reactive plasmonics

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Plasmonic Catalysis: new routes for sunlight into chemical energy conversion

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As of 2020, the majority of hydrogen (~95%) is produced from fossil fuels by steam reforming of natural gas, partial oxidation of methane, and coal gasification. Other methods of hydrogen production include biomass gasification and electrolysis of water. The production of hydrogen plays a key role in any industrialized society, since hydrogen is required for many essential chemical processes.

As of 2019, roughly **70 million tons of hydrogen are produced annually** worldwide for various uses, such as, oil refining, and in the production of ammonia (Haber process) and methanol (reduction of carbon monoxide), and also as a fuel in transportation. **The hydrogen generation market is expected to be valued at US$115.25 billion in 2017**.

Commercial hydrogen producers and petroleum refineries use steam-methane reforming to separate hydrogen atoms from carbon atoms in methane (CH_4). In steam-methane reforming, high-temperature steam (1,300°F to 1,800°F) under 3–25 bar pressure reacts with methane in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide.

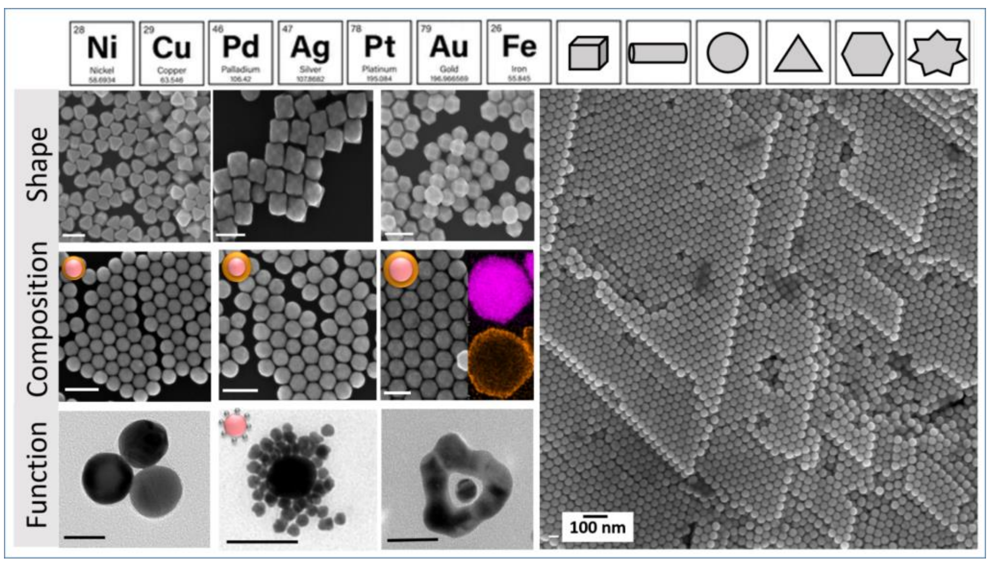


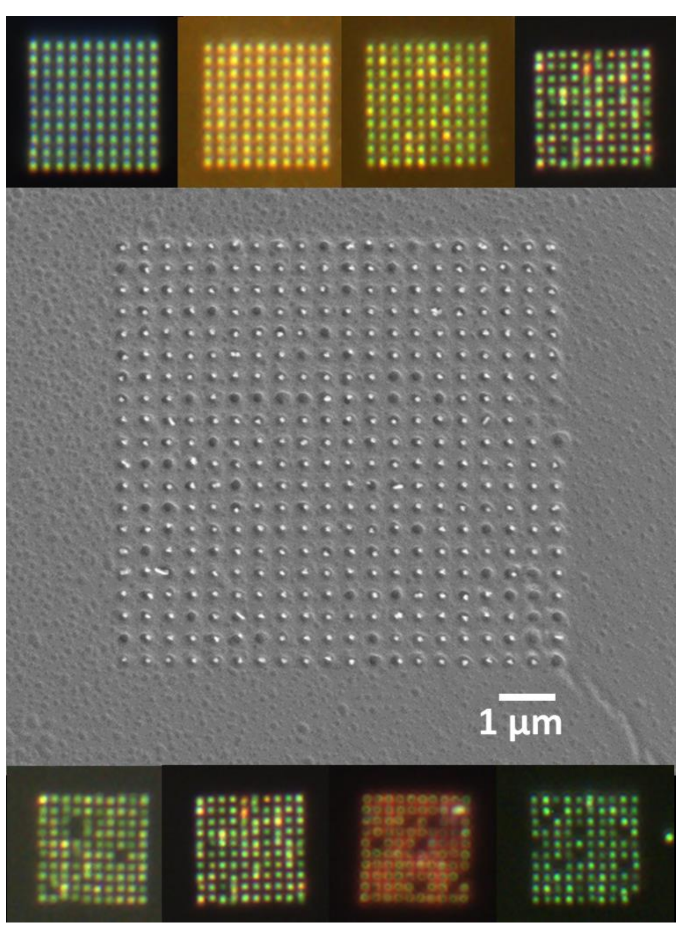
Figure 1: **Scalability.** Bottom-up chemical synthesis of new plasmonic-catalytic colloids. *Large-scale production of new photocatalysts. On a routine synthesis it is possible to obtain on the order of 10^{10} nanoparticles with low size dispersion and excellent optical and catalytic activity. Scale bars: 100 nm.*

Summary: Catalysis Condition and TOF in Published Papers

No.	Journal	Cat./Support	Additive	Visible Light /Dark	Temp. [°C]	H_2 production rate [mmol g^{-1} h^{-1}]
1	Adv. Mater. 2019	AuPd/NH2-N-rGO	No	Dark	25	41940
2	J. Mater. Chem. A, 2019	AgPd NWs/g-C3N4	No	Light	25	3925
3	J. Mater. Chem. A, 2018	Ag@AgPd NWs-PVP	No	Dark	25	3458
4	ACS Catal. 2019	AgPd@Pd-CTAC	Sodium Formate	Dark	30	850
4	ACS Catal. 2019	AgPd@Pd-CTAC	No	Dark	30	550
5	**Our Work**	**Au@AuPd/glass slide**	**No**	**Light**	**30**	**44.4**
6	J. Am. Chem. Soc. 2015	Pd-Tipped Au NRs-CTAB	No	Light	25	11
7	ACS Energy Lett. 2017	Au@Pd/MOFs	No	Light	30	5.46
8	RSC Adv., 2017	Au/Pd Nano-DogBones-CTAB	No	Light	15	1.05

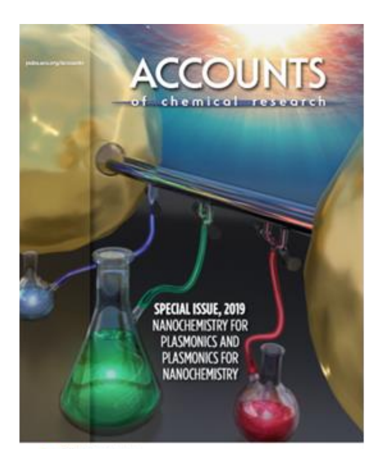
Figure 2: Hydrogen production using sunlight. *Comparison between different catalytic and photocatalytic materials towards hydrogen production. It is possible to obtain photocatalysts that can operate under sunlight conditions, close to the best outperforming catalysts.*

Figure 3: 2D-flow reactors. Large area AuNP patterning for electro- and photo electrochemistry. *Photographs of large-scale AuNP assembly printed on ITO glass substrate. Bright-field optical images of ITO, ITO-Au, ITO-PDMS, and ITO-PDMS-Au. Scale bars: 10 µm. Cyclic voltammogram of four samples for ferrocyanide/ferricyanide redox couple, demonstrating the capability of technique to create direct electrical contact for charge transfer. Schematic of band diagram of Au/TiO2 Schottky junction, whose barrier can be overcome by plasmon-induced hot electrons in Au, as shown in the photocurrent measurement next to it.*



Optical modes engineering in metallic and dielectric nanoparticles could open new paths for assisting chemical transformations using sunlight. In recent years, we have investigated these phenomena at the single nanoparticle level in order to unravel the mechanisms inducing catalytic transformations at these illuminated interfaces [1-11]. In both cases - plasmonic and photonic catalysis - the possibility to study the light-induced chemical transformations at the single particle level helped us to unravel:

the energy of the carriers [5], the spatial-resolved reactivity [3, 6, 9, 10, 11], the optimum geometry [2, 3, 4, 11], the dynamic processes affecting these catalysts [1, 3, 8], among others. Gaining a nanoscopic insight on these processes could aid in the rational design of novel plasmonic and photonic photocatalysts at Industrial levels.



Acc. Chem. Res. 2019, 52, 9, 2525–2535

Recent references of our work: [**1**] M. Barella, et al., ACS Nano, ASAP (**2020**) / [**2**] L. Hüttenhofer, et al., ACS Nano, 14 (2), 2456-2464 (**2020**) / [**3**] J. Gargiulo, et al., Acc. Chem. Res. 52, 2525-2535 (**2019**) / [**4**] S. Lee, et al., Angew. Chem. 58, 15890-15894 (**2019**) / [**5**] E. Pensa, et al., Nano Letters. 19, 1867-1874 (**2019**) / [**6**] S. Simoncelli, et al., Faraday Diss. 214, 73-87 (**2019**) / [**7**] E. Cortés, Science, 362, 28-29 (**2018**) / [**8**] R. Berte, at al., Phys. Rev. Lett. 121, 253902 (**2018**) / [**9**] S. Simoncelli, et al., Nano Letters 18, 3400–3406 (**2018**) / [**10**] S. Simoncelli et al., ACS Nano 12, 2184–2192 (**2018**) / [**11**] E. Cortés, et al., Nature Comm. 8, 14880 (**2017**).

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