Plasmonic metal-organic frameworks

Guangchao Zheng1 | Isabel Pastoriza-Santos2,3 | Jorge Pérez-Juste2,3 | Luis M. Liz-Marzán4,5,6

1School of Physics and Microelectronics, Key Laboratory of Material Physics, Ministry of Education, Zhengzhou University, Zhengzhou, China
2CINBIO, Universidade de Vigo, Departamento de Química Física, Vigo, Spain
3Galicia Sur Health Research Institute (IIS Galicia Sur), SERGAS-UVIGO, Vigo, Spain
4CIC biomaGUNE, Basque Research and Technology Alliance (BRTA), Donostia-San Sebastian, Spain
5Ikerbasque, Basque Foundation for Science, Bilbao, Spain
6Centro de Investigación Biomédica en Red, Bioingeniería, Biomateriales y Nanomedicina, CIBER-BBN, Donostia-San Sebastián, Spain

Correspondence
Luis M. Liz-Marzán, CIC biomaGUNE, Basque Research and Technology Alliance (BRTA) Paseo de Miramón 194, 20014 Donostia-San Sebastian, Spain.
Email: llizmarzan@cicbiomagune.es
Isabel Pastoriza-Santos and Jorge Pérez-Juste, Departamento de Química Física, CINBIO, Universidade de Vigo, Vigo, Spain; Galicia Sur Health Research Institute (IIS Galicia Sur), SERGAS-UVIGO, Vigo, Spain.
Email: pastoriza@uvigo.es and juste@uvigo.es

Funding information
Ministerio de Ciencia e Innovación, Spain, Grant/Award Numbers: MAT2017-88659-R, MDM-2017-0720, PID2019-108954R; National Natural Science Foundation of China, Grant/Award Number: 21902148; EU Horizon 2020 Research and Innovation Programme, Grant/Award Number: H2020-SUSECU-2019-883390 (SERSing)

Abstract
Plasmonic metal-organic frameworks are composite nanoparticles comprising plasmonic metal nanoparticles (NPs) embedded within a metal-organic framework (MOF) matrix. As a result, not only the functionalities of the individual components are retained, but synergistic effects additionally provide improved chemical and physical properties. Recent progress in plasmonic MOFs has demonstrated the potential for nanofabrication and various nanotechnology applications. Synthetic challenges toward plasmonic MOFs have been recently addressed, resulting in new opportunities toward practical applications, such as surface-enhanced Raman scattering, therapy, and catalysis. The impact of key parameters (thermodynamic vs. kinetic) on the synthetic pathways of plasmonic MOFs is reviewed, while providing insight into related progress toward structure-derived applications.

KEYWORDS
catalysis, drug delivery, metal-organic frameworks, nanocomposites, plasmonic metal nanoparticles, plasmonic MOFs, surface-enhanced Raman scattering

1 | INTRODUCTION

Metal-organic frameworks (MOFs) are crystalline networks of inorganic (metal ions/ clusters) and organic building units, linked through strong coordination bonds and resulting in an ordered porous structure with highly uniform pore size, high surface area and adjustable physical and chemical properties.1−8 The rational selection of their building units allows tailoring the pore size, crystallinity, and functionality for the precise design of novel functional materials. Moreover, MOFs offer great opportunities for accommodating...
myriad guest materials, ranging from ions or (bio) molecules to nanoparticles (NPs), which paves the way to create multifunctional nanocomposites.\(^9\)–\(^{14}\) As usually the guest does not alter the internal MOF structure, the inherent properties of MOFs are retained for further application. At the same time, the MOF pore size is uniform and adjustable, thus resulting in size-selective properties (molecular sieving effect), as well as enhanced stability of the active sites. For example, ultra-small Pt NPs embedded in the single crystal UiO-66 \((\text{Zr}_6\text{O}_4(\text{OH})_4(\text{fumarate})_6 [\text{BDC} = 1,4-\text{benzenedicarboxylate}])\) show 100% hydrogenation conversion rate of \(C_6\)-cyclic hydrocarbons, compared to low hydrogenation conversion by MOF-801 \((\text{Zr}_6\text{O}_4(\text{OH})_4(\text{fumarate})_6)\) due to its small pore size in comparison with the kinetic parameters of \(C_6\)-cyclic hydrocarbons.\(^{15}\)

The incorporation of guest materials in the MOF matrix is often carried out through the incorporation of specific functional groups in the organic ligands, metal ions/clusters, or even in the cavities.\(^{16}\) For instance, nucleic acid-MOFs were produced by the click reaction between the azide motif in UiO-66-N\(_3\) and dibenzyl cyclooctyne in DNA. The limited diffusion of DNA due to the MOF pore size contributed to the outer functionalization of the MOF, thereby improving cellular uptake.\(^{17}\) Imine-functionalized ZIF-92 (zeolitic imidazolate framework 92) can coordinate Pd ions through the N and O atoms of hydroxyethyl imine motifs in the imidazolate linker. The resulting Pd@ZIF-92 MOFs exhibited superior catalytic performance for Suzuki–Miyaura coupling reactions.\(^{18}\) Alternatively, the functionalization of a MOF with organic functional groups such as squaramides demonstrated excellent performance as active catalysts for the Friedel–Crafts reaction, or as sensors for the selective luminescence-based detection of lactose in milk.\(^{19}\)

Among the wide variety of guest materials that have been combined with MOFs, inorganic NPs are particularly attractive due to their outstanding properties at the nanoscale. In the particular case of plasmonic metal NPs, unique and tunable optical properties can be obtained due to the localized surface plasmon resonance (LSPR) effect. This collective oscillation of the free electrons at the metal-dielectric interface produced upon irradiation with light of specific energy, is highly efficient to manipulate and confine light at the nanoscale. The encapsulation of plasmonic NPs within an organic/inorganic matrix (e.g., silica, polymers, MOFs, proteins, etc.) has been used to modulate the LSPR through changes in the local refractive index, to enhance the electromagnetic near-field confined at the NP surface, or to simply improve the colloidal and chemical stability (which is also a critical issue in terms of optical properties). Although nanoplasmics can be considered as a young field, it has rapidly attracted intense interest, due to its major contribution to the development of various applications in (bio)sensing and bioimaging (surface-enhanced Raman scattering [SERS],\(^{20,21}\) surface-enhanced fluorescence [SEF],\(^{22,23}\) or LSPR sensing), gas separation/storage,\(^{24}\) (photo)catalysis,\(^{25–27}\) plasmonic optical activity,\(^{28}\) and so forth.

Given the excellent properties of plasmonic metal NPs and MOFs on their own, it has been proposed that multifunctional plasmonic MOFs, arising from the combination of one or more plasmonic NPs as the guest and MOFs as the host, can provide a unique platform to expand their applications into numerous fields. Plasmonic MOFs, NP@MOF core–shell (single or multiple core) or hetero-meric nanostructures, have been demonstrated to display either novel or enhanced properties. The MOF matrix does not only provide chemical and colloidal stability to the plasmonic counterpart, but can also act as a size-selective sieve or as a nanocarrier, by trapping different molecules in its porous matrix.\(^{25,30}\) For example, core–shell Ag@ZIF-8 (zeolitic imidazolate framework 8) nanowires have been successfully used for the separation of low concentrations of bioalcohols from an aqueous medium. While the ZIF-8 shell provided the nanocomposites with excellent adsorption capabilities, the photothermal properties of Ag nanowires allowed their recyclability and regeneration by triggering the bioalcohol release from the MOF matrix.\(^{31}\) Alternatively, the encapsulation of single Au nanorods (Au NRs) within ZIF-8 NPs exhibited a controlled photothermal effect in combination with a remarkable drug-loading capacity, which was triggered by pH changes.\(^{32}\)

Significant progress has been made regarding the synthetic strategies of plasmonic MOFs and their synergistic effects with potential application in important and diverse fields. Although many reviews have been published on the remarkable and promising properties of MOFs or MOF-based composite materials, we found that the emerging field of plasmonic MOFs has been poorly covered so far.\(^{33}\) Therefore, we attempted to summarize in this review the latest advances in plasmonic MOFs with well-defined size, composition, and morphology. Through these advances, the most successful synthetic strategies are reviewed, highlighting critical (kinetic and thermodynamic) parameters involved.\(^{34}\) Furthermore, combination of plasmonic properties with those characteristic of MOFs give rise to interesting synergistic effects in a number of fields such as SERS sensing, drug delivery for cancer therapy, and catalysis. We propose that plasmonic MOFs will become one of the leading
smart materials to offer solutions toward solving current critical issues.

2 | SYNTHESIS OF PLASMONIC MOFS

The different strategies to synthesize plasmonic MOFs, based on either single or multiple plasmonic NPs encapsulated within a MOF matrix, can be classified into one-pot and multiple-step approaches. In the one-pot approach, both the metal salt and MOF precursors are injected together in the reaction medium, so that metal NPs and MOFs grow concurrently. In the latter case, one of the components is synthesized first and plasmonic MOFs are subsequently obtained upon the corresponding reaction to obtain the second component. Alternatively, plasmonic MOFs can also be obtained by the combination of pre-synthesized MOF and plasmonic NPs, typically resulting in core-satellite nanostructures, but we intentionally left out this particular approach from this review because of its intrinsically different properties.

2.1 | One-pot synthesis

In the one-pot synthesis approach (Figure 1A), precursors of both a noble metal (typically a metal salt and a reducing agent) and MOFs (metal salts and coordination ligands) are mixed in the same reaction medium and the formation of plasmonic MOFs is triggered by temperature. Being performed in one vessel and a single step, one-pot synthesis methods are usually simple, and save time, space and energy consumption. However, the drawback of this approach is that it often gives rise to hybrid nanostructured materials with ill-defined properties, comprising randomly organized multiple NPs encapsulated within a MOF matrix. As a result, the obtained plasmonic-MOF NPs do not display a well-defined optical response and their tunability is severely limited. The synthesis of plasmonic NP-MOF core-shell NPs would require the adjustment of the growth rates for both plasmonic NPs and MOFs, through careful control of the reaction conditions. In a typical process, metal NPs would first be formed via chemical reduction of the corresponding metal precursor and MOF nucleation and growth would subsequently take place at the surface of the NPs, favored by the presence of certain capping ligands. This strategy was successfully developed by He et al. to obtain different core-shell plasmonic MOFs (Au@MOF-5 (Zn₄O(BDC)₃, BDC = 1,4-benzenedicarboxylate), Au@ZIF-8, Au@IRMOF-3 (Zn₄O(NH₂-BDC)₃, and Ag@MOF-5). The NPs were synthesized at high temperature (140 °C) by dissolving Au and MOF precursor salts, as well as polyvinylpyrrolidone (PVP), in a N,N-dimethylformamide (DMF)/ethanol mixture. While DMF plays a key role as the solvent for MOF precursors and reducing agent for the metal, PVP is required to maintain the colloidal stability of Au NPs before their encapsulation. Ethanol is added to modulate the coordination kinetics, so as to avoid self-nucleation and promoting MOF growth exclusively on the metal surface. Furthermore, the thickness of the MOF shell could be controlled through the amount of Au salt, so that larger amounts would lead to larger Au NPs and thinner MOF-5 shells.

2.2 | Multistep approaches

Most of the reported strategies for obtaining plasmonic MOFs involve several synthesis steps, based on either impregnation (MOF NPs are synthesized first) or seeded-growth methods, in which plasmonic NPs are synthesized first (Figure 1B,C).
2.2.1 | Impregnation

This is probably the most frequently used approach to prepare plasmonic MOFs. Well-defined MOFs are first prepared, followed by their impregnation with metal salts and their reduction to obtain multiple plasmonic NPs within the MOF matrix. Upon the synthesis of MOF NPs, these are incubated with the selected metal precursors in a liquid or gas phase, to promote the diffusion of metal ions through the pores, into the MOF matrix. Subsequently, the formation of metal NPs within MOFs' pores/cavities is typically carried out via chemical reduction (e.g., NaBH₄, H₂, sodium citrate, dopamine), photo-reduction, or thermal decomposition. On one hand, the pore size is expected to determine the size of the grown plasmonic NPs, which is thus limited to few nanometers, and on the other hand the well-defined MOF pore structure inhibits the aggregation and regrowth of the formed metal NPs. One of the main limitations of this method is that confinement effects hinder the modulation of size, shape and even composition of the NPs, and therefore their plasmonic response. However, since the synthesized metal NPs have small dimensions and often bare and clean surfaces, this strategy is especially attractive for catalytic applications. Unfortunately, their use as SERS sensing platforms is rather limited due to the NP small size, lack of reproducibility and poor homogeneity of the SERS signal.

It should be pointed out that most reports on plasmonic MOFs obtained via impregnation strategies usually rely on MOFs with dimensions ranging from several hundreds of nanometers to micrometers. One of the pioneering works was published by Hermes et al., by first exposing dried MOF-5 (bulk) to [(CH₃)Au(PMe₃)] vapor under static vacuum and then reduced in a H₂ stream at 190 °C. On an alternative approach, Xu et al. obtained Au@Ag core–shell NPs embedded in MOFs (ZIF-8) via sequential immersion in aqueous solutions of Au and Ag salts and also sequential reduction with NaBH₄. Interestingly, the reversed immersion sequence gave rise to Au@AuAg NPs embedded in ZIF-8, due to a galvanic replacement process. As a further step in the impregnation strategy, Chen et al. reported the synthesis of Pd@Ag NPs within the MOF pores by seed-mediated growth, where the reducing agent comprised activated hydrogen atoms. Table 1 summarizes some of the approaches reported based on the impregnation method including the type and size of the MOFs, as well as the size of the metal NPs.

2.2.2 | Seed-mediated growth

The growth of MOFs on pre-synthesized plasmonic metal NPs has emerged as an attractive alternative for the synthesis of plasmonic MOFs with either a core–shell or a multicore–shell structure. The modulation of the size and morphology of the plasmonic metal NPs allows tuning the LSPR wavelength that could be a requirement for specific applications (e.g., SERS-based applications with irradiation at a specific laser wavelength). Pre-synthesized plasmonic NPs are functionalized with capping ligands that trigger MOF growth on the metal surface. The advantage of this strategy is that it can be modulated to obtain plasmonic MOFs with controlled optical response by tuning the size, composition, and morphology of the plasmonic NPs. The critical issues in this approach are the colloidal stability of plasmonic NPs

![Figure 2](https://example.com/figure2.png)

**Figure 2** Impregnation strategy. (A) Schematic diagram for the synthesis of Au/Ag nanoparticles (NPs) embedded in ZIF-8 via sequential immersion in metal salt solutions. Reprinted with permission. (B) Schematic diagram for the synthesis of Pd@Ag NPs within the pores of a metal-organic framework through seed-mediated growth. Reproduced with permission.
The significant lattice mismatch between noble metals and MOFs leads to a large interfacial energy, which in principle might inhibit the heterogeneous nucleation and growth on the metal surface. To address this challenge, two main methodologies have been proposed: (i) the addition of different surfactants and polymers (such as cetyltrimethylammonium bromide [CTAB], PVP or polyethylene glycol [PEG]) to modify the surface chemistry of the metal and to promote MOF adsorption, and (ii) the surface functionalization of metal NPs with a sacrificial template, which eventually promotes MOF growth.

The first methodology, which implies the addition of promoting surfactants and polymers, has been widely explored for different MOFs. For instance, the presence of quaternary ammonium surfactants, such as cetyltrimethylammonium (CTA+), in the reaction medium induces the nucleation and growth of cubic-shaped ZIF-8 NPs with a size that is controlled through the selective adsorption and stabilization of hydrophobic hydrocarbon chains on {100} facets. Additionally, quaternary ammonium surfactants are common capping agents and stabilizers in the synthesis of plasmonic NPs. Therefore, Tsung et al. proposed the use of CTAB to promote the atomic-to-mesoscale lattice alignment between metal NPs and ZIF-8, leading to Pd or Au cubes encapsulated within single crystalline cubic ZIF-8 (Figure 3A). Interestingly, when Au octahedra enclosed by eight [111] surfaces were used instead of cubic NPs, the six vertices of the octahedra are pointing at the six faces of the outer ZIF-8 cube. It was proposed that the presence of small [100] surfaces resulting from truncated vertices of Au octahedra can promote ZIF-8 nuclei attachment (Figure 3B,C). Zheng et al. developed a similar approach for the encapsulation of single NPs within a polycrystalline ZIF-8 matrix, for plasmonic NPs with arbitrary shapes and compositions (Au and Au@Ag NRs, Au nanospheres, and nanostars, see Figure 3D,E). 3D tomography reconstructions of Au@Ag@ZIF-8 NPs evidenced a well-defined core–shell nanostructure, as well as the polycrystalline nature of the ZIF-8 shell. Interestingly, by fine-tuning CTAB concentration (below the critical micelle concentration) allowed the preparation of ZIF-8 shells with different thickness. Additionally, the combination of CTAB with other molecules such as tris(hydroxymethyl) aminomethane (TRIS), also allowed modulation of the ZIF-8 morphology (Figure 3F,G). Thus, pure ZIF-8 nanocrystals as well as core–shell plasmonic NP@ZIF8 with different morphologies (cubes, octahedra, hexapods, flowers, chair-like, burr-puzzle, etc.) were synthesized in the presence of CTAB and TRIS.

PVP has also been used as an important element toward coating plasmonic nanostructures with MOFs. PVP plays a two-fold role, by imparting stability to metal NPs under synthetic conditions (typically high ionic strength or the presence of nonpolar solvents), and promoting MOF growth from the metal surface through coordination and hydrophobic interactions. A suitable PVP concentration is necessary for the formation of core–shell nanostructures, considering that plasmonic NPs can easily aggregate in the absence of PVP, while MOF crystals may collapse if excessive PVP is added. Still at an optimal PVP concentration, the concentration of plasmonic seed can also influence the final core–shell morphology, due to changes in the active growth sites and residual surfactant. For instance, Li et al. reported that, by adding different concentrations of PVP-modified Ag nanowires into the MOF growth solution, necklace-like Ag

| Type of MOFs | Size of MOFs | Size of metal NPs (nm) |
|--------------|--------------|------------------------|
| UiO-66       | 146 ± 14 nm  | 2.4 ± 0.6              |
| Rb-CD-MOFs   | 2 × 2 × 1 mm | 2 ± 0.4                |
| MIL-101      | ca. 500 nm   | 2.35 ± 1.08            |
| MIL-101(Al)  | 0.2–0.8 μm   | 2.5 ± 0.2              |
| MIL-101(Cr)  | 0.4 μm       | 1.8 ± 0.2              |
| MOF-5        | 20–80 μm     | –                      |
| Zr-Carboxylate MOFs | ca. 0.4 μm | 2.0 – 6.0             |
| MIL-101(Cr)  | ca. 0.4 μm   | 2.0 – 5.0              |
| MIL-74(Ni)   | ca. 5 μm     | –                      |
| MIL-101      | ca. 0.5 μm   | 2.40 ± 0.63            |
| MIL-101(Cr)  | 0.5–5 μm     | ca. 3                  |
| MIL-101(Cr)  | 0.2 μm       | ca. 4                  |
| ZIF-8        | ca. 0.5 μm   | 4.0 – 9.0              |
| MIL-101(Cr)  | 0.3–1 μm     | 2.0 – 3.0              |
| UiO-67       | 0.3 μm       | 2.5                    |
| UiO-66       | 0.2 μm       | 1.7 ± 0.3              |

Abbreviations: MOFs, metal-organic frameworks; NPs, nanoparticles.
nanowires@ZIF-8 nanostructures were obtained. At low Ag nanowire concentrations, they were fully covered by polyhedron ZIF-8 particles, whereas increasing the amount of Ag nanowires resulted in smaller ZIF-8 NPs with a discontinuous distribution on the surface of Ag nanowires. Addition of PVP-stabilized plasmonic NPs to the reaction medium at different stages was implemented to control the ZIF-8 spatial distribution. In a representative example, Lu et al.68 demonstrated that simultaneous addition of 34 nm and 14 nm Au NPs resulted in a NP-rich core with a homogeneous distribution of NPs with both sizes. On the other hand, sequential addition led to a better-defined spatial distribution of the NPs within the transition shell (Figure 4A). On another example, Sindoro and Granick70 reported the growth of polycrystalline ZIF-8 on PVP-stabilized NPs with different geometries leading to a yolk–shell structure resembling the core shape. The origin of the yolk–shell configuration was ascribed to the anisotropic stress generated during polycrystalline shell growth, since the lattice symmetry of ZIF-8 is incompatible with an anisotropic growth preferentially perpendicular to the core. The initial stress would be reduced through outward recrystallization of the ZIF-8 shell, which requires the presence of an excess of metal and ligand precursors.

PEG is another capping ligand of choice, to obtain plasmonic Zr-based MOFs (Zr-MOFs). This type of MOFs crystallize under critical conditions (such as high temperatures) which can readily compromise the colloidal stability of metal NPs. Nevertheless, the energy barrier of MOF crystal formation can be decreased by injection of pre-formed small MOF crystals. Plasmonic Zr-MOFs were obtained under mild conditions by injecting tiny Zr-MOFs (previously obtained at high temperatures) into a growth solution containing PEG-coated Au NRs and Zr-MOF precursors. Surface functionalization with PEG triggered the heterogeneous growth of scu-topology Zr-MOFs to form a core–shell nanostructure, which resembles the prolate morphology of pristine Zr-MOF (NU-901), with scu-topology (Figure 4C),71 with Au NRs oriented parallel to the principal prolate axis. PEG provided colloidal stability while enriching the concentration of MOF precursors on the surface of metal NPs, because of the favorable interaction with MOF precursors and nuclei through its oxyethylene moieties.

An alternative approach to decrease the interfacial energy between metal NPs and MOFs is the NP surface functionalization with a sacrificial template, which promotes MOF growth. Metal oxides (CuO2,73,74 ZnO75–77, and Al2O373) are typical templates for the growth of MOFs. These materials can even provide metal ions in situ for the construction of the MOF shell. On the other hand, numerous metal oxides have been successfully...

**Figure 3** (A) Proposed mechanism for the encapsulation and alignment of individual plasmonic NPs within a single crystalline MOF via attachment of MOF to the metal surface with selective orientation, followed by growth with lattice alignment. (B) and (C) TEM images of an Au octahedron encapsulated within a cubic ZIF-8 in [001] and [010] view directions, respectively. Reproduced with permission.65 Copyright 2014, American Chemical Society. (D) TEM image of Au nanorods encapsulated within polycrystalline ZIF-8 crystals. The inset shows a SEM image of the NPs. Scale bars represent 100 nm. (E) 3D volume representation of a ZIF-8 coated Au@Ag core–shell NP reconstructed by electron tomography, demonstrating the core–shell configuration. Reproduced with permission.66 Copyright 2016, Wiley-VCH. (F) TEM image of Au@Ag nanorods encapsulated within burr puzzle ZIF-8 nanocrystals. (G) Visualization of the 3D reconstruction of one of the particles in (F). Reproduced with permission.67 Copyright 2017, Royal Chemistry of Society. MOF, metal–organic framework; NPs, nanoparticles; SEM, scanning electron microscope; TEM, transmission electron microscope.
FIGURE 4  (A) Scheme for the controlled encapsulation of PVP-stabilized NPs in ZIF-8 crystals. The spatial distribution of incorporated PVP-NPs can be controlled by the addition sequence, that is, addition at the beginning ($T_0$) or after a certain time ($T$) during MOF growth. Spatial distributions will be at (i) or off the central area (ii) of the MOF crystals, with two types of NPs in the central area (iii) or one type in the central area, and another type in the transition layer (iv) of the MOF crystals. (B) TEM image of hybrid nanocrystals obtained when Au NPs were introduced 15 min after the initiation of the reaction. Reproduced with permission.68 Copyright 2015, Nature publishing group. (C) TEM image of AuNR@NU-901 with parallel alignment of Au NRs along the principal axis of prolate crystallites. Reproduced with permission.71 Copyright 2019, American Chemical Society. (D) Procedure for the synthesis of nanocrystal@ZIF-8 yolk–shell nanostructures based on a Cu$_2$O sacrificial shell. (E) TEM image of a nanocrystal@ZIF-8 yolk–shell nanostructure. (D) and (E) reproduced with permission.72 Copyright 2012, American Chemical Society. MOF, metal-organic framework; NPs, nanoparticles; PVP, polyvinylpyrrolidone; TEM, transmission electron microscope.
combined with metal NPs for the preparation of core–shell metal@metal oxide nanostructures. Cu2O is a commonly employed oxide as coating material of Au and Ag NPs (nanoplates, nanorods, octahedra, etc.), which has also been used as a sacrificial template to obtain plasmonic MOFs (based on HKUST-1 and ZIF-8) with yolk–shell structure. Apart from providing chemical and colloidal stability, a Cu2O coating shell can favor the deposition of a ZIF-8 layer around plasmonic NPs. In the presence of ZIF-8 precursors, Cu2O is simultaneously etched off by the protons generated (lowering the pH) by deprotonation of 2-methylimidazole during ZIF-8 formation (Figure 4D). After removing the remaining Cu2O by addition of NH4OH in the final step, metal NP@ZIF-8 yolk–shell nanostructures were obtained (Figure 4E), and the size of the cavity was controlled by the thickness of the Cu2O shell. Cu2O can also provide metal ions to direct the growth of HKUST-1 on the NPs surface. Controlled dissolution of Cu2O under a mildly acidic solution with low polarity was used to encapsulate different types of plasmonic NPs (Au nanospheres and nanorods, Pd nanocubes, and Au@Pt dendritic NPs) within polycrystalline HKUST-1 shells, forming a yolk–shell nanostructure. HKUST-1 nucleates on different sites of the Cu2O surface, giving rise to the formation of a MOF shell constituted by multiple assembled nanocrystals.

Taking advantage of the ease of oxidation of aluminum nanocrystals, formation of an oxide layer of amorphous Al2O3 can also be used as a sacrificial template to grow Al-based MOFs. In acidic medium, Al2O3 slowly dissolves to produce Al3+ ions, which can directly coordinate with 2-aminoterephthalic acid (BDC-NH2) to form MIL-53-NH2 MOFs. This strategy was employed to encapsulate plasmonic aluminum nanocrystals within a Al-MOFs. The amorphous Al2O3 shell, resulting from the controlled oxidation of Al nanocrystals under acidic or polar conditions, releases Al ions to form a shell of MIL-53(Al) on the nanocrystal surface. The outer Al2O3 layer experienced four stages of “localized conversion mechanism,” including hydration of Al2O3 into aluminum oxyhydroxy species (AlOOH), generation of Al (H2O)n by Al3+ released from the neutralization between AlOOH and H+, formation of MIL-53(Al) nuclei by coordinating Al(H2O)n with the BDC2−, and nuclei overgrowth into MIL-53(Al) nanocrystals. The entire growth kinetics was governed by the pH of the reaction solution, which promoted dissolution of Al3+ but also inhibited deprotonation of H2BDC.

Recently, the seed-mediated approach has been applied to the encapsulation of other novel plasmonic materials within MOFs. For instance, plasmonic semiconductor NPs, such as Cu2−Se or indium tin oxide, have been encapsulated within ZIF-8 MOFs, preserving the plasmonic and structural properties of each system. Alternatively, Khan et al. proposed the incorporation of plasmonic oxides within MOFs such as ultra-thin degenerately doped molybdenum oxide with enhanced photostability compared to noble metal nanostructures.

### 2.2.3 Other multistep approaches

The Layer-by-Layer (LbL) technique has recently emerged as a suitable method for the growth of MOF thin films to obtain core–shell metal@MOF with subnanometer control over MOF shell thickness. This approach has been extensively developed for either plasmonic substrates or plasmonic NPs in solution, but in both cases proper surface modification or ligand exchange were needed to promote MOF growth. For instance, AuNRs were coated with HKUST-1 via this strategy, but successful coating required a ligand exchange of CTAB by 11-mercaptoundecanoic acid (MUA) on the Au NRs surface, prior to coating with HKUST-1 by alternating additions of copper(II) acetate and a tetraethylammonium salt of 1,3,5-benzenetricarboxylate (TMA-BTC). The carboxylic acid of MUA coordinates copper ions, thereby inducing HKUST-1 nucleation and overgrowth on the AuNR surface. The quality of the plasmonic MOFs improved by using the conjugate base of the organic linker BTC via enhancing the electrostatic stability and centrifuging the Au NRs between additions of MOF precursors to remove free HKUST-1 particles. The HKUST-1 shell thickness was increased by ca. 0.178 nm per deposited layer. In a different approach, Guselnikova et al. proposed the growth of a MOF-5 thin film on a plasmonic gold grating. The MOF-5 film was promoted by surface modification with 4-carboxyphenyl groups via diazonium chemistry, which then served as a linker for the surface-assisted nucleation and growth of MOF-5, and subsequent immersion in the mother liquid of MOF-5.

Alternatively, it has been proposed that MOF@NP nanostructures can act as seeds for the overgrowth of a secondary MOF shell, MOF@NP@MOF sandwiched structures can be obtained. Sandwiched plasmonic MOFs possess tunable activity and enhanced robust properties because of the capping effect of the secondary MOF shell. Engineering metal nodes and ligands in the secondary MOF can be used to adjust the electronic structures of plasmonic metal cores. For instance, Zr-MOFs in UiO-66@Pd@UiO-67 sandwiched MOFs composites renders the Pd surfaces more electron-deficient, due to the electron-withdrawing ability of the Zr metal nodes. Additionally, the MOF coating leads to an enrichment of phenylacetylene around the Pd NPs.
showing a significant catalytic performance for the semi-hydrogenation of alkynes.91

3 | SYNERGISTIC PROPERTIES OF PLASMONIC MOFS

Applications of MOFs in gas separation and storage, (bio)catalysis, drug delivery, biological imaging, (bio)sensing, magnetic and electronic devices, nonlinear optics, among others, have been reported so far. In the case of plasmonic MOFs, their applicability strongly relies on the properties of the individual components (metal NPs and MOFs), as well as on the synergistic effect resulting from their combination. For instance, apart from providing the composite with high porosity, MOFs can enhance the colloidal and chemical stability or even the sensing capabilities of the metal component, without altering its plasmonic properties. We highlight in this section selected synergistic effects that have been reported in the context of SERS-based (bio)sensing, drug delivery, imaging, and catalysis.

3.1 | SERS (bio)sensing

SERS is a powerful sensing tool to detect the presence of (bio)molecules, which can therefore be applied to a broad range of fields from materials and environmental science to medicine and biology.92-94 This technology is based on the enhancement of certain vibrational (Raman) signals of a molecule when it is adsorbed or located nearby a plasmonic surface. The amplification of the Raman signal is mainly attributed to the large electromagnetic near-field generated at the plasmonic metal surface upon LSPR excitation (electromagnetic enhancement mechanism), but can also be affected by electron transfer processes occurring between the metal nanostructure and the molecule (chemical enhancement mechanism). Both sources of enhancement are strongly determined by the surrounding medium and the surface chemistry of the nanostructures; molecules with stronger affinity to plasmonic surfaces are usually easier to detect by SERS.

The fabrication of SERS substrates that are highly reliable, reproducible and efficient has been one of the most critical issues in SERS science and technology. The unique properties of MOFs have attracted the attention of researchers working on SERS, since they have demonstrated improved sensing capabilities when combined with plasmonic materials.95,96 To start with, MOFs can improve the chemical and physical stability of plasmonic nanostructures in harsh environments; ZIF-8 coating of Ag-based SERS platforms has been demonstrated to enhance its resistance against oxidation, sulfidation, and enzymatic degradation, thereby preserving their sensing performance, even under harsh environmental conditions.97 In addition, MOFs can efficiently and selectively capture analytes, including gases, and bring them near the plasmonic surface, because of their larger surface area.98,99 This enrichment ability leads to a significant improvement of the SERS performance of plasmonic platforms.100-105 It has been shown that coating Au NPs with uniform and thin shells of MOF-5 allowed the selective SERS detection of CO2 in gas mixtures,38 due to the specific adsorption of CO2 molecules by MOF-5, leading to a significant enhancement of the Raman signal at 1395 cm⁻¹. The acquired SERS signal was found to depend on the MOF-5 thickness, being maximum for shells of ca. 3.2 nm. On the contrary, thick MOF coatings could cause shielding effects, inhibition of light absorption by the plasmonic NPs, and therefore a poorer SERS performance.98,106

Li et al.69 prepared a substrate made of necklace-like Ag@ZIF-8 core–shell heterostructured nanowires, where the distribution and dimensions of the ZIF-8 coating on the Ag nanowires could be tailored as needed (Figure 5A). Such heterostructures showed improved performance as compared to bare Ag nanowires, reaching a SERS enhancement factor (EF) of 4.2 × 10⁷ for crystal violet (CV) and showing large-area uniformity and good reproducibility. CV molecules were enriched in the ZIF-8 pores nearby the Ag surface, due to π–π electronic interactions between the CV molecule and the imidazole moiety. Importantly, when the effect of the MOFs mass-loading on the Ag nanowires surface was investigated, they found that a mass-loading of 28% generated the strongest SERS signal (Figure 5B), whereas larger ZIF-8 loadings on Ag nanowires gave rise to decreased signals, which was explained in terms of weaker “hot-spots” due to shielding effects by the ZIF-8 shells. Nevertheless, the larger dielectric constant of MOFs with respect to air or water was responsible for an enhancement of the electromagnetic near-field confined at the metal NP surface when embedded in a MOF matrix (Figure 5C). This phenomenon caused an enhancement in the SERS signal of the probe molecules (Figure 5D).107

One of the most interesting aspects of MOFs for SERS is given by their sieving properties endowed by the porous structure,66 which have been demonstrated to facilitate analyte identification and data analysis through size-selective sensing, of particular importance in complex samples.71,107,108 Qiao et al. employed Au NP ordered assemblies (which they termed superparticles) encapsulated within a ZIF-8 matrix (Figure 5E,F), to demonstrate by SERS the diffusion of molecules such as benzaldehyde, glutaraldehyde, and 4-ethylbenzaldehyde.
through ZIF-8, whereas larger aldehydes, such as 2-naphthaldehyde were excluded (Figure 5G).108 Only when the size of the molecule was smaller than the apertures and pores, molecules would be able to diffuse through MOF-based shells. Such Au superparticle@ZIF-8 nanostructures were tested for the selective detection of gaseous 4-ethylbenzaldehyde, a lung cancer biomarker in exhaled breath, through a Schiff base reaction (Figure 5H).
These authors claimed a limit of detection (LOD) of 10 ppb, as well as excellent selectivity in mixed mimetic exhalation, as determined by principal component analysis (PCA) (Figure 5A).

On the other hand, MOF surfaces often show numerous coordinatively unsaturated metal sites, enabling their bioconjugation with polyhistidine-tagged proteins and peptides, and therefore offering excellent opportunities for bio-targeting. The modular assembly of ZIF-8 coated Au@Ag core–shell nanorods encoded with Raman reporters and carrying immunoglobulins and recombinant antibodies, enabled the detection of EGFR and CD44 cell surface receptors in vitro. Apart from facilitating the encoding with Raman reporters, MOFs allowed bioconjugation of SERS nanotags with polyhistidine-tagged protein G and SpyCatcher through interactions between polyhistidine and coordinatively unsaturated Zn$^{2+}$ sites.

### 3.2 Drug delivery and cancer therapy

MOFs in general and ZIF-8 in particular have been demonstrated as suitable candidates for applications in cancer diagnosis and therapy. A drug carrier should exhibit high loading capacity and biodegradability, provide molecule protection, or enable controlled release and efficient targeting. Indeed, the therapeutic efficiency of MOFs is commonly better than that of conventional drug molecules per dose, thereby allowing to decrease the amount of drug molecules and reduce side effects. Such a performance is in part due to the slow release of drugs, triggered by the physiological environment (e.g., pH), temperature, or light irradiation. Apart from small molecule drugs such as ibuprofen, curcumin, or doxorubicin, MOFs have been used for the encapsulation and delivery of a wide variety therapeutic agents including gasotransmitters, proteins, nucleic acids, viruses, and cells. Plasmatic MOF composites possess enhanced properties, as the plasmatic components can help improve the space and time control of drug release, due to their efficient photothermal properties, even providing high near-infrared (NIR) absorption for NIR thermal and photoacoustic imaging.

Excellent drug delivery performance has been demonstrated for Au NR@ZIF-8 core–shell nanostructures, with high drug loading capacity and dual stimuli-responsive release (Figure 6A). These plasmatic MOFs showed a remarkable drug-loading capacity when tested with doxorubicin hydrochloride (DOX), as a model anticancer drug. The study found that drug release could be triggered by both pH and NIR irradiation. On one hand, Zn–O and Zn–N bonds between DOX and ZIF-8 and Zn$^{2+}$ and imidazolate, respectively, break at low pH; on the other hand, NIR irradiation generates a plasmon-induced photothermal effect that contributes to the dissociation of coordination bonds, as well as an increase of molecular mobility. Importantly, both in vitro and in vivo anticancer experiments performed with DOX-loaded AuNR@ZIF-8 nanoparticles under NIR irradiation (808 nm) showed a higher toxicity at cellular and animal levels, compared with those for single treatment (chemotherapy or photothermal therapy). The lack of stability of the ZIF-8 matrix in the biological medium can be enhanced by coating with an amphiphilic polymer shell. Thus, highly stable thermoresponsive plasmonic nanocarriers were obtained by coating Au nanostar@ZIF-8 core–shell nanostructures with poly(isobutylene-alt-maleic anhydride)-graft-dodecyl (PMA). The polymer shell provided stability to the MOF matrix, while activating cargo release inside living cells upon plasmon excitation. The thermoplasmonic effect was found to give rise to a temperature increase that can trigger diffusion of the cargo (active bisbenzimide molecules) into living cells in a more efficient manner than by conventional heating.

Au nanostar@ZIF-8 yolk–shell NPs were also tested as remote-controlled and stimuli-responsive drug carriers, exhibiting excellent synergistic anticancer effects. In addition, Au@MOF NPs demonstrated suitable properties as a contrast agent for in vivo photoacoustic and NIR photothermal imaging. Zhang et al. also incorporated luminescent NPs (Ag$_2$S, Ag$_2$Se, or uponversion NPs) in a ZIF-8 matrix, together with DOX, to fabricate plasmonic AuNR-MOF heterodimers for cancer theranostics using combined therapy. After intravenous injection in HeLa-tumor bearing female nude mice, DOX was gradually released in the vicinity of the cancer tissue, triggered by low pH conditions. The luminescent NPs allowed in vivo trimodal (fluorescence, photoacoustic, and NIR fluorescence) imaging to monitor tumor evolution during chemotherapeutic treatment under NIR irradiation. In vivo triple-modality imaging, involving computed tomography, magnetic resonance imaging, and photoacoustic imaging, was achieved by combining Au nanorods with a Fe-based MOF such as MIL-88 (Figure 6B). The resulting core–shell Au@MIL-88(Fe) NP probes showed high penetration depth, high contrast, and high spatial resolution for imaging and diagnosis of glioma.

As a final example, porphyrinic MOFs feature the properties of porphyrins (high absorption and luminescence) but also high porosity for molecular trapping. Thus, porphyrinic MOFs have been used for cancer therapy and sensing. Zeng et al. fabricated a multifunctional theranostic platform combining Au NRs and a porphyrinic MOFs such as Zr$_6$(TCPP)$_{1.5}$ (TCPP = tetraakis (4-carboxyphenyl)porphyrin), which is composed of a connected Zr$_6$ cluster ($Zr_6$O$_4$(OH)$_4$(H$_2$O)$_6$(OH)$_6$(COO)$_6$) and a
tetrapotopic linker (TCPP). The resulting AuNR@MOF core–shell nanostructures showed theranostic performance, as nanocarriers for light-induced drug delivery, fluorescence imaging probes and producers of reactive oxygen species for photothermal therapy. It was reported that AuNR@MOFs loaded with camptothecin could inhibit tumor growth and metastasis in vivo (Figure 6C).

3.3 | Catalysis

Noble metal NPs have been intensively used in the field of catalysis. Their catalytic behavior depends on NP size, shape, structure, composition, and NP-support interaction. Besides, in the case of plasmonic metal NPs, they can act as efficient photocatalysts upon light irradiation, driving a wide variety of chemical reactions. On the other hand, MOFs exhibit several properties that commend them as catalytic platforms, although just a small fraction of existing MOFs have been investigated in catalysis. Thus NiCo–MOF nanosheets have been used for oxygen evolution reaction (OER) in alkaline conditions, polymolybdate-based MOFs for hydrogen generation from water, porphyrinic Ti MOFs for alcohol oxidation, or Co-porphyrin MOF for CO2 reduction, and among others. Nevertheless, both plasmonic NPs and MOFs suffer from several drawbacks as catalysts, which may be overcome when they are combined. The plasmonic component can either act as a catalyst or enhance the
catalytic performance of the MOF through plasmon-based processes (hot electron injection or thermal effects).

On the other hand, MOFs can improve the catalytic performance of metal NPs by improving their stability, avoiding catalyst poisoning, enhancing the adsorption of the catalytic substrate, providing molecular size-selective properties, facilitating tandem reactions, and so on. Therefore, plasmonic MOFs have demonstrated improved catalytic performance compared with their corresponding building blocks. We provide some examples in what follows.

Multiple plasmonic Pd nanocubes encapsulated inside a ZIF-8 matrix showed high catalytic efficiency for selective hydrogenation of olefins under ambient conditions and visible-light irradiation (Figure 7A). While Pd nanocubes provided catalytic active sites as well as plasmon-induced photothermal effects, the MOF shell enhanced the catalytic performance through H2 enrichment, providing selectivity (molecular sieving effect) and improving catalyst reusability. Through investigation of the hydrogenation of 1-hexene at room temperature and under visible-light excitation (100 Mw/cm2), it was found that Pd@ZIF-8 NPs provided yields similar to those obtained by heating at 50 °C. Pd@ZIF-8 also showed better 1-hexene conversion than Pd nanocubes under similar experimental conditions. Finally, olefin conversion strongly depended on the molecule size: while for 1-hexene the conversion was approximately 100% in 90 min, conversions of 37%, 27%, and 0% were achieved for 1-octene (ca. 4 Å), cyclohexene (ca. 4.2 Å), and cyclooctene (ca. 5.5 Å), reflecting the size selectivity of the Pd NCS@ZIF-8 catalyst.

The MOF matrix can enhance the photocatalytic efficiency of plasmonic NPs. UiO-66 was employed as a template (NPs or membranes) to confine and provide stability to bare Au NPs improving their photocatalytic activity to produce NH3 through N2 reduction reaction under ambient conditions. Besides, UiO-66 also promotes the diffusion of N2 molecules and hydrated molecules towards the catalytic surface. Interestingly, upon light irradiation Au NPs play a triple role: (1) generating hot electrons and transferring them to the N2 molecules, (2) absorbing N2 molecules and catalyzing the N2 reduction reaction upon the addition of electrons and protons, and (3) boosting the activation of N2 molecules and intermediates induced by LSPR effects (photothermal, near electromagnetic fields, etc.). In another study focused on Al@MIL-53(Al) core–shell NPs, the MOF coating also enhanced the photocatalytic activity of Al NPs toward CO2 reduction in reverse water-gas shift (rWGS) reactions. MIL-53 exhibits CO2 trapping and storage capabilities (Figure 7B) restricting CO2 diffusion away from the substrate, and additionally Al is a photocatalyst for CO2 reduction, to selectively produce CO instead of both CH4 and CO (typically obtained in thermally driven processes). Combination of both materials in the form of Al@MIL-53(Al) core–shell NPs produced a higher CO yield than that obtained from bare Al NPs under laser irradiation (Figure 7B). High selectivity toward CO2 hydrogenation under light-heat dual activation was also achieved using plasmonic MOF catalysts comprising multiple Au@Pd core–shell NPs encapsulated within an UiO-66-NH2 (Zr6O4(OH)8(BDC-NH2))6+ matrix. It was proposed that the multiple Au NP cores acted as a plasmonic nanoantenna generating hot-electrons, while the thin Pd coating (<1 nm) further improved CO2 reduction by a decrease of the HOMOLUMO gap and the reaction energy barrier of CO2* to COOH*. Finally, UiO-66-NH2 contributed to enhancing the conversion and selectivity into CO.

On a related example, plasmonic Ag nanocubes were encapsulated within a Zr-based MOF (UiO-67) which contains a CO2-to-CO conversion photocatalyst. Re(CO)6(2,2'-bipyridine-5,5'-dicarboxylate)Cl (Figure 7C). Immobilization of the photocatalyst (ReTCS) inside the MOF matrix not only prevents deactivation through dimerization, but also allows tuning its density toward cooperatively enhanced photocatalytic activity. The MOF also acts in this case as a support to spatially confine the photocatalyst inside the electromagnetic near-field generated at the Ag nanocube surface upon light excitation, which results in an enhancement of the photocatalytic activity. Since the quadrupolar LSPR mode of Ag nanocubes overlaps with the absorption band of the photocatalyst, upon LSPR excitation the electromagnetic field can be absorbed by ReTCS. As a result, Ag@Re-MOF NPs show a remarkable enhancement of the catalytic activity with respect to Re-MOF, 5-fold or 7-fold for MOF shells of 34 nm or 16 nm, respectively (Figure 7C).

Finally, with the aim of fabricating a photocatalyst with a broadband spectral response from the UV to the NIR, a multifunctional plasmonic MOF (UCNPs-Pt@MOF/Au) was fabricated by combining UiO-66-NH2 (absorption band at 300–450 nm), Au NPs (LSPR band at 500–600 nm), upconversion NPs (UCNPs, absorption band at 980 nm) and Pt NPs. The resulting nanocomposites consisted of UCNPs decorated with tiny Pt NPs and coated with UiO-66-NH2, doped with 10 nm Au NPs, thereby being able to capture UV, visible, and NIR photons (Figure 7D). As schematically shown in Figure 7D, UCNPs can convert NIR light into UV and visible light, which is again harvested by UiO-66-NH2 and plasmonic NPs. While the excited MOF transfers the electrons to Pt NPs, which behave as electron reservoirs and active sites, excited Au NPs generate hot electrons that are injected into the MOF and then rapidly transferred to Pt sites. Therefore, the role of the MOF shell is very important.
FIGURE 7  (A) Schematic representation of plasmon-driven selective catalysis of the hydrogenation of olefins in the presence of Pd@ZIF-8 nanoparticles and hydrogenation yields of 1-hexene obtained using 1 atm H₂ under full-spectrum irradiation with different light intensities at room temperature or upon heating at different temperatures. (B) Top: Low-pressure CO₂ adsorption isotherm for Al@MIL-53(Al) and bare Al nanoparticles measured at 273 K. The solid and open symbols represent adsorption and desorption, respectively. Bottom: Photocatalytic performance of Al@MIL-53(Al) (blue line), Al (red line), and MIL-53(Al) (black line) nanoparticles on rWGS reaction (CO₂ + H₂ → CO + H₂O) under white-light irradiation. The green line represents the performance of the photocatalyst in an inert He atmosphere. Reproduced with permission. Copyright 2019, AAAS. (C) Left: Scheme for CO₂ conversion on the Ag@Re-MOF photocatalyst. Right: TEM image of Ag@Re-MOF nanoparticles and magnified image of Re-MOF shell and photocatalytic performance of Re-MOF (blue line), Cu@Re-MOF (green dot), and Ag@Re-MOF with MOF thickness of 16 nm (red dot) and 33 nm (orange dot). Reproduced with permission. Copyright 2017, American Chemistry Society. (D) Top: Scheme for the photocatalysis mechanism of multifunctional plasmonic MOF (UCNPs-Pt@MOF/Au). Bottom: H₂ generation rate of UCNPs/Pt@MOF and UCNPs/Pt@MOF/Au under irradiation with UV light, visible light, NIR light, and solar light Reproduced with permission. Copyright 2019, Wiley-VCH. MOF, metal-organic framework; NIR, near infrared; TEM, transmission electron microscope; UV, ultraviolet
Recycling experiments (Figure 7D, bottom) also revealed high recyclability and stability.

4 | SUMMARY AND OUTLOOK

We have recently witnessed major progress in the design of synthetic strategies toward the fabrication of plasmonic MOFs in various configurations, which require consideration of key issues such as colloidal stability or high temperature, often required to synthesize MOFs. We selected what we considered the most relevant strategies so far, which we expect will guide further development of new plasmonic MOFs. The growing interest in MOFs per se, together with the myriad well-established methods for the tailored synthesis of plasmonic NPs with pre-designed surface chemistry, will definitely allow a rapid progress in the field. Despite the large variety of MOFs, only a small fraction of them have been implemented for the preparation of plasmonic-MOF hybrids. In particular, plasmonic MOFs with core–shell configuration are essentially limited to ZIFs, MILs, HKUSTs, or UiOs; it would be very interesting therefore to employ MOFs with unique functions such as conductive MOFs, magnetic MOFs or biomimicking MOFs, among others. The library of MOF building blocks in plasmonic hybrids could be expanded by employing new synthetic procedures that would not involve harsh conditions. Indeed, high temperatures and pressures can often compromise the integrity of metal NPs, leading to aggregation, reshaping, and/or degradation.

We have highlighted some of the most relevant applications that have been reported so far for plasmonic MOFs, in the fields of sensing, therapy and catalysis. We made a special effort to select those works where synergistic effects arising from the combination of the different components are purposely exploited. Given the plethora of applications that have been reported for either plasmonic NPs or MOFs alone, we suggest that the development and application of plasmonic MOF nanocomposites is still in its infancy. Additional endeavors will be required to achieve efficient applications of plasmonic MOFs in the market in the near future. In our opinion, the main goal to be achieved will be a tight and reproducible synthetic control that leads to well-defined optical properties, that is, narrow and tunable LSPR bands. In this way, the potential of different MOFs in catalysis through cascade or simultaneous reactions could be optimized by means of plasmon-mediated photocatalysis. Another topic that will surely deserve further attention from a NP perspective is the combination of (recently developed) metal NPs with plasmonic optical activity (chirality) and selected MOFs, which will open up new avenues in the fields of chemical sensing, circularly polarized photocatalysis, and photodynamic therapy.

ACKNOWLEDGMENTS

G. Zheng acknowledges the National Natural Science Foundation of China (Grant Number: 21902148). Financial support was also provided by the Spanish Ministerio de Ciencia e Innovación (Grant No. PID2019-108954R to I. Pastoriza-Santos and J. Pérez-Juste; Grants No. MAT2017-86659-R and MDM-2017-0720 to L. M. Liz-Marzán) and EU Horizon 2020 research and innovation programme under grant agreement no. 883390 (SERSing).

CONFLICT OF INTERESTS

The authors declare no conflict of interest.

ORCID

Guangchao Zheng https://orcid.org/0000-0003-0736-8409
Isabel Pastoriza-Santos https://orcid.org/0000-0002-1091-1364
Jorge Pérez-Juste https://orcid.org/0000-0002-4614-1699
Luis M. Liz-Marzán https://orcid.org/0000-0002-6647-1353

REFERENCES

1. Eddaoudi M, Kim J, Rosi N, et al. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. Science. 2002;295:469-472.
2. Lee S, Jeong H, Nam D, Lah MS, Choe W. The rise of metal–organic polyhedra. Chem Soc Rev. 2020;50:528-555.
3. Park KS, Ni Z, Côté AP, et al. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. Proc Natl Acad Sci USA. 2006;103:10186-10191.
4. Farha OK, Eryazici I, Jeong NC, et al. Metal-organic framework materials with ultrahigh surface areas: is the sky the limit? J Am Chem Soc. 2012;134:15016-15021.
5. Jiang HL, Feng DW, Liu TF, Li JR, Zhou HC. Pore surface engineering with controlled loadings of functional groups via click chemistry in highly stable metal-organic frameworks. J Am Chem Soc. 2012;134:14960-14963.
6. Deng H, Grunder S, Cordova KE, et al. Large-pore apertures in a series of metal-organic frameworks. Science. 2012;336:1018-1023.
7. Sindoro M, Yanai N, Jee AY, Granick S. Colloidal-sized metal-organic frameworks: synthesis and applications. Acc Chem Res. 2014;47:459-469.
8. Furukawa H, Cordova KE, O’Keeffe M, Yaghi OM. The chemistry and applications of metal-organic frameworks. Science. 2013;341:1230444.
9. Wang SZ, Chen YJ, Wang SY, Li P, Mirkin CA, Farha OK. DNA-functionalized metal-organic framework nanoparticles for intracellular delivery of proteins. J Am Chem Soc. 2019;141:2215-2219.
10. Poddar A, Conesa JJ, Liang K, et al. Encapsulation, visualization and expression of genes with biometrically mineralized zeolitic imidazolate framework-8 (ZIF-8). Small. 2019; 15:1902268.

11. Liu Y, Zhang W, Li S, et al. Designable yolk-shell nanoparticle@MOF petalous heterostructures. Chem Mater. 2014; 26:1119-1125.

12. Wang C, deKrafft KE, Lin WB. Pt nanoparticles@photoactive metal-organic frameworks: efficient hydrogen evolution via synergistic photoexcitation and electron injection. J Am Chem Soc. 2012;134:7211-7214.

13. Chen Y, Lykourinou V, Vetromile C, et al. How can proteins enter the interior of a MOF? Investigation of cytochrome c translocation into a MOF consisting of mesoporous cages with microporous windows. J Am Chem Soc. 2012;134:13188-13191.

14. Lyu FJ, Zhang YF, Zare RN, Ge J, Liu Z. One-pot synthesis of protein-embedded metal-organic frameworks with enhanced biological activities. Nano Lett. 2014;14:5761-5765.

15. Na K, Choi KM, Yaghi OM, Somorjai GA. Metal nanocrystals embedded in single nanocrystals of MOFs give unusual selectivity as heterogeneous catalysts. Nano Lett. 2014;14:5979-5983.

16. Razavi SAA, Morsali A. Linker functionalized metal-organic frameworks. Coord Chem Rev. 2019;399:213023.

17. Morris W, Briley WE, Auyeung E, Cabezas MD, Mirkin CA. Nucleic acid-metal-organic framework (MOF) nanoparticle conjugates. J Am Chem Soc. 2014;136:7261-7264.

18. You L-X, Zhao B-B, Yao S-X, et al. Engineering functional group decorated ZIFs to high-performance Pd@ZIF-92 nanocatalysts for C(sp2)-C(sp2) couplings in aqueous medium. J Catalysis. 2020;392:80-87.

19. Jiang M, Li P, Wu P, et al. A squaramide-based metal-organic framework as a luminescent sensor for the detection of lactose in aqueous solution and in milk. Chem Commun. 2018; 54:9131-9134.

20. Xu JY, Wang J, Kong LT, Zheng GC, Guo Z, Liu JH. SERS detection of explosive agent by macromyc compound functionalized triangular gold nanoprisms. J Raman Spectrosc. 2011;42:1728-1735.

21. Zheng GC, Polavarapu L, Liz-Marzan LM, Pastoriza-Santos I, Perez-Juste J. Gold nanoparticle-loaded filter paper: a recyclable dip-catalyst for real-time reaction monitoring by surface enhanced Raman scattering. Chem Commun. 2015;51:4572-4575.

22. Zheng GC, Wang J, Kong LT, Cheng HF, Liu JH. Cellular-like gold nanoefet: synthesis, functionalization, and surface enhanced fluorescence detection for mercury contaminations. Plasmonics. 2012;7:487-494.

23. Kong LT, Wang J, Zheng GC, Liu JH. A highly sensitive protocol (FRET/SIMNSEF) for the determination of mercury ions: a unity of fluorescence quenching of graphene and enhancement of nanogold. Chem Commun. 2011;47:10389-10391.

24. Zlatea C, Campesi R, Cuevas F, et al. Pd nanoparticles embedded into a metal-organic framework: synthesis, structural characteristics, and hydrogen sorption properties. J Am Chem Soc. 2010;132:2991-2997.

25. Qiu L, Pang GA, Zheng GC, Bauer D, Wieland K, Haich C. Kinetic and mechanistic investigation of the photocatalyzed surface reduction of 4-nitrothiophenol observed on a silver plasmonic film via surface-enhanced raman scattering. ACS Appl Mater Interfaces. 2020;12:21133-21142.

26. Chen Z, Chen C, Zhang J, et al. Zeolite Y microspheres with perpendicular mesochannels and metal@Y heterostructures for catalytic and SERS applications. J Mater Chem A. 2018;6:6273-6281.

27. Zheng GC, Carbo-Argibay E, Gonzalez-Romero E, Pastoriza-Santos I, Perez-Juste J. Pd-Au heteropentamers: selective growth of Au on Pd tetrahedral nanoparticles with enhanced electrocatalytic activity. Cryst Growth Des. 2020;20:5863-5867.

28. Zheng G, Bao Z, Perez-Juste J, et al. Tuning the morphology and chiroptical properties of discrete gold nanorods with amino acids. Angew Chem Int Ed. 2018;57:16452-16457.

29. Wang J, Xu H, Ao C, et al. Au@Pt nanotubes within CoZn-based metal-organic framework for highly efficient semi-hydrogenation of acetylene. Iscience. 2020;23:101233.

30. Zhou Z, Vazquez-Gonzalez M, Willner I. Stimuli-responsive metal–organic framework nanoparticles for controlled drug delivery and medical applications. Chem Soc Rev. 2021;50:4541-4563.

31. Liu X, He L, Zheng J, et al. Solar-light-driven renewable butanol separation by core-shell Ag@ZIF-8 nanowires. Adv Mater. 2015;27:3273-3277.

32. Li Y, Jin J, Wang D, et al. Coordination-responsive drug release inside gold nanorods@metal-organic framework core-shell nanostructures for near-infrared-induced synergistic chemophotothermal therapy. Nano Res. 2018;11:3294-3305.

33. Wang SZ, McGuirk CM, d’Aquino A, Mason JA, Mirkin CA. Metal-organic framework nanoparticles. Adv Mater. 2018;30:1800202.

34. Troyano J, Carne-Sanchez A, Avci C, Imaz I, Maspoch D. Colloidal metal-organic framework particles: the pioneering case of ZIF-8. Chem Soc Rev. 2019;48:5534-5546.

35. Wang S, McGuirk CM, Ross MB, et al. General and direct method for preparing oligonucleotide-functionalized metal-organic framework nanoparticles. J Am Chem Soc. 2017;139:9827-9830.

36. Ishida T, Nagaoka M, Akita T, Haruta M. Deposition of gold clusters on porous coordination polymers by solid grinding and their catalytic activity in aerobic oxidation of alcohols. Chem-Eur J. 2008;14:8456-8460.

37. Pastoriza-Santos I, Liz-Marzan LM. N,N-Dimethylformamide as a reaction medium for metal nanoparticle synthesis. Adv Funct Mater. 2009;19:679-688.

38. He L, Liu Y, Liu J, et al. Core shell noble-metal@metal-organic-framework nanoparticles with highly selective sensing property. Angew Chem Int Ed. 2013;52:3741-3745.

39. Zhu QL, Li J, Xu Q. Immobilizing metal nanoparticles to metal-organic framework with microporous windows. J Mater Chem A. 2014;3:9827-9830.

40. Aijaz A, Akita T, Tsumori N, Xu Q. Metal-organic framework-immobilized polyhedral metal nanocrystals:
reduction at solid-gas interface, metal segregation, core-shell structure, and high catalytic activity. *J Am Chem Soc.* 2013; 135:16356-16359.

43. Cao X, Hong S, Jiang Z, et al. SERS-active metal-organic frameworks with embedded gold nanoparticles. *Analyst.* 2017;142: 2640-2647.

44. Huang PC, Ma WI, Yu P, Mao LQ. Dopamine-directed in-situ and one-step synthesis of Au@Ag core-shell nanoparticles immobilized to a metal-organic framework for synergistic catalysis. *Chem-Asian J.* 2016;11:2705-2709.

45. Ameeloot R, Roefaeers MB, De Cremer G, et al. Metal-organic framework single crystals as photoactive matrices for the generation of metallic microstructures. *Adv Mater.* 2011;23: 1788-1791.

46. Shen LJ, Wu WM, Liang RW, Lin R, Wu L. Highly dispersed palladium nanoparticles anchored on UiO-66(NH2) metal-organic framework as a reusable and dual functional visible-light-driven photocatalyst. *Nanoscale.* 2013;5:9374-9382.

47. Hermes S, Schröter MK, Schmid R, et al. Metal@MOF: loading of highly porous coordination polymers host lattices by metal organic chemical vapor deposition. *Angew Chem Int Ed.* 2005;44: 6237-6241.

48. Jiang HL, Akita T, Ishida T, Haruta M, Xu Q. Synergistic catalysis of Au@Ag core-shell nanoparticles stabilized on metal-organic framework. *J Am Chem Soc.* 2011;133:1304-1306.

49. Liu GF, Qiao XX, Cai YL, et al. Aluminum metal-organic framework-silver nanoparticle composites for catalytic reduction of nitrophenols. *ACS Applied Nano Materials.* 2020;3:11426-11433.

50. Rodríguez-Gonzalez B, Burrows A, Watanabe M, Kiely CJ, Liz-Marzan LM. Multishell bimetallic AuAg nanoparticles: synthesis, structure and optical properties. *J Mater Chem.* 2005;15: 1755-1759.

51. Polavarapu L, Zanaga D, Altantzis T, et al. Galvanic replacement coupled to seeded growth as a route for shape-controlled synthesis of plasmonic nanorattles. *Adv Mater.* 2016;138: 11453-11456.

52. Chen LY, Huang BB, Qiu X, Wang X, Luque R, Li YW. Seed-mediated growth of MOF-encapsulated Pd@Ag core-shell nanoparticles: toward advanced room temperature nanocatalysts. *Chem Sci.* 2016;7:228-233.

53. Chen LW, Hao YC, Guo Y, et al. Metal-organic framework membranes encapsulating gold nanoparticles for direct plasmonic photocatalytic nitrogen fixation. *J Am Chem Soc.* 2021; 143:5727-5736.

54. Wei YH, Han SB, Walker DA, Fuller PE, Grzybowski BA. Nanoparticle core/shell architectures within MOF crystals synthesized by size-diffusion. *Angew Chem Int Ed.* 2012;51: 7435-7439.

55. Liu HL, Liu YL, Li YW, Tang ZY, Jiang HF. Metal-organic framework supported gold nanoparticles as a highly active heterogeneous catalyst for aerobic oxidation of alcohols. *J Phys Chem C.* 2010;114:13362-13369.

56. Aijaz A, Karkamkar A, Choi YJ, et al. Immobilizing highly catalytically active Pt nanoparticles inside the pores of metal-organic framework: a double solvents approach. *J Am Chem Soc.* 2012; 134:13926-13929.

57. Liu J, Strachan DM, Thallapally PK. Enhanced noble gas adsorption in Ag@MOF-74Ni. *Chem Commun.* 2014;50: 466-468.

58. Long JL, Liu HL, Wu SJ, Liao SJ, Li YW. Selective oxidation of saturated hydrocarbons using Au-Pd alloy nanoparticles supported on metal-organic frameworks. *ACS Catal.* 2013;3: 647-654.

59. El-Shall MS, Abdelsayed V, Khder AERS, Hassan HMA, El-Kaderi HM, Reich TE. Metallic and bimetallic nanocatalysts incorporated into highly porous coordination polymer MIL-101. *J Mater Chem.* 2009;19:7625-7631.

60. Khajavi H, Stil HA, Kuipers HPCE, Gascon J, Kapteijn F. Shape and transition state selective hydrogenations using egg-shell Pt-MIL-101(Cr) catalyst. *ACS Catal.* 2013;3: 2617-2626.

61. Dang TT, Zhi YH, Ngiam JSY, Ghosh SC, Chen AQ, Seayad AM. Palladium nanoparticles supported on ZIF-8 as an efficient heterogeneous catalyst for aminocarboxylation. *ACS Catal.* 2013;3:1406-1410.

62. Pascaru V, Yao Q, Bermejo Gómez A, et al. Sustainable catalysis: rational Pd loading on MIL-101Cr-NH2 for more efficient and recyclable Suzuki-Miyaura reactions. *Chem-Eur J.* 2013;19:17483-17493.

63. Liu HL, Chang LN, Bai CH, Chen LY, Luque R, Li YW. Controllable encapsulation of "Clean" metal clusters within MOFs through kinetic modulation: towards advanced heterogeneous nanocatalysts. *Angew Chem-Int.* 2016;55: 5019-5023.

64. Pan Y, Heryadi D, Zhou F, et al. Tuning the crystal morphology and size of zeolitic imidazolate framework-8 in aqueous solution by surfactants. *CrystEngComm.* 2011;13: 6937-6940.

65. Hu P, Zhuang J, Chou LY, et al. Surfactant-directed atomic to mesoscale alignment: metal nanocrystals encased individually in single-crystalline porous nanostructures. *J Am Chem Soc.* 2014;136:10561-10564.

66. Zheng G, de Marchi S, López-Puente V, et al. Encapsulation of single plasmonic nanoparticles within ZIF-8 and SERS analysis of the MOF flexibility. *Small.* 2016;12:3935-3943.

67. Zheng G, Chen Z, Sentosun K, et al. Shape control in ZIF-8 nanocrystals and metal nanoparticles@ZIF-8 heterostructures. *Nanoscale.* 2017;9:16645-16651.

68. Lu G, Li S, Guo Z, et al. Imparting functionality to a metal-organic framework material by controlled nanoparticle encapsulation. *Nat Chem.* 2012;4:310-316.

69. Li QQ, Gong SS, Zhang H, Huang FZ, Zhang LN, Li SK. Tailored necklace-like Ag@ZIF-8 core/shell heterostructure nanowires for high-performance plasmonic SERS detection. *Chem Eng J.* 2019;371:26-33.

70. Sindoro M, Granick S. Voids and yolk-shells from crystals that coat particles. *J Am Chem Soc.* 2014;136:13471-13473.

71. Osterrrieth JW, Wright D, Noh H, et al. Core-shell gold nanorod@zirconium-based metal-organic framework composites as in situ size-selective raman probes. *J Am Chem Soc.* 2019;141:3893-3900.

72. Kuo CH, Tang Y, Chou LY, et al. Yolk-shell nanocrystal@ZIF-8 nanostructures for gas-phase heterogeneous catalysis with selectivity control. *J Am Chem Soc.* 2012;134:14345-14348.

73. Yang Q, Liu W, Wang B, et al. Regulating the spatial distribution of metal nanoparticles within metal-organic frameworks to enhance catalytic efficiency. *Nat Commun.* 2017;8:14429.
74. Zhan GW, Zeng HC. Synthesis and functionalization of oriented metal-organic framework nanosheets: toward a series of 2D catalysts. *Adv Funct Mater.* 2016;26:3268-3281.

75. Zhan WW, Kuang Q, Zhou JZ, Kong XJ, Xie ZX, Zheng LS. Semiconductor-metal-organic framework core-shell heterostructures: a case of ZnO@ZIF-8 nanorods with selective photoelectrochemical response. *J Am Chem Soc.* 2013;135:1926-1933.

76. Li SZ, Zhang WN, Zhu YN, Zhao Q, Huo FW. Synthesis of MOFs and their composite structures through sacrificial-template strategy. *Cryst Growth Des.* 2015;15:1017-1021.

77. Zanchetta E, Malfatti L, Ricco R, et al. ZnO as an efficient nucleating agent for rapid, room temperature synthesis and patterning of Zn-based metal-organic frameworks. *Chem Mater.* 2015;27:690-699.

78. Hu Z, Mi Y, Ji Y, et al. Multiplasmon modes for enhancing the photocatalytic activity of Au/Ag/Cu3O core-shell nanorods. *Nanoscale.* 2019;11:16445-16454.

79. Tao S, Yang M, Chen HH, Ren MY, Chen GW. Microfluidic synthesis of Ag@Cu3O core-shell nanoparticles with enhanced photocatalytic activity. *J Colloid Interface Sci.* 2017;486:16-26.

80. Kuo CH, Hua TE, Huang MH. Au nanocrystal-directed growth of Au-Cu3O core-shell heterostructures with precise morphological control. *J Am Chem Soc.* 2009;131:17871-17878.

81. Yu Y, Wu XJ, Zhao M, et al. Anodized aluminum oxide templated synthesis of metal-organic frameworks used as membrane reactors. *Angew Chem Int Ed.* 2017;56:578-581.

82. Robatjazi H, Weinberg D, Swearengin DF, et al. Metal-organic frameworks tailor the properties of aluminum nanocrystals. *Sci Adv.* 2019;5:eaaav3340.

83. Wolf A, Diestel L, Lübkmann F, et al. Plasmonic semiconductor nanocarriers in a metal-organic framework structure and their in situ cation exchange. *Chem Mater.* 2016;28:7511-7518.

84. Khan MW, Zhang BY, Xu K, et al. Plasmonic metal-organic framework nanocomposites enabled by degenerately doped molybdenum oxides. *J Colloid Interface Sci.* 2021;586:305-314.

85. So MC, Jin S, Son HJ, Wiederscheidt GP, Farha OK, Hupp JT. Layer-by-layer fabrication of oriented porous thin films based on porphyrin-containing metal-organic frameworks. *J Am Chem Soc.* 2013;135:15698-15701.

86. Shekhah O, Wang H, Strunskus T, et al. Layer-by-layer growth of oriented metal organic polymers on a functionalized organic surface. *Langmuir.* 2007;23:7440-7442.

87. Himman JG, Turner JG, Hofmann DM, Murphy CJ. Layer-by-layer synthesis of conformal metal-organic framework shells on gold nanorods. *Chem Mater.* 2018;30:7255-7261.

88. Guselnikova O, Postnikov P, Elashnikov R, Miliutina E, Svoricik V, Lyutakov O. Metal-organic framework (MOF-5) coated SERS active gold gratings: a platform for the selective detection of organic contaminants in soil. *Anal Chim Acta.* 2019;1068:70-79.

89. Zhao M, Yuan K, Wang Y, et al. Metal-organic frameworks as selectivity regulators for hydrogenation reactions. *Nature.* 2016;539:76-80.

90. Dolgopolova EA, Brandt AJ, Ejegbavwo OA, et al. Electronic properties of bimetallic metal-organic frameworks (MOFs): tailoring the density of electronic states through MOF modularity. *J Am Chem Soc.* 2017;139:5201-5209.

91. Choe K, Zheng F, Wang H, et al. Fast and selective semi-hydrogenation of alkenes by palladium nanoparticles sandwiched in metal-organic frameworks. *Angew Chem Int Ed.* 2020;59:3650-3657.

92. Reguera J, Langer J, de Aberasturi DJ, Liz-Marzan LM. Anisotropic metal nanoparticles for surface enhanced Raman scattering. *Chem Soc Rev.* 2017;46:3866-3885.

93. Schluicker S. Surface-enhanced raman spectroscopy: concepts and chemical applications. *Angew Chem Int Ed.* 2014;53:4756-4795.

94. Langer J, Jimenez de Aberasturi D, Aizpurua J, et al. Present and future of surface-enhanced Raman scattering. *ACS Nano.* 2020;14:28-117.

95. Lai HS, Li GK, Xu FG, Zhang ZM. Metal-organic frameworks: opportunities and challenges for surface-enhanced Raman scattering—a review. *J Mater Chem C.* 2020;8:2952-2963.

96. De Marchi S, Vázquez-Iglesias L, Bodelón G, et al. Programmable modular assembly of functional proteins on Raman-encoded zeolitic imidazolate framework-8 (ZIF-8) nanoparticles as SERS tags. *Chem Mater.* 2020;32:5739-5749.

97. Koo WT, Kim SJ, Jang JS, Kim DH, Kim ID. Metal-organic framework coating for the preservation of silver nanowire surface-enhanced Raman scattering platform. *Adv Mater Interfaces.* 2019;6:1900427.

98. Xue DX, Cairns AJ, Belmabkhout Y, et al. Tunable rare-earth fcu-MOFs: a platform for systematic enhancement of CO2 adsorption energetics and uptake. *J Am Chem Soc.* 2013;135:7660-7667.

99. Li G, Kobayashi H, Taylor JM, et al. Hydrogen storage in Pd nanocrystals covered with a metal-organic framework. *Nat Mater.* 2014;13:802-806.

100. Fu YZ, Xin MY, Chong J, Li RP, Huang MJ. Plasmonic gold nanostars@ZIF-8 nanocomposite for the ultrasensitive detection of gaseous formaldehyde. *J Mater Sci.* 2020;56:4151-4160.

101. Lai HS, Shang WJ, Yun YY, Chen DJ, Wu LQ, Xu FG. Uniform arrangement of gold nanoparticles on magnetic core particles with a metal-organic framework shell as a substrate for sensitive and reproducible SERS based assays: Application to the quantitation of Malachite Green and thiram. *Microchim Acta.* 2019;186:144.

102. Xu FG, Shang WJ, Ma GR, Zhu YM, Wu MJ. Metal organic framework wrapped gold nanourchin assembled on filter membrane for fast and sensitive SERS analysis. *Sens Actuators B Chem.* 2021;326:128968.

103. Rodenas T, Luz I, Prieto G, et al. Metal-organic framework nanosheets in polymer composite materials for gas separation. *Nat Mater.* 2015;14:48-55.

104. Chen EX, Qiu M, Zhang YF, et al. Acid and base resistant zirconium polyphenolate-metalloporphyrin scaffolds for efficient CO2 photoreduction. *Adv Mater.* 2018;30:1704388.

105. Li JF, Huang YF, Ding Y, et al. Shell-isolated nanoparticle-enhanced Raman spectroscopy. *Nature.* 2010;464:392-395.
107. Qiao X, Su B, Liu C, et al. Selective Surface enhanced Raman scattering for quantitative detection of lung cancer biomarkers in superparticle@MOF structure. *Adv Mater*. 2018;30:1702275.

108. Ding Q, Wang J, Chen X, et al. Quantitative and sensitive SERS platform with analyte enrichent and filtration function. *Nano Lett*. 2020;20:7304-7312.

109. Röder R, Preiß T, Hirschle P, et al. Multifunctional nanoparticles by coordinate self-assembly of its tagged units with metal organic frameworks. *J Am Chem Soc*. 2017;139:2359-2368.

110. Sugikawa K, Nagata S, Furukawa Y, Kokado K, Sada K. Stable and functional gold nanorod composites with a metal-organic framework crystalline shell. *Chem Mater*. 2013;25:2565-2570.

111. Zhuang J, Kuo CH, Chou LY, Liu DY, Weerapana E, Tsung CK. Optimized metal-organic-framework nanospheres for drug delivery: evaluation of small-molecule encapsulation. *ACS Nano*. 2014;8:2812-2819.

112. He CB, Lu KD, Lin WB. Nanoscale metal-organic frameworks for real-time intracellular pH sensing in live cells. *J Am Chem Soc*. 2014;136:12253-12256.

113. Khaletskaya K, Reboul J, Meilikhov M, et al. Integration of porous coordination polymers and gold nanorods into core-shell mesoscopic composites toward light-induced molecular release. *J Am Chem Soc*. 2013;135:10998-11005.

114. Lu KD, He CB, Lin WB. Nanoscale metal-organic framework for highly effective photodynamic therapy of resistant head and neck cancer. *J Am Chem Soc*. 2014;136:16712-16715.

115. Lawson HD, Walton SP, Chan C. Metal-organic frameworks for drug delivery: a design perspective. *ACS Appl Mater Interfaces*. 2021;13:7004-7020.

116. Deng X, Liang S, Cai X, et al. Yolk-shell structured Au nanostar@metal-organic framework for synergistic chemophotothermal therapy in the second near-infrared window. *Nano Lett*. 2019;19:6772-6780.

117. Li Y, Zhang K, Liu P, et al. Encapsulation of plasmid DNA by nanoscale metal-organic frameworks for efficient gene transportation and expression. *Adv Mater*. 2019;31:1901570.

118. Carrillo-Carrión C, Martinez R, Navarro Poupard MF, et al. Aqueous stable gold nanostar/ZIF-8 nanocomposites for light-triggered release of active cargo inside living cells. *Angew Chem Int Ed*. 2019;58:7078-7082.

119. Zhang H, Hao C, Qu A, et al. Heterostructures of MOFs and nanorods for multimodal imaging. *Adv Funct Mater*. 2018;28:1805320.

120. Shang W, Zeng C, Du Y, et al. Core-shell gold nanorod@metal-organic framework nanoprobes for multimodality diagnosis of glioma. *Adv Mater*. 2017;29:1604381.

121. Chen JJ, Zhu YF, Kasel S. Porphyrin-based metal-organic frameworks for biomedical applications. *Angew Chem Int Ed*. 2021;60:5010-5035.

122. Zeng JY, Zhang MK, Peng MY, Gong D, Zhang XZ. Porphyrinic metal-organic frameworks coated gold nanorods as a versatile nanoplateform for combined photodynamic/photothermal/chemotherapy of tumor. *Adv Funct Mater*. 2018;28:1705451.

123. Zheng G, Kaeler K, Mourikoudis S, et al. Palladium nanoparticle-loaded cellulose paper: a highly efficient, robust, and recyclable self-assembled composite catalytic system. *J Phys Chem Lett*. 2015;6:230-238.

124. Zheng GC, Mourikoudis S, Zhang ZC. Plasmonic metallic heteroneric nanostructures. *Small*. 2020;16:16.

125. Rodrigues TS, da Silva AGM, Camargo PHC. Nanocalysis by noble metal nanoparticles: controlled synthesis for the optimization and understanding of activities. *J Mater Chem A*. 2019;7:5857-5874.

126. Han PF, Martens W, Waclawik ER, Sarina S, Zhu HY. Metal nanoparticle photocatalysts: synthesis, characterization, and application. *Part Part Syst Char*. 2018;35:1700489-370.

127. Yang D, Gates BC. Catalysis by metal organic frameworks: perspective and suggestions for future research. *ACS Catal*. 2019;9:1779-1798.

128. Qin JS, Du DY, Guan W, et al. Ultrastable polyolymbydate-based metal organic frameworks as highly active electrocatalysts for hydrogen generation from water. *J Am Chem Soc*. 2015;137:7169-7177.

129. Yuan S, Liu TF, Feng D, et al. A single crystalline porphyrinic titanium metal-organic framework. *Chem Sci*. 2015;6:3926-3930.

130. Kornienko N, Zhao Y, Kley CS, et al. Metal-organic frameworks for electrocatalytic reduction of carbon dioxide. *J Am Chem Soc*. 2015;137:14129-14135.

131. Meyer K, Ranaocchiari M, van Bokhoven JA. Metal organic frameworks for photo-catalytic water splitting. *Energy Environ Sci*. 2018;11:1923-1937.

132. Zhao S, Wang Y, Dong J, et al. Ultrathin metal-organic framework nanosheets for electrocatalytic oxygen evolution. *Nat Energy*. 2016;1:1-10.

133. Diercks CS, Liu Y, Cordova KE, Yaghi OM. The role of reticular chemistry in the design of CO₂ reduction catalysts. *Nat Mater*. 2018;17:301-307.

134. Guo J, Wan Y, Zhu YF, Zhao MT, Tang ZY. Advanced photocatalysts based on metal nanoparticle/metal-organic framework composites. *Nano Res*. 2020. https://doi.org/10.1007/s12274-020-3182-1

135. Yang QH, Xu Q, Yu SH, Jiang HL. Pd nanocubes@ZIF-8: integration of plasmon-driven photothermal conversion with a metal-organic framework for efficient and selective catalysis. *Angew Chem Int Ed*. 2016;55:3685-3689.

136. Sumida K, Rogow DL, Mason JA, et al. Carbon dioxide capture in metal-organic frameworks. *Chem Rev*. 2012;112:724-781.

137. Zhang W, Lu G, Cui C, et al. A family of metal-organic frameworks exhibiting size-selective catalysis with encapsulated noble-metal nanoparticles. *Adv Mater*. 2014;26:4056-4060.

138. Wang SB, Wang XC. Multifunctional metal-organic frameworks for photocatalysis. *Small*. 2015;11:3097-3112.

139. Zhao M, Deng K, He L, et al. Core-shell palladium nanoparticle@metal-organic frameworks as multifunctional catalysts for cascade reactions. *J Am Chem Soc*. 2014;136:1738-1741.

140. Li XL, Guo ZY, Xiao CX, Goh TW, Tesfagaber D, Huang WY. Tandem catalysis by palladium nanoclusters encapsulated in metal-organic frameworks. *ACS Catal*. 2014;4:3490-3497.

141. Zhang X, Fan Y, You E, et al. MOF encapsulated sub-nm Pd skin/Au nanoparticles as antenna-reactor plasmonic catalyst for light driven CO₂ hydrogenation. *Nano Energy*. 2021;84:105950.

142. Choi KM, Kim D, Rungtaweevoranit B, et al. Plasmon-enhanced photo catalytic CO₂ conversion within metal organic frameworks under visible light. *J Am Chem Soc*. 2017;139:556-362.

143. Li D, Yu S-H, Jiang H-L. From UV to near-infrared light-responsive metal-organic framework composites: plasmon and
upconversion enhanced photocatalysis. *Adv Mater.* 2018;30:1707377.

**AUTHOR BIOGRAPHIES**

**Guangchao Zheng** obtained his MSc degree in Chemistry from University of Science and Technology of China in 2012. He received his PhD degree in 2015 from University of Vigo (Spain) under the supervision of Professors Jorge Pérez-Juste and Luis M. Liz-Marzán. Then, he worked as research associate (2016–2017) and research fellow (2017–2019) in The Hong Kong Polytechnic University. Now he works at Zhengzhou University (China) as Associate Professor. His current research interests include the structure-oriented application of noble metal nanoparticles in the field of surface-enhanced spectroscopy (SERS/SEF), catalysis and chiral nanoplasmonics.

**Isabel Pastoriza-Santos** obtained her PhD degree in chemistry at the Universidad de Vigo (2001). She worked as a postdoctoral fellow at the University of Melbourne (Australia) between 2002 and 2003. In 2004 she got a postdoctoral research position at the University of Vigo. In 2009, she obtained a faculty position at the Department of Physical Chemistry of the University of Vigo. She is co-author of about 145 articles. Her current interests include the synthesis of plasmonic nanoparticles and nanocomposites, as well as their use in sensing and catalysis.

**Luis M. Liz-Marzán** is Ikerbasque Professor and Scientific Director of CIC biomaGUNE, in San Sebastián (Spain), since 2012. He graduated in chemistry from the University of Santiago de Compostela, was postdoc at Utrecht University and Professor at the University of Vigo (1995–2012). He is a member of the Spanish Royal Academy of Sciences and Academia Europaea, among other awards and recognitions. Liz-Marzán is considered a pioneer in the colloidal synthesis and self-assembly of metal nanocrystals, as well as the characterization and application of their plasmonic properties. His recent research focuses on the biomedical applications of plasmonic nanostructures.

**How to cite this article:** Zheng G, Pastoriza-Santos I, Pérez-Juste J, Liz-Marzán LM. Plasmonic metal-organic frameworks. *SmartMat.* 2021;2:446-465. https://doi.org/10.1002/smm2.1047