It is an ideal approach to utilize solar energy instead of heat to drive organic reactions. In this communication, we report the use of Pd–Ag alloy nanocages for light-driven catalytic hydrogenation, in which Pd provides active sites for hydrogenation reactions and Ag offers plasmonic properties to convert light into heat.

Catalysis is a process that increases the rate of a chemical reaction due to the participation of a catalyst so that the reaction can occur more efficiently with less energy input. Given the fact that fossil fuels have been excessively consumed, it is imperative to explore the possibilities of harvesting solar energy to perform chemical transformations for energy conversion and storage. Despite the success in conventional semiconductor-based photocatalysis, it remains a grand challenge to overcome the limitation that most semiconductor materials cannot provide active sites for many chemical reactions such as organic reactions. In contrast, metallic nanostructures are often active catalysts for a variety of organic reactions. For this reason, the surface plasmon of metals, which converts light into heat through a photothermal effect to sustain the reactions, can offer an alternative approach to solar-to-chemical energy conversion at the intersection with catalysis. In one of our recent works, we have designed a class of unique Pd concave nanostructures that can achieve the catalytic hydrogenation efficiency under 100 mW cm\(^{-2}\) full-spectrum irradiation at room temperature comparable to that thermally driven at 70 °C. The nanostructures possess a large quantity of active sites for the reaction with local heat intensively generated through the photothermal effect, while the effect of plasmonic hot electrons disfavors the hydrogenation process.

To achieve high efficiency in such plasmonic-driven organic reactions, the catalysts should have a large number of active catalytic sites for the reactions and sufficient plasmonic cross-sections for light harvesting. In most cases, these two requirements can hardly be both met in a single material despite the existing success. For instance, catalytic hydrogenation is one of the simplest transformations in organic chemistry, which has been extensively involved in various chemical processes. Pd is the most active catalyst for the hydrogenation among various noble metals and alloys due to its strong interactions with molecular hydrogen (H\(_2\)). However, Pd nanoparticles generally possess significantly smaller plasmonic cross sections than Ag and Au due to intrinsic factors such as dielectric functions, and are often considered as a non-plasmonic material. In addition, the Pd nanocrystals synthesized in the solution phase typically exhibit plasmonic bands in the UV region with small cross sections limited by their small sizes, although well-defined shapes and surface facets can be achieved for tuning catalytic activities in thermal reactions. In this communication, we propose to combine the active sites offered by Pd with the strong plasmonic properties provided by Ag, which enables efficient plasmonic-driven hydrogenation reactions as illustrated in Fig. 1. As such, the chemical transformations can be accomplished by utilizing solar energy instead of conventional heat.

In terms of solar energy utilization, ideally it prefers to tune the plasmonic band of metallic nanostructures to cover a wide range of wavelengths simply because UV light only accounts for a small portion of the solar spectrum (ca. 5%) in comparison with visible (400 < \(\lambda\) < 800 nm, ca. 43%) and near-infrared (NIR) light (800 < \(\lambda\) < 2500 nm, ca. 52%). In principle, their plasmonic bands can be tuned toward the visible-NIR spectral region or be broadened by increasing particle sizes, lowering shape symmetries or making hollow structures. In consideration of catalytic activities, we decide to take hollow structures as a model system to demonstrate our concept, as the high surface-
to-volume ratio enabled by the hollow nature may help increase the number of active reaction sites.

The selected hollow structures, Pd–Ag alloy nanocages, are synthesized via a galvanic replacement method using Ag nanocubes as sacrificial templates. In the synthesis, the Ag nanocubes enclosed by {100} facets are first prepared by following our well-established polyol protocol in which silver trifluoroacetate is used as an Ag precursor, and sodium hydrosulfide and hydrochloride acid serve as a catalyst and an etchant, respectively. As displayed in Fig. 2a, such a protocol typically produces Ag nanocubes with sharp corners and edges with an average edge length of 60 nm. Further, the Ag nanocubes are transformed into Pd–Ag alloy nanocages through their galvanic replacement with K2PdCl4 solution in the presence of stabilizer poly(vinyl pyrrolidone) (PVP). As different amounts of K2PdCl4 are added into this synthesis (see Table S1† for the added amounts of K2PdCl4), the morphologies of nanocrystals are significantly altered. As displayed in transmission electron microscopy (TEM) images (Fig. 2a–(g)), Ag nanocubes gradually evolve into hollow structures with pinholes formed on walls, edges and corners (namely, nanocages). The evolution process that turns the Pd–Ag alloy nanocrystals more hollow and porous has been identified by scanning transmission electron microscopy (STEM) (Fig. S1†). The high-resolution TEM (HRTEM) image in Fig. 1h shows that the resulting nanocages are still single crystals enclosed by {100} facets as indicated by the continuous lattice fringes. According to inductively coupled plasma mass spectrometry (ICP-MS) measurements, their compositions are transformed from pure Ag to Pd–Ag with Pd contents up to 62.67% in weight. To further verify the alloy nature of samples, we have collected X-ray diffraction (XRD) patterns (Fig. S2†). For the four samples with different compositions, the diffraction peaks gradually shift to higher 2θ in the range of the standard peaks from pure Ag (JCPDS #04-0783) and pure Pd (JCPDS #46-1043) as the Pd composition increases, in agreement with Vegard’s law. This set of data clearly shows that our obtained nanocages are Pd–Ag alloys.

We first evaluate the plasmonic properties of Pd–Ag alloy nanocages. As Pd is the active component for catalyzing hydrogenation reactions, we intend to maintain the same amount of Pd for all the samples used in the characterization. Fig. 3a displays the UV-vis extinction spectra of samples, showing the extension of plasmonic bands toward NIR with the...
increase of Pd content. This band shift should be ascribed to the shape evolution into hollow structures, as the reduction in the wall thickness of hollow structures generally induces a red-shift of the extinction peak. According to the calculation results in the literature, the magnitudes of plasmonic extinction cross sections only slightly depend on the wall thickness (i.e., the formation of hollow structures). Furthermore, with some holes formed on the hollow structures (i.e., the formation of porous structures in the nanocages), a significant reduction in the magnitudes of cross sections can be observed although the positions of extinction peaks are not further altered. On the other hand, we use the amounts of Pd to determine the concentrations of particles in suspensions in our measurements, and as a result, the number of particles in the suspensions should be substantially reduced when the Pd contents in the alloy nanoparticles are increased. As a sum effect, the extinction of the nanoparticle suspension reaches a turning point at the Pd content of 25.84%. Note that the extinction is the sum of scattering and absorption (i.e., photothermal effect), and the hollow structures particularly favour the absorption. Given that the absorption is the major effect for the surface plasmon of nanocages, we would anticipate that the photothermal effect increases local temperature surrounding the nanocages under light illumination. To assess the photothermal effect, we have measured the temperature changes in the aqueous suspension of Pd–Ag alloy nanocubes under 50 mW cm\(^{-2}\) irradiation (\(\lambda > 400\) nm) (Fig. 3b). It shows that the nanocages can harvest light and induce temperature increase in water. The trend for temperature increase is very consistent with the extinction peak. The positions of extinction peaks are not further altered.

As displayed in Fig. 3b, the yields are still promoted by increasing the ratios of Pd to Ag at room temperature (15 °C). As shown in Fig. 4b, the yields are still promoted by increasing the ratios of Pd to Ag; however, unlike the thermally driven reaction, the activity promotion becomes subtle beyond the point of 44.08% Pd. This feature should be ascribed to the reduction in photothermal capability when the Pd content is too high (shown in Fig. 3b). Thus the dependence of catalytic activities on Pd-to-Ag ratios is the combinative result of active sites and the photothermal effect. To minimize the material cost, 44.08%-Pd Ag alloy nanocubes would be ideal candidates for plasmonic-driven hydrogenation given the higher price of Pd than Ag.

We thus perform systematic studies using the 44.08%-Pd nanocages as catalysts. As shown in Fig. 5a, one can see that the catalytic yields of styrene hydrogenation in the dark gradually increase with the increase of reaction temperatures, which can approach 98% at 70 °C for 1 h. Apparently, this catalytic performance can be readily achieved by switching heating to light illumination.
light illumination. When the light intensities are increased from 0 to 50 mW cm\(^{-2}\), the catalytic performance can be boosted with the yields of ethylbenzene up to 97%. Remarkably, the yield under 50 mW cm\(^{-2}\) irradiation at room temperature is comparable to that thermally driven at 70 °C. In comparison, we have performed the same light-driven hydrogenation reactions using Pd nanocubes and Ag nanocubes as catalysts (Fig. S5†). As expected, the plasmonic band of Pd nanoparticles is mainly confined in the UV spectral region with very small optical cross-sections (see Fig. S3†), no obvious activity enhancement by light irradiation has been observed in the case of Pd nanocubes, limiting the yield to 38%. Although Ag nanocubes have large plasmonic cross sections, they cannot provide an active surface for the hydrogenation. To further confirm the importance of the surface plasmon to catalytic hydrogenation, we have compared the performance of Pd–Ag alloy nanocages with Pd\(_{16}\)Ag\(_{84}\) alloy nanoparticles with a solid structure at a size of 5 nm. As shown in Fig. S5†, the solid alloy nanoparticles show faint activities under \(\lambda > 400\) nm illumination despite their smaller particle sizes (which usually favors the promotion of catalytic activities), as the nanoparticles have limited plasmonic properties in this spectral range (see Fig. S3†). This series of results proves the key role of photothermal conversion in catalytic hydrogenation.

On the other hand, we notice from Fig. 4 that the light irradiation significantly enhances the catalytic performance for the Pd–Ag nanocrystals with a Pd content below 44.08% except the sample with 25.84% Pd (i.e., 52% yield at 60 °C in the dark versus 50% yield at room temperature under 50 mW cm\(^{-2}\) illumination). To decode the mechanism, we have performed the light intensity-dependent catalytic hydrogenation from 0 to 75 mW cm\(^{-2}\). As indicated by Fig. 5b, the yields of ethylbenzene using the 44.08%-Pd sample are reduced from 97% to 87% when the light intensity is increased from 50 to 75 mW cm\(^{-2}\). According to our previous research,\(^7\) the dominant effect of plasmonic hot electrons under very strong light illumination would disfavor the hydrogenation process, resulting in this performance decay. Similarly, we have observed the yield reduction from 90% to 40% for the 25.84%-Pd sample by increasing the light intensity from 20 to 75 mW cm\(^{-2}\) (see Fig. S6†). The dominant side effect from plasmonic hot electrons at relatively low light intensity (i.e., the turning point of catalytic yield versus light intensity) observed for the 25.84%-Pd sample should be ascribed to the fact that this sample possesses stronger plasmonic properties than the 44.08%-Pd nanocages. By controlling the light intensity to 20 mW cm\(^{-2}\), the 25.84%-Pd sample can achieve the yield of 90% (Fig. S6†), significantly higher than that obtained at 60 °C in the dark (52%, Fig. 4a). It demonstrates that the photothermal conversion can dramatically facilitate the hydrogenation reaction as long as the hot-electron side effect is not dominant. Thus the light intensity should be a key parameter to the surface plasmon-driven hydrogenation reactions.

In summary, we have developed Pd–Ag alloy nanocages in tunable compositions and structures for light-driven catalytic hydrogenation. In the catalysis, Pd provides active sites for hydrogenation reactions, while Ag offers plasmonic properties to convert light into heat on the nanocrystal surface. With the increase of Pd content, the structures of Pd–Ag alloy nanocrystals turn more hollow and porous, which affect both the number of active sites and plasmonic cross sections. In consideration of Pd usage, one has to minimize the amount of Pd used in catalysts so that the alloy nanocages with 25.84% and 44.08% Pd are the best candidates. As compared with our previous success in bare Pd nanostructures,\(^7\) the 44.08%-Pd nanocages can achieve the same catalytic yield with only half illumination intensity (50 mW cm\(^{-2}\) versus 100 mW cm\(^{-2}\)) and 1/5 Pd (0.04 mg Pd/0.2 mmol styrene versus 2 mg Pd/2 mmol styrene) used. This work provides new insights into the design of plasmonic catalytic materials, and paves the way toward low-cost catalysts for light-driven organic reactions.

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### Notes and references


