\text{D}}$ value obtained upon light irradiation is 2.94 (Figure 11), higher than that in dark, which shows the increased role of O-H oxidative addition in the rate-limiting step compared to that upon reaction in the dark. This is in agreement with the electronic enrichment of the Rh site facilitating this O-H oxidative addition step.

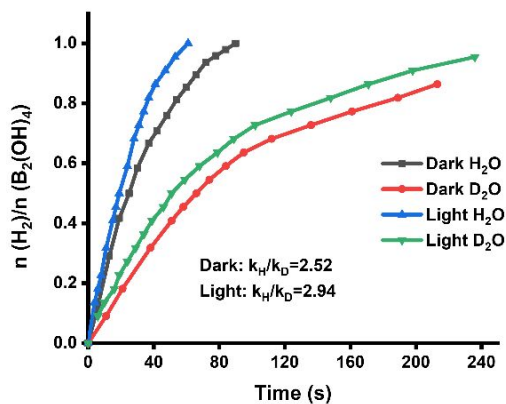


Figure 11. Time plot of hydrogen evolution catalyzed by 0.1 mol % Au₄Rh₁NPs in H₂O and D₂O in dark and light at 15 ± 1 °C.

Successive reactions, in which the hydrolysis of B₂(OH)₄ and the hydrogenation of styrene utilizing the H₂ gas produced in the former step, were conducted in the same system. These experiments were then carried out in order to investigate the fate of the deuterium atoms. D₂ gas evolution occurred upon hydrolysis of B₂(OH)₄ catalyzed by Au₄Rh₁ NZ in D₂O in the left tube, meanwhile this gas was directed to the right

tube to initiate the hydrogenation of styrene in CD₃OD in the presence of commercial Pd/C at room temperature (Figure S21). Hydrogenation of styrene occurs in methanol, while the nanocatalyst was in aqueous solution. The solid heterogeneous Pd/C hydrogenation catalyst was employed in the right tube. The product in the right tube was collected 24 h later, for analysis by ¹H NMR spectroscopy and gas chromatography–mass spectrometry. In the ¹H NMR spectra (Figure S22), a cluster of peaks at 7.11–7.28 ppm with 5-H integration reflects the existence of aromatic H atoms. No signals appear at 5–7 ppm, indicating 100% conversion of styrene to deuterated ethylbenzene. Compared to normal ethylbenzene, reduced integration values of the peaks at 2.6 and 1.22–1.17 ppm were observed, showing deuteration of ethylbenzene in the right tube. Besides, in the mass spectrum (Figure S23), there were three peaks at around 107, 108 and 109 m/z corresponding to substitution of one, two and three H atom by D atoms in deuterated ethylbenzene. The mass spectrum of deuterated ethylbenzene contains not only the peak corresponding to bis-deuterated ethylbenzene as expected, but also minor peaks corresponding to mono- and tris-deuterated ethylbenzene. The presence of these odd numbers of D atoms in the ethylbenzene product is due to the stability of the styryl radical intermediate Ph-CH·-CH₃ (or deuterated analogues) that can exchange H (or D) atoms with the Pd_n-H or Pd_n-D catalytic species, Pd_n-H species being formed by reaction of partly deuterated ethylbenzene with the Pd_n catalyst, and Pd-D by oxidative addition of D₂ on Pd_n (SI 3.4). The formula found is Ph-CH_{0.08}D_{1.92}-CH_{2.71}D_{0.29}, in which the total number of D atoms in the deuterated ethylbenzene obtained is 2.2 ± 0.2 for 2 D expected. Between

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3 B₂(OH)₄ and D₂O, fast H/D exchange occurs between these two oxo-acids, but D₂O is in
4 such a very large molar excess (450/1), so that the final proportion of H atoms in D₂ formed
5 is negligible.
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All these results confirm those obtained by direct alkene hydrogenation⁵ and verify that both hydrogen atoms of the produced hydrogen gas are originated from water. Accordingly, a mechanism of $B_2(OH)_4$ hydrolysis catalyzed by Au-Rh NZs is proposed

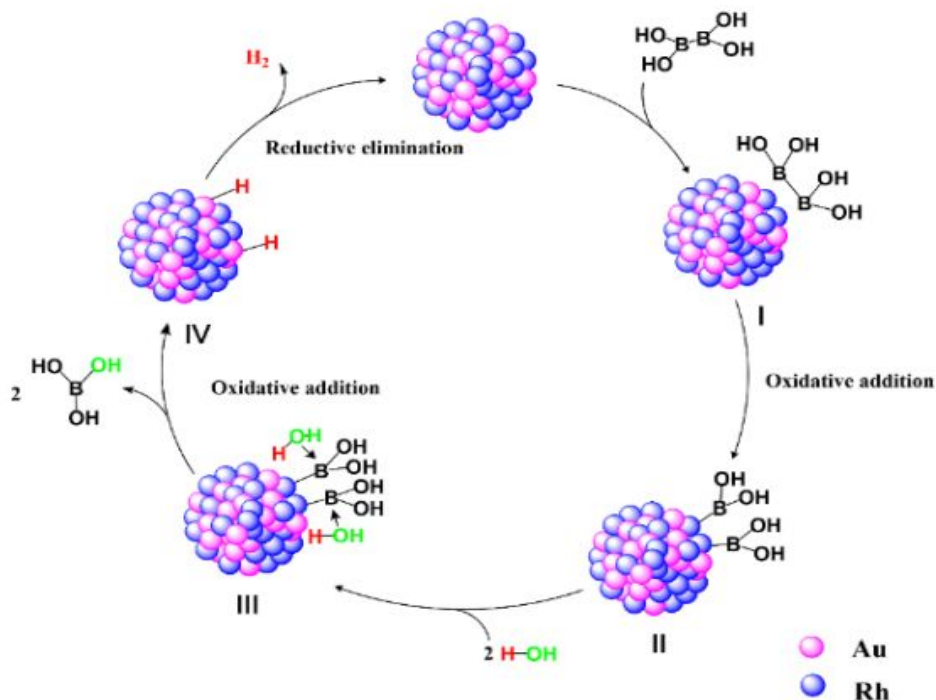


Figure 12. Schematic illustration of the confirmed mechanism of the $B_2(OH)_4$ dehydrogenation catalyzed by the nanozyme catalysts Au-RhNZ @click dendrimer.

here (Figure 12). In the first step of the catalytic cycle, $B_2(OH)_4$ is adsorbed onto the catalyst surface to give the intermediate **I**. Subsequently, the intermediate **II** is obtained following oxidative addition of the B-B bond onto the metal surface.^{5,9} Owing to the electron-deficiency of the Lewis-acidic B-containing species, two H_2O molecules obviously act as Lewis base to coordinate two boron atoms giving the intermediate **III**. At this point, the oxidative addition of an O-H bond of H_2O is facilitated by the initial H_2O coordination to the boron atoms bringing these O-H bonds close to the catalyst surface. The result is the formation of the two NP-H bonds, as shown by the D_2O experiments, and the release of 2 $B(OH)_3$ whose formation was demonstrated earlier,⁹ giving intermediate **IV**. Finally, the generated hydride-[M]-hydride intermediate **IV** produces H_2 upon reductive elimination.⁵³

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3 As indicated in the introduction, there are similarities between this mechanism and that
4 of hydrogenase including, first, the origin (water) of both atoms forming H₂. Then,
5 mechanistically, in hydrogenase, two water protons are successively transferred to
6 heteroatoms of the ligand bound to the metal site together with electrons, before their
7 transfer to the metal site, followed by reductive elimination to yield H₂. Here, the metal
8 site of the NZs is played by the bimetallic NP. The two water protons are transferred via
9 the two boron species before subsequent transfer to the NP, which is also followed by
10 reductive elimination like in the hydrogenase enzyme. These mechanistic features are in
11 sharp contrast with those involved in borohydride or ammonia-borane hydrolysis, whereby
12 first a hydride is transferred from the borane precursor followed by proton transfer from
13 water in the second step. The beneficial use of visible light for the NZs is compatible with
14 the same B₂(OH)₄ hydrolysis mechanism, just clearly accelerating the last step, reductive
15 elimination, by increasing the electron density on Rh through electronic donation upon
16 transfer from the plasmonic metal, Au.
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28 **4. Conclusion**

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30 A series of alloyed Au-Rh NP catalysts supported and encapsulated by a “click”
31 dendrimer (called nanozymes, NZs) were prepared, extensively characterized, then utilized
32 for H₂ production upon B₂(OH)₄ hydrolysis and convenient hydrogenation reactions with
33 produced H₂. These Au-Rh NZs with different molar ratios of the two metals in the alloys
34 were shown to exhibit different catalytic efficiencies, the optimized composition being
35 Au₄Rh₁ with sharp volcano-type synergies of 3.4-fold and 8.9-fold increased TOF_s,
36 compared to the monometallic Au and Rh NZs, respectively. The plasmonic Au-Rh NZs
37 also exhibit remarkable additional enhancement of catalytic activity under visible-light
38 illumination provoking what appears to be hot electron injection from plasmonic Au to Rh-
39 adsorbed substrates at the nearby Rh atom and giving the highest light enhancement rate
40 of 1.4 for Au₁Rh₂ NZ. Although the synergistic sharp volcano-type enhancement in the
41 dark and light-induced enhancements show their maxima for distinct proportions of the
42 two metals in the alloy, the two effects are cumulative, and the maximum combined
43 enhancement effect is obtained for the Au₄Rh₁ NZ. In the alloy, Au plays both roles of
44 most efficient partner in the synergistic volcano-type effect and source of plasmonic charge
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3 transfer, which explains why the percentage of the part of Au atoms among the two metals
4 is much larger than the Rh part in the optimized catalyst, Au₄Rh₁ NZ. Kinetic and isotopic
5 studies along with successive reactions confirm the mechanism of B₂(OH)₄ hydrolysis,
6 indicating that both hydrogen atoms of formed H₂ are coming from water (contrary to
7 ammonia borane), like with hydrogenase. This work illustrates a rational design of the
8 function of plasmonic metal in light-accelerated bimetallic photo-catalysis and a facile
9 strategy for H₂ (or D₂) evolution from H₂O (resp. D₂O) based on B₂(OH)₄ hydrolysis
10 together with application of H₂ (resp. D₂) formed.
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18 ASSOCIATED CONTENT

20 4.Supporting Information.

21
22 Materials and methods, nanomaterials characterizations, and kinetics and compared
23 performances of Au-Rh nanocatalyzed in B₂(OH)₄ hydrolysis.
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27 AUTHOR INFORMATION

29 5. Corresponding Author

30
31
32 **Didier Astruc** - ISM, UMR CNRS N° 5255, Univ. Bordeaux, 33405 Talence Cedex,
33 France; orcid.org/000-0001-6446-8751; E-mail: didier.astruc@u-bordeaux.fr
34
35

36 6. Authors

37
38 **Qiuxia Zhao**- LCC, CNRS & University of Toulouse III, 205 Route de Narbonne, 31077
39 Toulouse Cedex, France. ISM, UMR CNRS N° 5255, Univ. Bordeaux, 33405 Talence
40 Cedex, France; <https://orcid.org/0000-0002-5618-1379>; E-mail: zqx52028@gmail.com
41
42

43 **Naixin Kang**- ISM, UMR CNRS N° 5255, Univ. Bordeaux, 33405 Talence Cedex,
44 France; <https://orcid.org/0000-0001-8364-4343>; Email: knxcarnation@foxmail.com
45
46

47 **Marta Martinez Moro** - Soft Matter Nanotechnology Lab, CIC biomaGUNE,
48 Paseo Miramón 182. 20014. Donostia-San Sebastián, Gipuzkoa, Spain ;
49 <https://orcid.org/0000-0001-9380-9973>; E-mail : mmartinez@cicbiomagune.es
50
51

52 **Eduardo Guisasola Cal** - Soft Matter Nanotechnology Lab, CIC biomaGUNE,
53 Paseo Miramón 182. 20014. Donostia-San Sebastián, Gipuzkoa, Spain;
54 <https://orcid.org/0000-0002-2549-1745>
55
56
57
58
59
60

1
2
3 E-mail : eguisasola@cicbiomagune.es

4 **Sergio Moya** - Soft Matter Nanotechnology Lab, CIC biomaGUNE, Paseo Miramón 182.
5 20014. Donostia-San Sebastián, Gipuzkoa, Spain ; [https://orcid.org/0000-0002-7174-](https://orcid.org/0000-0002-7174-1960)
6 1960. Email : smoya@cicbiomagune.es

7
8 **Emerson Coy**- NanoBioMedical Centre, Adam Mickiewicz University in Poznań,
9 Wszechnicy Piastowskiej 3, 61-614 Poznań, Poland; [https://orcid.org/0000-0002-4149-](https://orcid.org/0000-0002-4149-9720)
10 9720.

11 E-mail : coyeme@amu.edu.pl

12 **Lionel Salmon**- LCC, CNRS & University of Toulouse III, 205 Route de Narbonne,
13 31077 Toulouse Cedex, France ; <https://orcid.org/0000-0002-8064-8960>. E-mail :
14 lionel.salmon@lcc-toulouse.fr

15 E-mail : lionel.salmon@lcc-toulouse.fr

16
17 **Xiang Liu**- College of Materials and Chemical Engineering, Key Laboratory of
18 Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges
19 University, Yichang 443002, Hubei, China; <https://orcid.org/0000-0002-0213-637X>; E-
20 mail : xiang.liu@ctgu.edu.cn

21 Notes

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