Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

A novel AgPd hollow spheres arched on graphene as an efficient catalyst for the dehydrogenation of formic acid at room temperature

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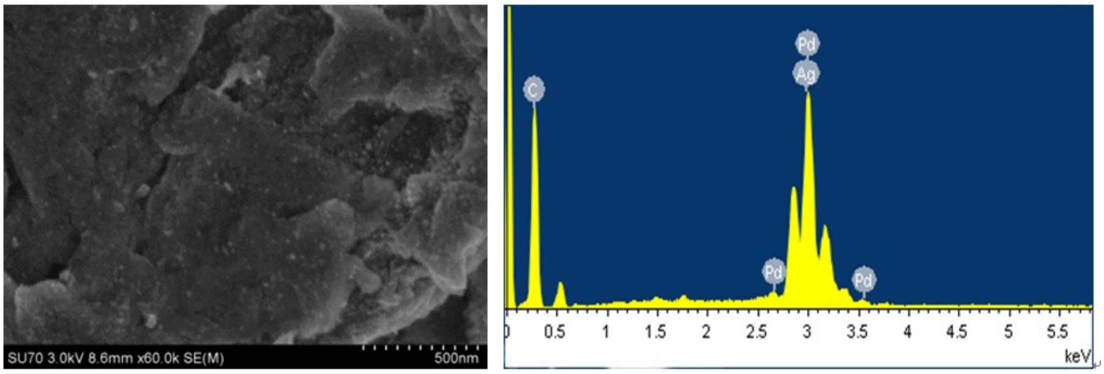

Fig. S1 SEM image and EDS spectrum of AgPd-Hs/G.

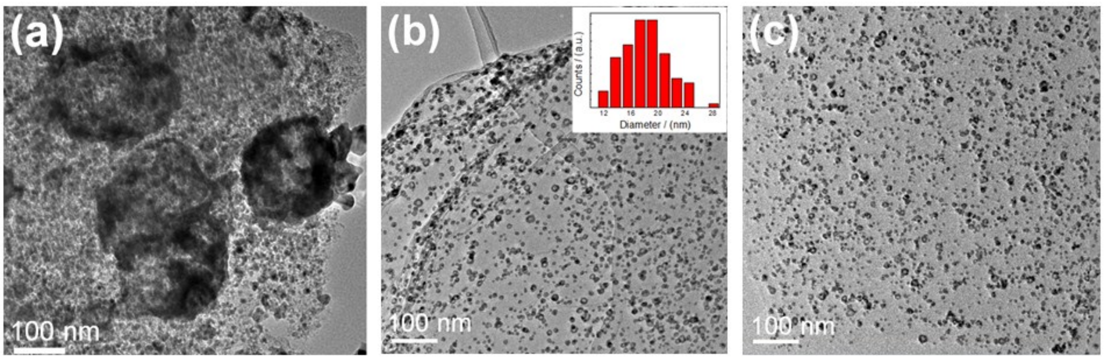

Fig. S2 TEM images of (a) AgPd/C, and AgPd-Hs/G (b) before and (c) after the catalytic performance test. The inset of (b) is the corresponding histograms of particle size distribution.

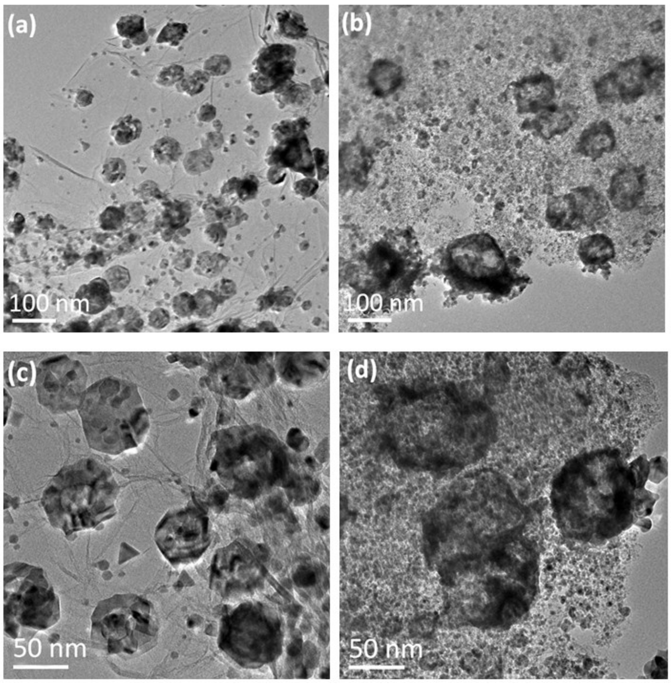

Fig. S3 TEM images of catalysts synthesized without trisodium citrate dihydrate (a, c) and using activated carbon rather than graphene as the support (b, d).

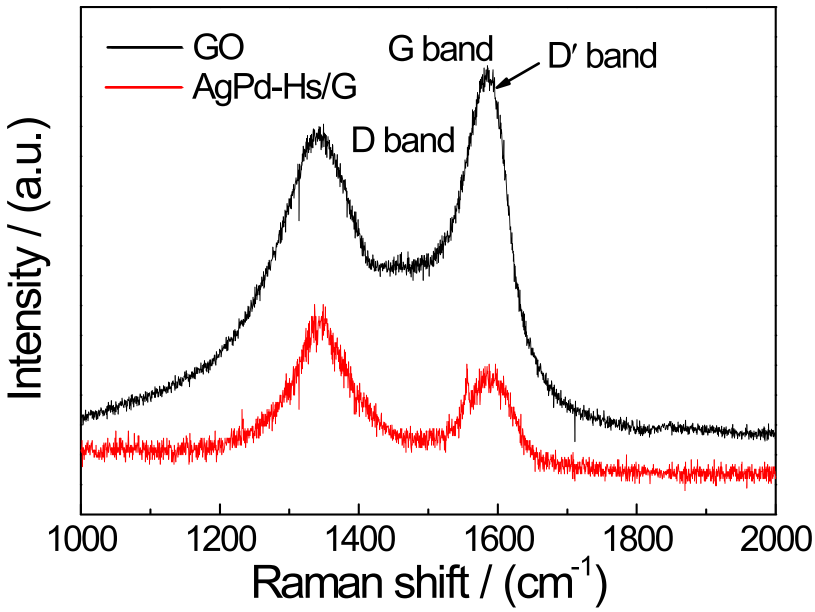

Fig. S4 Raman spectra of GO and AgPd-Hs/G.

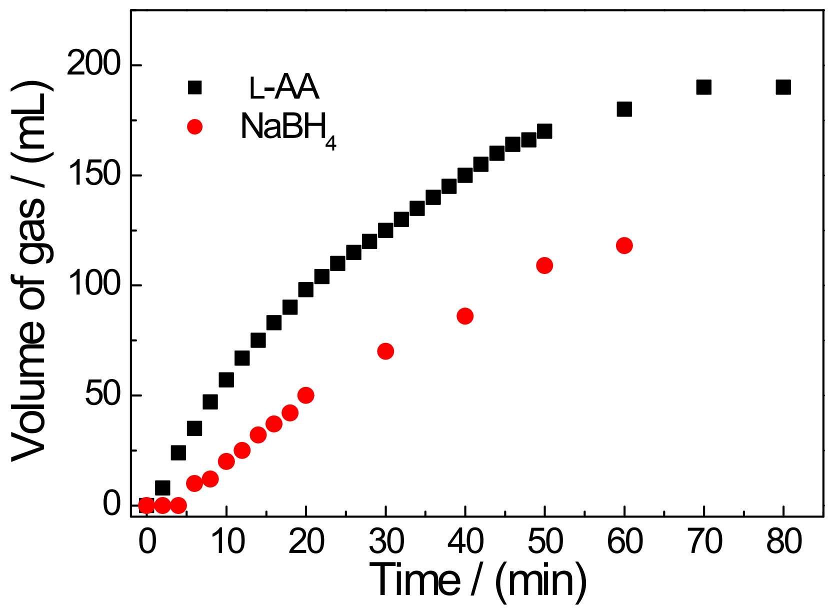

Fig. S5 Gas generation by the decomposition of FA/SF (2.5 M/2.5 M, 2 mL) versus time using different catalysts reduced by L-AA and $NaBH_4$ at 25 ^oC under ambient atmosphere ($m_{catalyst}$=10 mg).

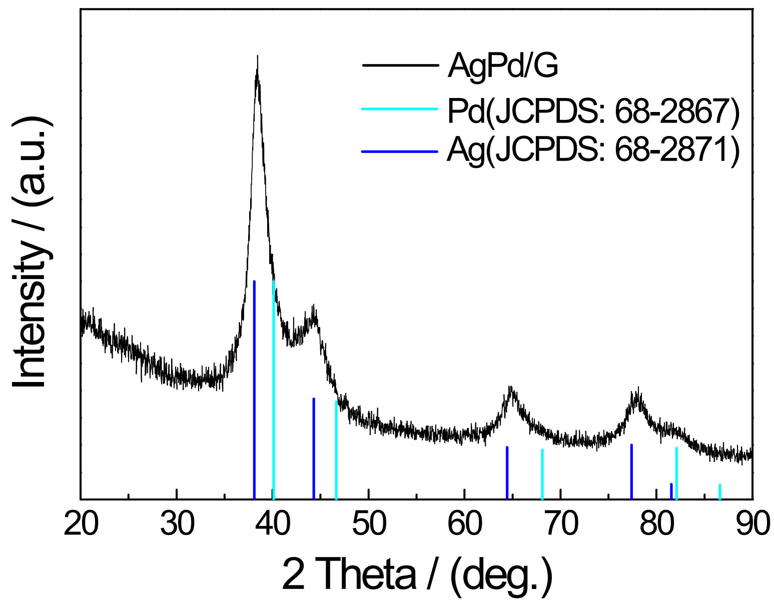

Fig. S6 XRD patterns for the as-synthesized AgPd/G.

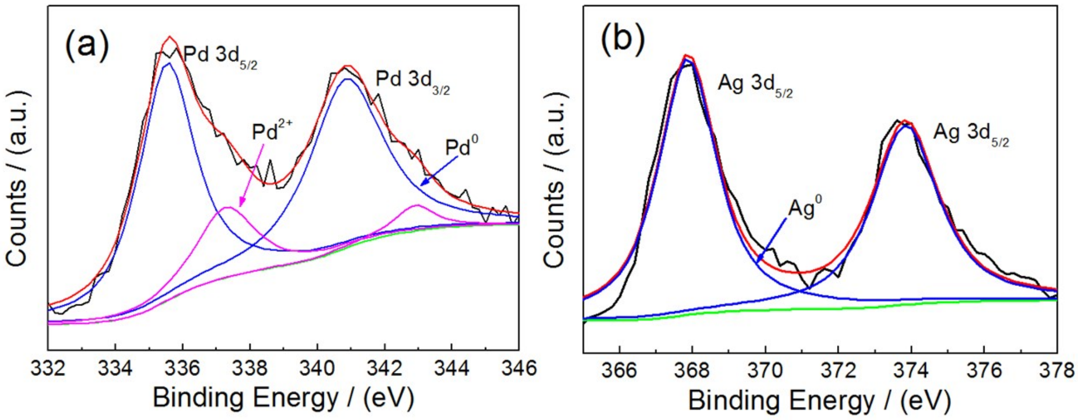

Fig. S7 XPS spectra of Pd 3d (a) and Ag 3d (b) of AgPd/G.

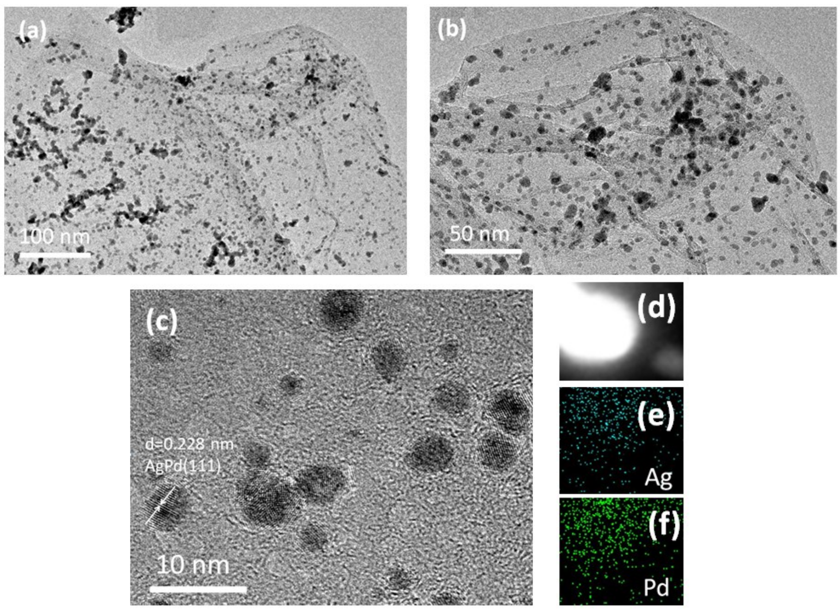

Fig. S8 TEM (a), enlarged TEM (b), HRTEM (c) and HAADF-STEM-EDS mapping images (h, i, j) of AgPd/G.

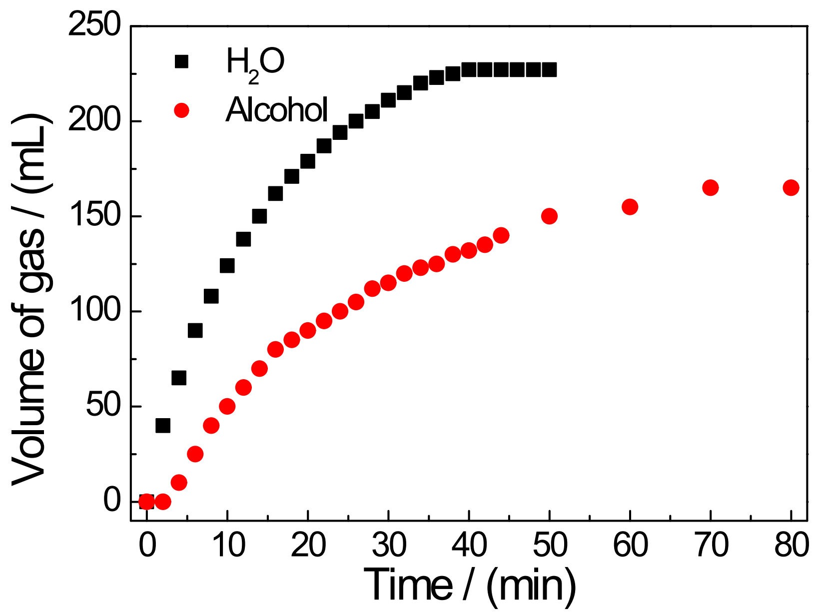

Fig. S9 Gas generation by the decomposition of FA/SF (2.5 M/2.5 M, 2 mL) versus time using different solvents i.e. water and alcohol at 25 ^{o}C under ambient atmosphere ($m_{catalyst}$=10 mg).

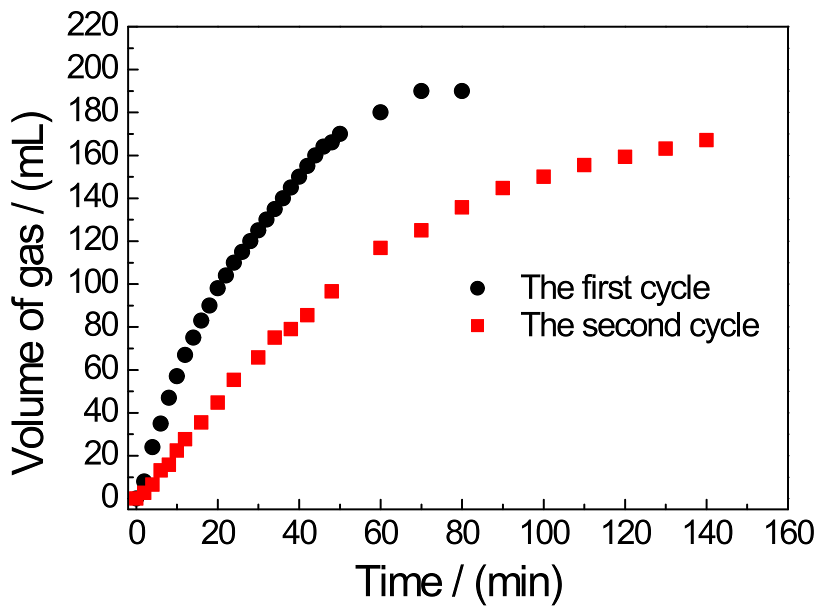

Fig. S10 Two repeated testings of graphene supported AgPd hollow spheres at room temperature ($m_{catalyst}$=10 mg).

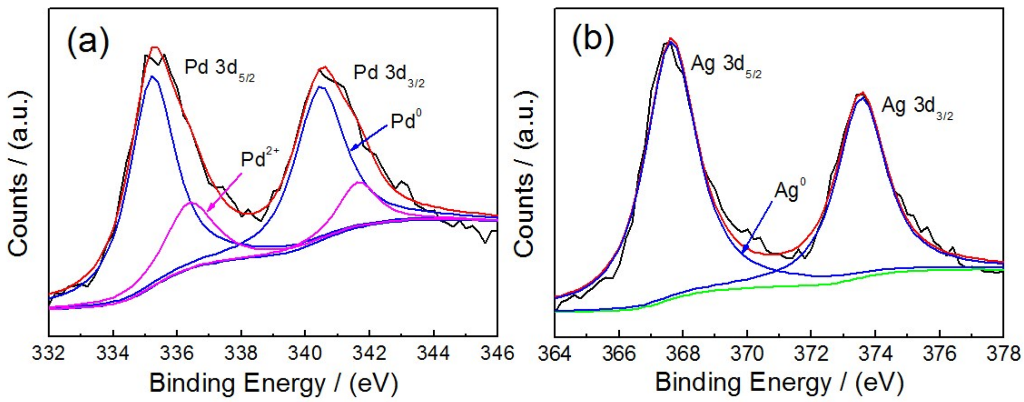

Fig. S11 XPS spectra of Pd 3d (a) and Ag 3d (b) of AgPd-Hs/G after the catalytic performance test.

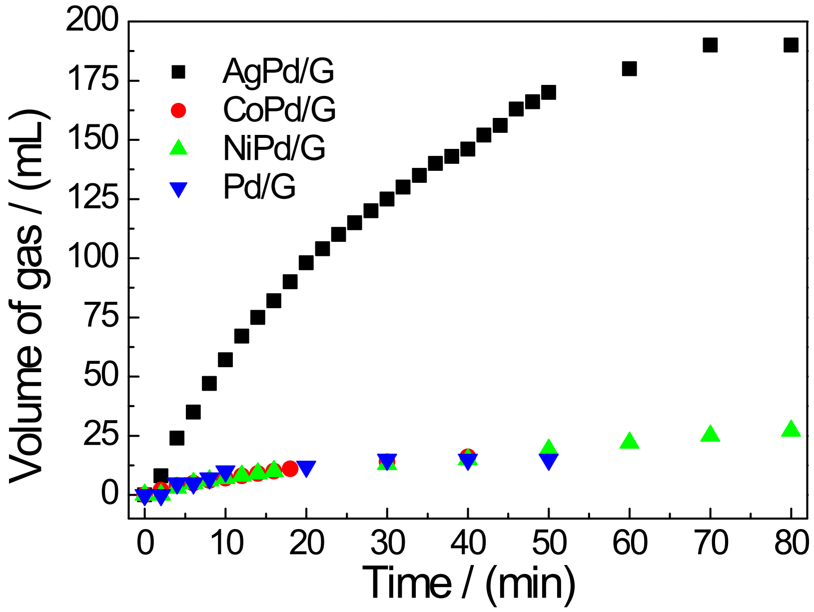

Figure S12 Gas generation by decomposition of FA/SF (2.5 M/2.5 M, 2 mL) versus time using different alloy catalysts at 25 ^{o}C under ambient atmosphere.

Table S1 ICP-MS analysis for the AgPd-Hs/G

catalyst	Pd content (%)	Ag content (%)
AgPd-Hs/G	24.2	16.6

Table S2 Comparison of activities of different catalysts for hydrogen generation from formic acid

Catalyst	T(°C)	TOF	E_a(kJ/mol)	Ref.
AgPd-Hs/G	**25**	**333**	**28**	**Present work**
AgPd/rGO	25	105.2	—	R[1]
Citric acid modified Pd/C	25	143.1	—	R[2]
AgPd	25	150	—	R[3]
CoAuPd/C	25	80	—	R[4]
PdNiAg/C	50	85	20.5	R[5]
Au-Pd	50	230	28	R[6]
AuPd@ED-MIL-101	90	240	—	R[7]
Ag@Pd	20	125	—	R[8]
Pd/C	30	228	—	R[9]
AgAuPd/rGO	25	57.6	—	R[10]
Pd-MnO_x/SiO_2-NH_2	30	290	—	R[11]
Au/CeO_2	80	—	56	R[12]
Pt-Ru-BiO_x/C	80	312	37.3	R[13]
Pd-Au-Dy/C	92	269	98.3	R[14]
PdAu@Au/C	92	300	—	R[15]

Calculation methods:

$$\text{TOF}_{\text{initial}} = \frac{P_{atm}V_{H_2} / RT}{\text{n}_{AgPd}t} \qquad (\text{R}^6)$$

Where TOF is the initial turnover frequency, P_{atm} is the atmospheric pressure, V_{H_2} is the generated volume of H_2 during the first 10 min of the reaction, R is the universal gas constant, T is the temperature (25 °C), n_{AgPd} is the total mole number of Ag and Pd, and t is the reaction time of the first 10 min.

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