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Nanocatalosomes as Plasmonic Bilayer Shells with Interlayer Catalytic Hot Nanospaces for Solar-Light-Induced Reactions

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Abstract: Paramount interest and challenges remain in designing and synthesizing catalysts with nature-like complexities at few-nm scale to harness unprecedented functionalities by using sustainable solar light. We introduce "nanocatalosomes"— bio-inspired bilayer-vesicular design of nanoreactor with metallic bilayer hollow shell-in-shell structure, having numerous controllable confined cavities within fewnm interlayer space, customizable with different noble metals. The intershell-confined plasmonically-coupled hot-nanospaces within the few-nm cavities play pivotal role in harnessing synergistic catalytic effects for various important organic transformations, as demonstrated by 'acceptorless dehydrogenation', 'Suzuki-Miayura cross-coupling' and 'alkynyl-annulation' affording clean conversions and TOF at least one order of magnitude higher than state-of-the-art Au-nanorod-based plasmonic-catalysts. This work paves the way towards next-generation nanoreactors, craftable at few-nm scale to maximize their functionality and customizable to carry out diverse chemical transformations efficiently with green solar energy.

Introduction

In nature, bilayer-membrane-based hollow structures are prevalent as cellular vesicles, exosomes, carboxysomes, vacuoles, capsids and various organelles, where they not only maintain critical pH, ion/molecular-channeling and concentrations but also endow biocatalytic functionalities through the membranebound enzymes and polypetidic sub-nanometer (nm) confined spaces through directed compartmentalization and activation of the substrates.^[1-2] However, in the synthetic realm, it is immensely challenging to design and synthesize bio-inspired nextgeneration catalysts, which can assimilate kev intricate morphological features of natural systems at few-nm scale and functionally diversify to carry out various thermodynamically challenging and industrially useful chemical reactions, most preferably by harvesting sustainable natural solar light and thereby overcoming the fossil-fuel-based energy-intensive thermal conditions.^[3-6] Metal-based hollow nanostructures such as shells, capsules, boxes, rattles, yolk-shells, colloidosomes and others have drawn tremendous interest due to their unique optical, chemical and cargo-loading properties mainly emerging from high surface area, low density and confined quantum mechanical effect.^[7-16] So far, in these nano or microsized nanostructures, interior (hollow)/exteiror surfaces or intershell gaps can only be manipulated at several tens or hundreds nm-scale with no control over randomly emerging few/sub-nm cavities within the shell or intershell region which are critical for exploiting structuredependent physicochemical and catalytic properties.^[17-19] For example, the plasmonic metal-based nanostructures consisting of controllable few-nm ultra-narrow gaps, junctions and cavities, can dramatically augment the broad optical extinction and generate electromagnetic fields many orders higher than the isolated nanoparticle (NP) units, originated from the collective excitation and extensive multimodal plasmonic coupling; these nanoscale effects in turn result efficient generation of energetic charge-carriers and localized increase in photothermal temperatures, highly advantageous in promoting interfacial catalytic reactions.^[20-28] So far, it is elusive to achieve such controllable structural intricacy at few-nm scale in a single nanostructure, providing massive density of confined cavities for highly efficient plasmon-induced catalysis. In the present work, we introduce "nanocatalosomes (NCat)", similar to the nature's bilayer vesicular-design of plasmonic-catalytic nanoreactors, having metal-bilayer hollow shell-in-shell structure composed of arrays of closely gapped NP-units creating a fewnm interlayer catalytic space for organic reactions (Figure 1). The interlayer space of NCat is equipped with the massive number of plasmonic nanocavities (few-nm size) intimately interfaced with the choice of catalytic noble metals (Au/Pt/Pd). As a proof-ofconcept for the catalytic performance of NCat, acceptorless dehydrogenation (AD) reactions of N-heterocycles were tested. AD-reactions have enormous value as a key step in the synthesis of numerous pharmaceutical and bioactive heterocyclic scaffolds and to facilitate organic hydrides as hydrogen-storage materials for commercial fuel-cells. Previously, the benchmark two-step highly endothermic AD-reactions of tetrahydroquinolines (THQs) have been carried out with metal-based homogeneous catalysts which are rarely recyclable and air-sensitive, with heterogeneous

noble-metal NP based catalysts under unavoidable harsh

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Figure 1. Synthesis and applications of nanocatalosomes. (a) Schematic for the synthesis of metallic-bilayer nanocatalosomes with controllable interlayer few-nm cavities (right side), red shadows depicting change in interlayer cavity-structure. (b) Catalytic applications of different nanocatalosomes for different solar light-induced reactions.

conditions (temperature > 135 °C, reaction time >24 h) and requiring additional oxidizers, bases, and hydrogen-acceptors and also with few photocatalysts which are complicated to synthesize, requiring high furnace temperatures (~1250 °C) under toxic ammonia flow, have narrow light absorption profile and take long reaction hours with using high catalyst-amounts.[29-32] Impressively, Pt-Au-based NCat demonstrated very clean AD reaction (yield >99%) within short reaction time (~30 min) showing up to ~11 times increased turn over frequencies (TOFs) as compared to the state-of-the-art plasmonic-catalytic platforms [eg. Pt-gold nanorod (Pt-AuNR)] under ambient solar light irradiation (0.7 W/cm²) at constant 25 °C. In addition, Pd-Au-based NCat also performed highly useful and industrially important Suzuki-Miayura C-C cross-coupling reaction^[33-36] affording efficient and clean production of biaryl products (>99% yield, reaction time <15 min) with low Pd (0.01 mol%) and highest TOF (up to 17.5 s⁻¹) reported so far, which is an impressive ~20 times increase in TOF previously obtained from Pd-AuNR. Finally, Au-based NCat were also found to be highly active for [Au]-mediated alkyne-activationannulation reactions (conversion up to 99%, 30 min); such reactions were previously accomplished with only homogeneous Au(I/III)-based catalysts.[37-39] We rationalized the consistent high catalytic performance of NCat-structures in variety of reactions is due to the presence of abundant and controllable few-nm cavities in bilayer structure of NCat, where highly coupled plasmonic hotspots are well-overlapped with confined catalytic sites, exhibiting synergistically enhanced reaction rates.

Results and Discussion

Synthesis of Nanocatalosomes

We started the synthesis of NCat from hollow and porous aminated silica nanoshells (h-SiO₂, 75±3 nm diameter, ca. 10 nm thickness)[40] modified with Au-seeds (AuNC@h-SiO2) and coated with a thin conformal film (~3 nm) of TA-Fe coordination polymer using a modified reported chemistry (Figure S1).^[22] Next, the TA-Fe-coated AuNC@h-SiO2 were dispersed in aqueous solution of PVP (1 mL, 2%) followed by the addition of HAuCl₄ (900 µL, 5 mM) and hydroguinone (900 µL, 50 mM) leading to the growth of Au-seeds in to the homogeneously larger and closely spaced AuNP-units simultaneously, on the outer and inner surfaces of h-SiO₂-template (Figure 2a & Figure S2), resulting Aubilayer structures of NCat, designated as Au-1-NCat, Au-2-NCat, Au-3-NCat and Au-4-NCat, [collectively represented as Au-1~4-NCat] prepared from the increasing amounts (0.38, 0.6, 0.75 and 0.9 mL) of 5 mM HAuCl₄ (Figure S2 & Figure 2a). As shown in the transmission electron microscopy (TEM) image of Au-4-NCat (Figure 2a), the outer Au-layer grew slightly thicker (14±1 nm) than the inner Au-layer (11±1 nm), forming a structure collectively evolving as a hollow concentric metallic bilayer configuration, where each Au-layer is composed of arrays of closely spaced AuNP-units; and the interlayer space comprises massive

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Figure 2. Structural characterization of different nanocatalosomes. (a) TEM images of different metal bilayer nanocatalosomes [Au-4-NCat (*i*), Pt-NCat (*ii*), and Pd-NCat (*iii*)]. (b) TEM image (*i*), HRTEM images (*ii*), STEM, STEM-EDS elemental maps (*iii*) and EDS-elemental line profiling (*iv*) of Pt/Au-4-NCat. (c) TEM image (*i*), HRTEM images (*ii*), STEM and STEM-EDS elemental maps (*iii*) of Pd/Au-4-NCat.

number of few-nm cavities confined by AuNPs, which remain accessible through the narrow interparticle channels among the non-coalesced AuNP-units. In the plausible Au-growth mechanism, the TA-Fe nanofilm deassembles in the presence of HAuCl₄, due to the pH-dependent reversible Fe(III)-TA coordination chemistry and generates TA-oligomers having plenty of free catecholic moieties on the surface of **AuNC@h-SiO2**;^[22] followed by the directed approach of Au³⁺ towards outer and inner Au-seeds permeating through microporous aminosilica-layer (Figure 1a).^[40] Replacing hydroquinone with other reducing agents didn't result the desired Au-bilayer structure (Figure S3).

When Au-bilayer synthesis was attempted starting from thicker h-SiO₂ (*ca.* 15 nm) template (Figure S4), closely located (<1 nm gap size) AuNP-units (individual unit size *ca.* 8 nm) were grown throughout the silica volume, resulting a multilayered arrangement (designated as **Au-M-NCat**). The strategy was also applied to synthesize bilayer structures of other noble metals such as Pt and Pd (namely, **Pt-NCat** and **Pd-NCat**), by replacing HAuCl₄ with Na₂PtCl₄ and Na₂PdCl₄, respectively, (Figure 2b). For the diverse catalytic applications, plasmonic bilayer structure of **Au-4-NCat** was functionalized with different catalytic metals (Pt and Pd) by reducing Na₂PtCl₄ (5 mM) and Na₂PdCl₄ (5 mM),

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Figure 3. Structure-dependent plasmonic properties of nanocatalosomes. (a) TEM images of Pt/Au-1~4-NCat prepared from increasing amounts of metal precursors (i-iv, left to right). (b) UV-vis spectra of Pt/Au-1~4-NCat. (c) Representative SERS spectra (i) with average C-S (ii) and C-C (iii) Raman peaks intensities of 4-aminothiophenol (4-ATP)-modified Au-1~4-NCat, recorded at 10 different spots of the sample in each case. (d) Raman thermometry experiments: SERS Stokes peak intentistiy (Is) and anti-Stokes peak intensity (IAS) of C-S peak in 4-ATP modified Au-1~4-NCat (i) and corresponding temperatures estimated from the populations of their respective vibrational states given by the Boltzmann distribution (ii), Is and IAS were recorded at 10 different spots of the sample in each case.

respectively with ethylene glycol at 70 °C, leading to the bimetallic bilayer structures, namely, Pt/Au-4-NCat and Pd/Au-4-NCat respectively (Figure 2b-c); which were characterized by highangle annular dark-field scanning TEM (HAADF-STEM), energydispersive X-ray scattering (EDS) elemental mapping, lineprofiling and X-ray photoelectron spectroscopy (XPS) (Figure 2bc, Figure S5-6). Detailed HRTEM-based investigation revealed the granular Pt- and thin layered Pd-metallic species were coated onto plasmonic AuNP-units in both outer and inner layers, maintaining the consistent interparticle nanogaps among adjacent AuNP-units and intershell nanospaces; notably, plenty of three dimensional nanocavities were constructed within the hollow shell-in-shell arrangement (Figure S7-8). Our synthetic strategy allowed to finely modulate the size and spatial configurations of plasmonic (Au)-components depending on the amounts of metal precursors used in the synthesis for example, using lesser amounts of HAuCl₄ resulted in smaller AuNPs having larger interparticle separations and wider spaces between inner and outer layers and the difference between the thicknesses of outer and inner layers grew larger upon successively using higher amounts of Au³⁺ (Figure 3a for Pt/Au-1~4-NCat and Figure 2c & S6 for Pd/Au-1~4-NCat, controlling Pt/Pd : Au = 20 : 80 as estimated by ICP). The thickness of outer and inner Au-layers, interparticle distances among AuNP-units and thereby, the size and geometries of interlayer nanocavities, can be finely tuned; such structural modulation is crucial for tuning and optimizing the plasmonic coupling and geometries of 'hot-spots' which would have tremendous influence on the optical, thermoplasmonic and catalytic properties of different structures.

Plasmonic Properties of Nanocatalosomes

As shown in Figure 3b, as the size of AuNP-units successively increased in different Pt/Au-1~4-NCat structures, the enhancement in optical absorption and significant broadening of UV-vis spectra from visible to NIR region were observed which were due to the extensive plasmonic coupling effect when interparticle nanogaps among AuNP-units became ultranarrow

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Figure 4. Catalytic performance of nanocatalosome for acceptorless dehydrogenation reaction. (a) Comparison of the performance of **Pt/Au-4-NCat** with previously reported catalysts. (b) Schematic for [**Pt**]-catalyzed dehydrogenation of THQ and conversion yields at different reaction times using **Pt/Au-1~4-NCat**. (c) Conversion yields at different reaction times of dehydrogenation of THQ using **Pt/Au-4-NCat** after repetitively switching on and off the light source (Xe lamp, 1 W/cm²). (d) Low (up) and high magnification (down) TEM images of Au-monolayer shell (**s-Pt/Au-Ncat**), used as the control catalyst. (e) TOF(h⁻¹) for dehydrogenation of THQ using **Pt/Au-Ncat**. (f) Substrate scope with TOF(h⁻¹) and product yields of dehydrogenation reaction using **Pt/Au-4-NCat**. The error bars in (b), (e) and (f) show the standard deviations obtained from three repetitive experiments.

(~1 nm) and confined cavities were extensively formed within the intershell nanospaces.^[41] Pt/Au-1~4-NCat also harnessed high

photothermal conversion efficiencies with solar light (300 W Xe lamp, 1W/cm²) and the photothermal temperature was well

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Figure 5. Catalytic performance of nanocatalosome for Suzuki-Miayura cross-coupling reaction. (a) Schematic for [Pd]-catalyzed cross-coupling of aryl halides with aryl boronic acids. (b) Conversion yields for cross-coupling of iodobenzene with phenyl boronic acid at different reaction times using **Pd/Au-1~4-NCat**. (c) TOF(s⁻¹) for cross-coupling of iodobenzene with phenyl boronic acid using different catalysts. (d) Substrate scope with TOF(s⁻¹) Suzuki-Miayura cross-coupling reactions using **Pd/Au-4-NCat**. The error bars in (b) and (c) show the standard deviations obtained from three repetitive experiments.

controllable with the structures and concentrations of different NCat: in the case of Pt/Au-4-NCat, the temperature rose highest (~90 °C) among different structures of Pt/Au-1~4-NCat at the NP concentration 0.5 mg/mL within 6 min of light exposure; whereas solution temperature can be maintained close to ambient (~ 28 °C) by decreasing the NP concentration to 0.05 mg/mL under identical solar flux (Figure S9). Notably, the plasmonic UV-vis absorptions and photothermal conversions didn't show any significant change among Pt/Au-4-NCat, Pd/Au-4-NCat and Au-4-NCat, signifying the minimal influence of catalytic components (Pt/Pd) on the optical and thermoplasmonic properties (Figure S9). As the bulk-solution photothermal temperatures originate exclusively from the NP-surface-bound plasmonic effects, it can be deduced that M/Au-4-NCat (M=Pt,Pd) would have highest local temperature. In order to validate the presence of electromagnetic hot-spots, surface-enhanced Raman scattering (SERS) spectra of 4-aminothiophenol (4-ATP, Raman reporter)modified on Au-1~4-NCat (via facile Au-S bonding) were recorded for different structures: as shown in Figure 3c, SERS signals intensities at 1072 cm⁻¹ (C-S stretching) and 1572 cm⁻¹ (C-C stretching) dramatically increased (ca. 34 times than AuNC@hSiO₂) in the case of Au-4-NCat, where the narrowest plasmonic nanocavities were formed in the bilayer which generate maximum number of highly coupled electromagnetic hot-spots.^[41] Further, to estimate exact photothermal local temperature on different Au-1~4-NCat, previously reported Raman thermometry method was used, which is based on the stokes and anti-stokes SERS peakproportional intensities, to the temperature-dependent populations of vibrational states in Boltzmann distribution (details in SI): the estimated local temperature was found to be as high as ca. 180 °C in the case of Au-4-NCat (Figure 3d).^[42] We have also performed electromagnetic field (EF)-simulation on the simplified 2D-models of Au-1~4-NCat through finite-difference time-domain (FDTD) method to verify the EF concentration and the enhancement mainly occur at interlayer cavities and close junctions of adjacent Au-units in Au-4-Ncat with minimal effect of overall nanostructure size increase (Figure S10). In addition, the plasmonic properties of Pt/Au-1~4-Ncat and Pd/Au-1~4-Ncat are mainly contributed by the parent Au-component (Au-1~4-Ncat) due to the much higher plasmonic response and relative amounts of Au as compared to the Pt/Pd. After synthesizing diverse NCat with controllable structures, composition and

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Figure 6. Catalytic performance of nanocatalosome for alkynyl annulation reaction. (a) Schematic for [Au]-catalyzed alkynyl annulation of different phenolic esters of phenylpropiolic acids. (b) Conversion yields for alkynyl annulation of 6(i) at different reaction times using **Au-1~4-NCat**. (c) Substrate scope with conversion yields for alkynyl annulation reactions using **Au-4-NCat**. The error bars in (b) show the standard deviations obtained from three repetitive experiments.

optical/plasmonic properties and establishing the presence of highly coupled electromagnetic and thermal hot-spots in the bilayer structure, stage was set to test them for potential catalytic applications.

Catalytic Properties of Nanocatalosomes

First, we subjected Pt/Au-1~4-NCat for accomplishing highly important and challenging dehydrogenation reactions of Nheterocycles under solar light as the only energy source with no other additive (Figure 4); such reactions have been previously conducted under high temperatures (>135 °C), long reaction times (>24 h) and use of additional oxidizers, bases, and hydrogen-acceptors and difficult to synthesize photocatalysts (Figure 4a).^[29-32] We chose the conversion of 1,2,3,4tetrahydroquinoline (THQ) as a model substrate for investigating catalytic AD reaction in the presence of Pt/Au-1~4-NCat (0.5 mol% Pt) and solar light (300 W Xe lamp, 0.7 W/cm²) and the reaction was monitored by the time-course yield measurement of the product quinoline by ¹H NMR (Figure 4b). With Pt/Au-4-NCat, the product guinoline started forming within the 5 min and the yield reached >99% within 30 min (TOF_{Pt} = 430 h⁻¹) at the bulk reaction temperature 25 °C. The temperature of bulk reaction solution did not rise significantly due to the highly localized phothothermal effect in the confined bilayer structure of NCat. Whereas, in the absence of solar light, no formation of guinoline was detected up to 2 h, however, 92% yield of quinoline could be obtained upon increasing the bulk solution temperature to 180 °C by an oil bath for 12 h (Figure S11). Under identical reaction conditions, Pt/Au-1~3-NCat with fewer and wider interlayer cavities and plasmonic gaps, affected much slower reactions, affording 10%, 17% and 48% yields, respectively, suggesting that structure of NCat has significant influence on their catalytic performance (Figure 4b); also, Au-4-NCat (having no Pt) could only show moderate catalytic activity affording ca. 30% yield of quinoline, signifying crucial role of Pt as the catalytic component (Figure S12). When a single reaction using Pt/Au-4-NCat was monitored with light on/off sequence over a time-course: smooth transformation of THQ into quinoline was observed under solar-irradiation lapse (Figure 4c), but the transformation stopped when the light was turned off; this result suggested that the reaction can only be proceeded with continuous plasmonic excitation. For deconvoluting the effect of plasmonic component of Pt/Au-4-NCat on the catalytic efficacy, Pt-NCat (Pt-bilayer with no Aucomponent) was tested for dehydrogenation of THQ under solar light which afforded only <5% yield (TOF_{Pt} < 10 h^{-1}), suggesting the critical function of plasmonic component in high performance of Pt/Au-4-NCat under solar light. In order to further verify the effect of metallic bilayer structure and thereby interlayer plasmonic-catalytic nanocavities, we synthesized a surrogate

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nanocatalyst having only monolayer shell composed of noncoalesced Pt-modified-AuNP-units around silica nanosphere (Figure 4d), creating a nanostructure compositionally similar to Pt/Au-4-NCat except the absence of internal Au-Pt layer (designated as s-Pt/Au-NCat); it could only afford 25% yield of THQ to quionline (TOF = 65 h^{-1}), performing much inferior to the Pt/Au-4-NCat having bilayer structure (Figure 4e). Notably, TOF_{Pt} (h-1) of Pt/Au-4-NCat was found to be impressively ~11 times higher than Pt-AuNR,^[43] a conventional plasmonic catalyst under identical reaction conditions, indicating a huge advantage of bilayer-confined plasmonic-catalytic structure of NCat over isolated plasmonic NP-based catalyst. Also, compared to the previously reported photocatalyst h-BCN for AD reaction (83% conversion in 12 h using 10 mg of catalyst for 0.3 mmol of substrate), Pt/Au-4-NCat shows much faster reaction (>99% conversion, 30 min using 0.5 mol% [Pt] for 0.11 mmol substrate).[31] In another experiment, solar light activated Pt/Au-4-NCat showed ~35 times higher TOF (at bulk reaction temperature 25 °C) as compared to the thermally activated commercial Pt/C (at bulk reaction temperature 120 °C), signifying the huge advantage of solar-light induced Pt/Au-4-NCat (Figure 4e). After reaction, Pt/Au-4-NCat can be easily recovered by centrifugation (10,000 rpm, 5 min) and reused for fresh reaction with minimal loss in activity, showing overall ~13% loss in TOF after 5 cycles, still accomplishing >99% conversion; on the other hand, the product yield using Pt-AuNR catalyst after only first use dropped by ~90% in the second cycle (Figure S13-14). As represented in Figure 4f, Pt/Au-4-NCat converted range of Nheterocycles to the corresponding dehydrogenated products with excellent yields and TOFs, except the substrate with bulky size 1ix, which didn't show any detectable dehydrogenated product 2-ix even after 6 h of the reaction; such noticeable specific nonreactivity indicated the possible restricted approach of such a bulky substrate towards the reactive intershell cavities. Also, Ocontaining heterocycles (such as tetrahydrobenzofuran, 1-viii) were unreactive to the dehydrogenation using Pt/Au-4-NCat, such inertness is due to the lack of Lewis basic nitrogen, which is crucial for noble-metal-mediated dehydrogenation step.[44] The high catalytic performance of Pt/Au-4-NCat can be rationalized as follows: in the unique and robust composite bilayer structure of Pt/Au-4-NCat, closely spaced Pt-modified AuNP-units at the inner and outer layers encompass high numbers of plasmoniccatalytic nanocavities within the interlayer region which not only provide plenty of few-nm confined catalytically reactive sites but also endow highly coupled plasmonic hot-spots in the direct contact of interfacial catalytic sites which can harness enormous electromagnetic fields and generate localized photothermal effect and hot charge-carriers,[20] efficiently harvested during [Pt/Au]mediated elimination of H₂ from N-heterocycles within the confined bilayer-nanospace; these structural features have synergistic influence on the overall catalytic performance of Pt/Au-4-NCat. We also performed the dehydrogenation of THQ with Pt/Au-4-NCat under two monochromatic sources, NIR laser (785 nm, 0.7 W/cm²) and green laser (514 nm, 0.7 W/cm²): under green laser irradiation, conversion yields were found to be lower (ca. 46%) than NIR laser irradiation (ca. 95%), possibly due to the lower absorbance of Pt/Au-4-NCat at 514 nm as compared to the absorbance at 785 nm. Such dependence of conversion yields on excitation wavelengths clearly validates that the reactions are driven by surface plasmon resonance (SPR)-based mechanism (Figure S15). Notably, the interlayer confined space is most

crucial structural feature in the design of **NCat**, as corroborated from the results: i) structure-dependent catalytic performance of **Pt/Au-1~4-NCat**, where **Pt/Au-4-NCat** is most reactive having extensive confined plasmonic-catalytic nanocavities within bilayer space; ii) inferior performance of monolayer shell (**s-Pt/Au-NCat**), where interlayer space is absent and iii) non-reactivity of bulkysize substrates which can't approach the confined cavities present in bilayer structure of **Pt/Au-4-NCat**.

Next, the application scope of NCat was further extended towards industrially important and extensively applied Suzuki-Miyaura cross-coupling reactions of aryl halides and boronic acids resulting biaryls using Pd/Au-1~4-NCat; previously, such reactions have been demonstrated under plasmon-induced conditions using simple Pd-AuNR and Pd-AuNP based catalysts.^[33-35] As a test reaction between phenyl boronic acid and iodobenzene, Pd/Au-4-NCat (0.01 mol% Pd) afforded clean conversion to biaryl product in quantitative yield (TOF = $\sim 18 \text{ s}^{-1}$) upon solar light irradiation (300 W Xe lamp, 0.7 W/cm²) with keeping the bulk reaction temperature at 25 °C; whereas, the conversion yield dropped to ~6% under dark-conditions (Figure 5a-b). Under identical reaction conditions, the control catalysts **Pd-NCat** (Pd-bilayer with no Au-component, TOF = 0.9 s^{-1}), physical mixture of Pd-NCat and Au-4-NCat (TOF = 1.2 s⁻¹) and Pd-AuNR (TOF = 2.1 s⁻¹), performed much inferior to Pd/Au-4-**NCat** (TOF = \sim 18 s⁻¹) (Figure 5c). Also, the TOF (s⁻¹) was found to be linearly dependent on the light intensity (Figure S16-17), signifying the characteristic plasmon-induced catalysis. As shown in Figure 5d, Pd/Au-4-NCat (0.01 mol% Pd) afforded clean conversion of broad range of aryl halides and boronic acids to the corresponding biaryl products in quantitative yields within short reaction times upon solar light irradiation (300 W Xe lamp, 0.7 W/cm²). To the best of our knowledge, among so far reported Pdcatalyzed cross-coupling reactions, we achieved TOF (up to 18 s⁻ ¹) which is ~20 times higher than previously reported Pd-AuNR and best among so far reported Pd-based catalysts.[33-36] In the metal-bilayer design, plethora of few-nm plasmonic-catalytic interlayer cavities play key role in the high reactivity of Pd/Au-4-NCat, where localized photothermal effect and abundant hotelectrons produced in the highly coupled electromagnetic hotspots can be efficiently harnessed for promoting [Pd]-catalyzed dissociation of C-I bond in aryl halide, which is elemental step in overall cross-coupling reaction.[35] Also, Au-4-NCat (having no Pd) didn't result any cross-coupled product, validating that the cross-coupling reaction undergoes via [Pd]-catalyzed pathway (Figure S18).

Au-based catalysts have special place in organic synthesis due their selective affinity towards coordination with alkyne-group in the presence of other functional groups, resulting a number of unique molecular transformations useful in pharmaceutical synthesis and biorthogonal chemistry;[37-39] however, most of these alkyne-activation-based chemistries are only possible with non-recyclable homogeneous Au(I/III)-complexes with only very few examples of AuNP-based recyclable green catalysts showing low reactivity.^[45] With the use of metal-bilayer structure of Au-1~4-NCat and by harnessing the interlayer plasmonic-catalytic nanocavities for catalysis, we envisioned to compensate the low reactivity of [Au]-catalyzed alkyne-activation. We chose the reaction of different phenolic esters of phenylpropiolic acid 6(i-iv), which undergo annulation via [Au]-pi-acidic coordination with alkyne-moiety followed by intramolecular Michael-type C-C bond formation with aryl moiety of phenolic-part, affording 7(i-iv) in good

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to excellent yields under solar light irradiation (300 W Xe lamp, 0.7 W/cm²) (Figure 6). Reaction rates depended on the different structures of Au-1~4-NCat, showing highest reactivity in the case of Au-4-NCat and similar to the Au-multilayer NCat (Au-M-NCat), validating the influence of bilayer/multilayer-confined plasmonic effect on reaction rates (Figure 6b and Figure S19). In the bilayer structure of nanocatalosomes, closely located plasmonic units with narrow interparticle gaps and cavities can form extensively coupled plasmonic hot-spots which can concentrate high electromagnetic fields and other plasmon-induced effects such as: instantaneous production/transfer of hot charge-carriers and their equilibration with lattice through an electron-phonon coupling resulting the photothermal increase in localized temperature;[46-47] all these factors together are responsible for solar-light induced high catalytic activities of nanocatalosomes. In order to investigate the individual role of photothermal effect, we tested the folding/unfolding of proteins in the presence of Au-4-NCat under light irradiation. Under controlled conditions, such protein denaturation can only be affected upon exposure to high temperatures; monitoring of this phenomenon can evidence the localized photothermal effect on Au-4-NCat.[48] In a mixture of bovine serum albumin (BSA) and Au-4-NCat, the intensity of characteristic fluorescence band at 300-500 nm reduced up to ca. 37% upon exposing to the NIR laser (785 nm, 0.7 W/cm²) for 25 min (Figure S20). Next, to further evidence the surface-mediated energy transfer processes involving the plasmonic hot charge carriers, we studied the conversion of normal oxygen $({}^{3}O_{2})$ to singlet oxygen (¹O₂).^[49] For testing the presence of ¹O₂ in the O₂saturated solution of Au-4-NCat after exposure of NIR laser (785 nm, 0.7 W/cm²), we used fluorescence-based singlet oxygen assay (SOSG Assay): the production of ¹O₂ gradually increases with the amounts of Au-4-NCat and the light exposure time (Figure S21), clearly evidencing the plasmon-induced conversion of ${}^{3}O_{2}$ to ${}^{1}O_{2}$.

Conclusion

Inspired from the nature's favorite bilayer-membrane-based vesicular structures, we have designed and synthesized metalbilayer-based hollow-nanostructures: "nanocatalosomes", as a new class of highly customizable and catalytically diverse nanoreactors having controllable bilayer-space. In diverse plasmonic-catalytic nanocatalosomes, bilayer shell having plenty of few-nm nanogaps/cavities within intershell nanospace is the key structural feature which endow controllable plasmonic coupling effect, and efficiently harness broad range of solar light to generate localized photothermal heating and plasmonic charge-carriers, highly useful for variety of catalytic reactions. By implementing suitably customized nanocatalosomes, challenging acceptorless dehydrogenation reactions of N-heterocycles were accomplished with unprecedented rates and TOF (h-1) up to ~11 times higher than conventional Pt-AuNR plasmonic catalyst, under low power solar irradiation; otherwise, such reactions with conventional catalysts take very long times (> 24 h) and energyintensive harsh thermal conditions (temperatures up to 150 °C). Diverse functional customization scope of nanocatalosomes was also demonstrated by performing extensively applied and industrially important Suzuki-Maiyura C-C cross-coupling (TOF up to ~18 s⁻¹) and alkynyl annulation reactions with good to excellent yields in maximum recorded TOFs, reported so far. Such diversely active nanocatalosomes show substantially distinguished and consistently high catalytic performance than the reported NP-based catalysts owing to the unique bilayer structure. By this work, we have opened the avenues towards advanced next-generation metallic-bilayer-based nanoreactors and extended the scope of their structural and functional tunability by including controllable intricacies at few-nm scale. By expanding the utility of solar energy in fueling the nanocatalosomes, this research will add enormous value to the sustainable development of the highly functional catalytic chemistry.

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Keywords: nanocatalyst • hollow nanostructure • bilayer structure • plasmonic-catalytic material • nano-space confinement

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Entry for the Table of Contents



"Nanocatalosome" — a bio-inspired bilayer-vesicular design of nanoreactors with hollow metallic-bilayer shells where few-nm intershell nanospace can be controlled and customized with different noble metals to generate numerous interlayer-confined catalytically active cavities harnessing synergistic plasmonic-catalytic effects and performing highly efficient solar light induced organic reactions with unprecedented rates.