Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Amine Functionalized Graphene Nanosheets Supported PdAuNi Alloy Nanoparticles: Efficient Nanocatalyst for the Formic Acid Dehydrogenation

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(Supporting Information)

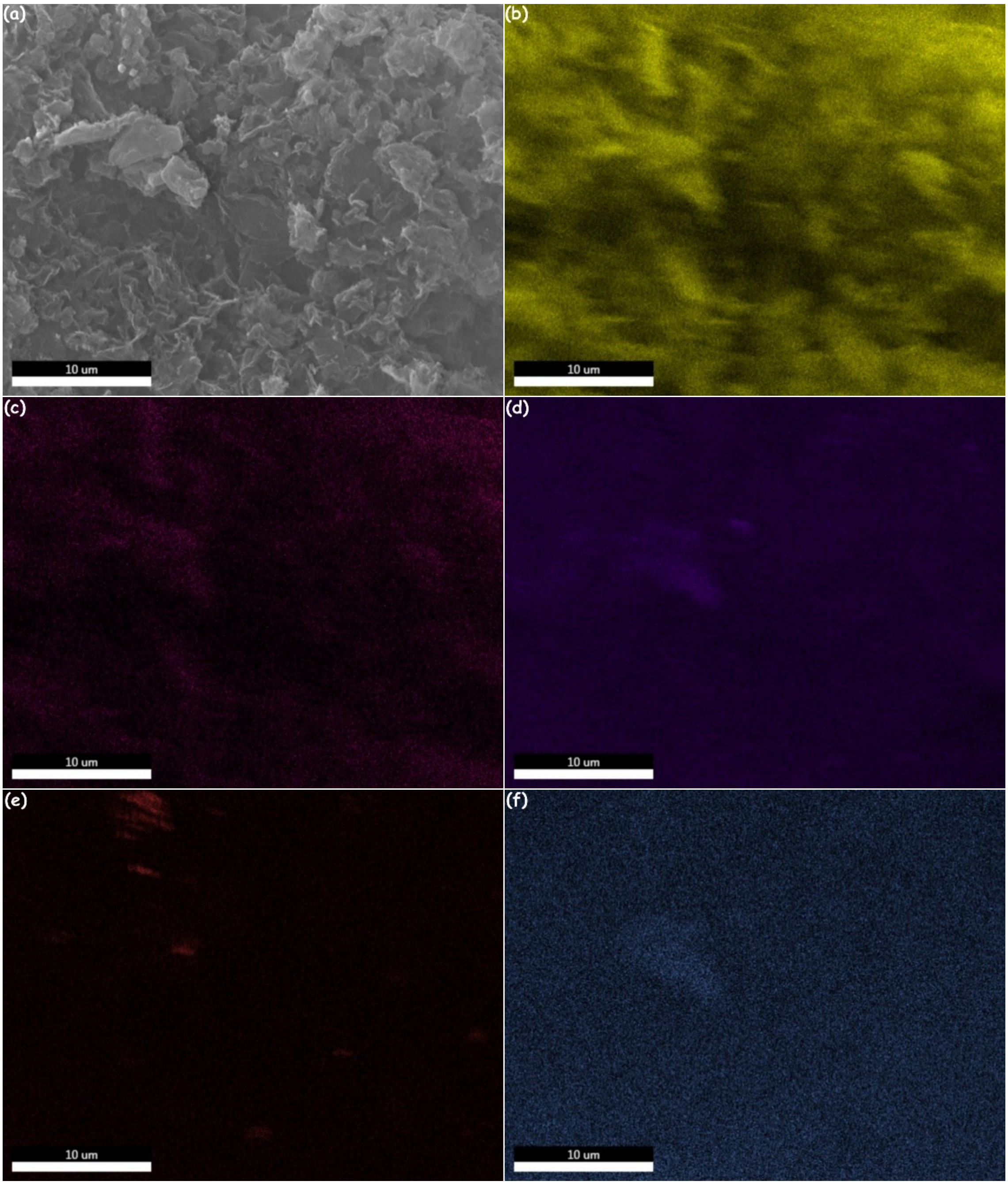

Figure S1. (a) SEM image of PdAuNi/f-GNS and SEM-EDX elemental mapping of PdAuNi/f-GNS for the elements of (b) C, (c) N, (d) Pd, (e) Au and (f) Ni (in all scale bar = 10 μm).

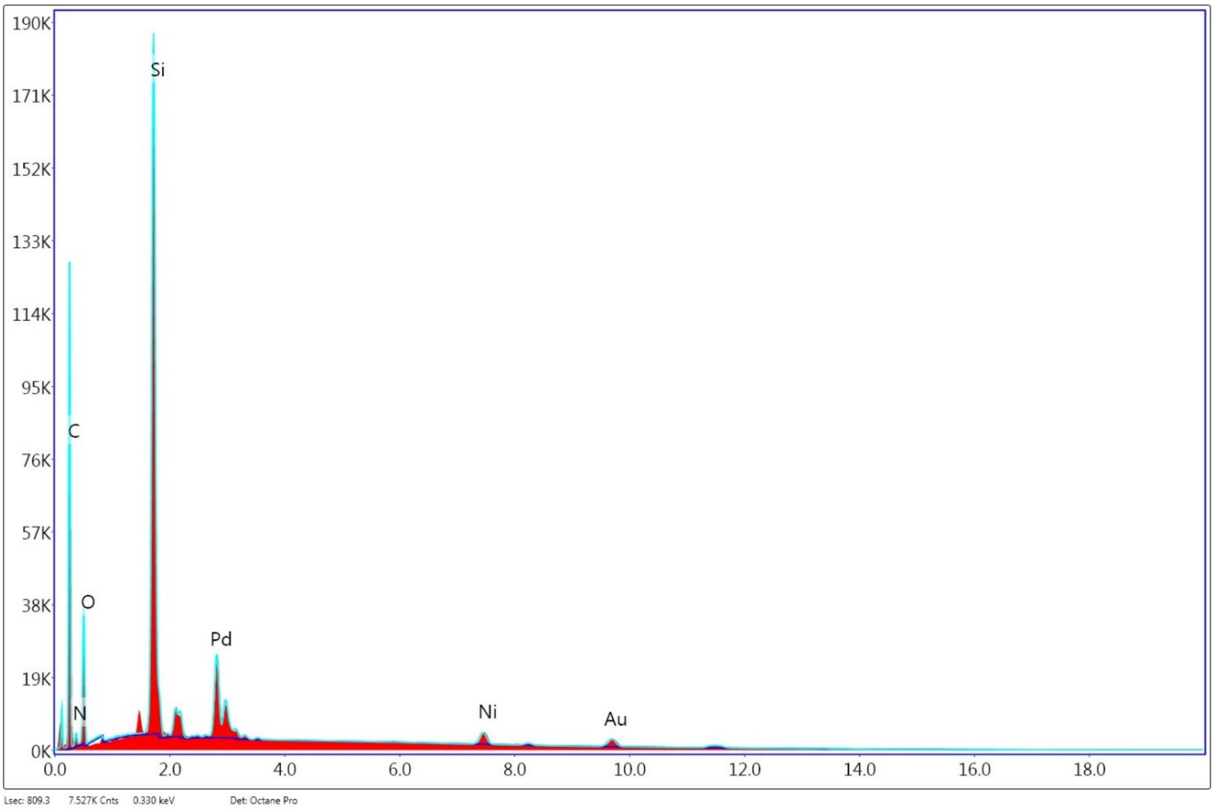

Figure S2. SEM-EDX spectrum of PdAuNi/f-GNS.

NaOH Trap Experiment

NaOH trap (10.0 M NaOH solution) was placed between the jacketed reactor and gas burette. The generated gas during the reaction was passed through the NaOH trap where CO2 was captured (1). Next, the volume of the gas generated from the dehydrogenation of FA was monitored and compared to those without the trap experiment. We observed that the volume of the generated gas decreased by a factor of 2 in the presence of the NaOH trap (Figure S3). This result is indicative of the complete adsorption of CO_2 in NaOH solution (1) and the presence of equivalent molar amounts of CO_2 and H_2 (1.0:1.0) in the product mixture of the PdAuNi/f-GNS catalyzed additive-free aqueous FA dehydrogenation.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \ (\mathbf{1})$$

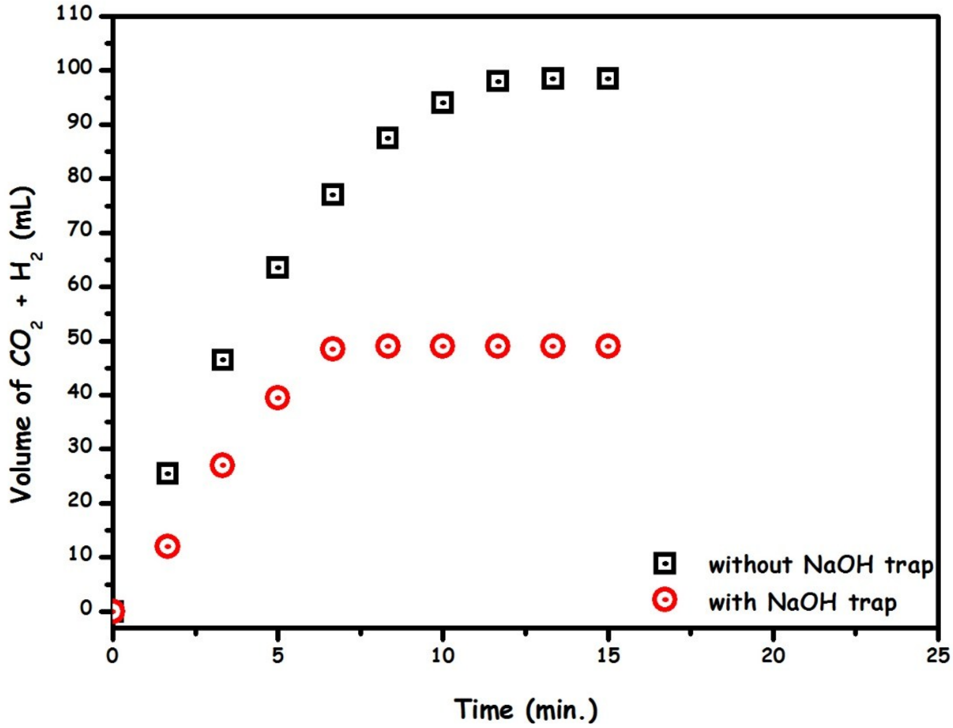

Figure S3. The volume of generated gas (H_2+CO_2) versus time graphs for $Pd_{0.60}Au_{0.20}Ni_{0.20}$/f-GNS ($n_{metal}$ = 20 µmol) catalyzed dehydrogenation of aqueous FA solution (0.22 M) at room temperature in the presence and absence of 10.0 M NaOH trap solution.

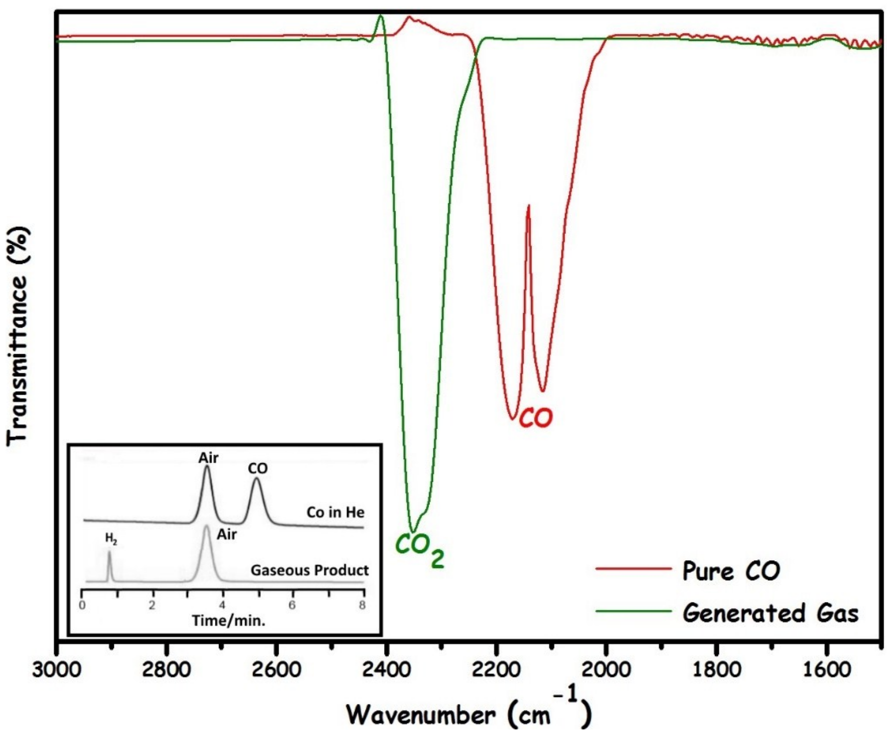

Figure S4. FTIR spectrum and GC chromatograms (inset) of pure CO and the generated gas over $Pd_{0.60}Au_{0.20}Ni_{0.20}$/f-GNS ($n_{metal}$ = 20 µmol) catalyzed dehydrogenation of aqueous FA solution (0.22 M) at room temperature.

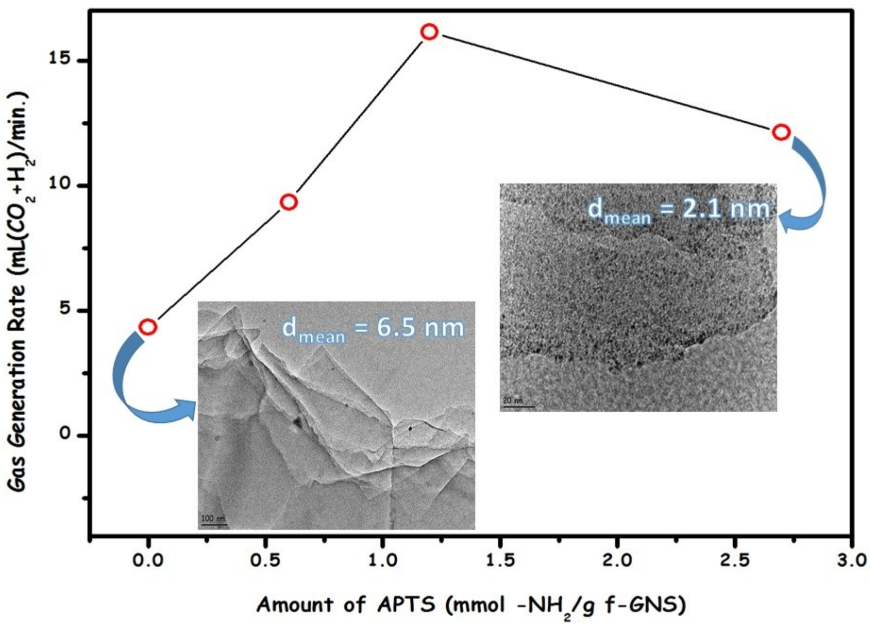

Figure S5. Gas generation rate versus amount of APTS loading for $Pd_{0.60}Au_{0.20}Ni_{0.20}$/f-GNS ($n_{metal}$ = 20 μmol) catalyzed additive-free dehydrogenation of aqueous FA solution (0.22 M) at room temperature and BFTEM images of $Pd_{0.60}Au_{0.20}Ni_{0.20}$/f-GNS samples with 0.0 (d_{mean} = 6.5 nm) and 2.7 mmol NH_2/g GNS (d_{mean} = 2.1 nm) APTS loadings.

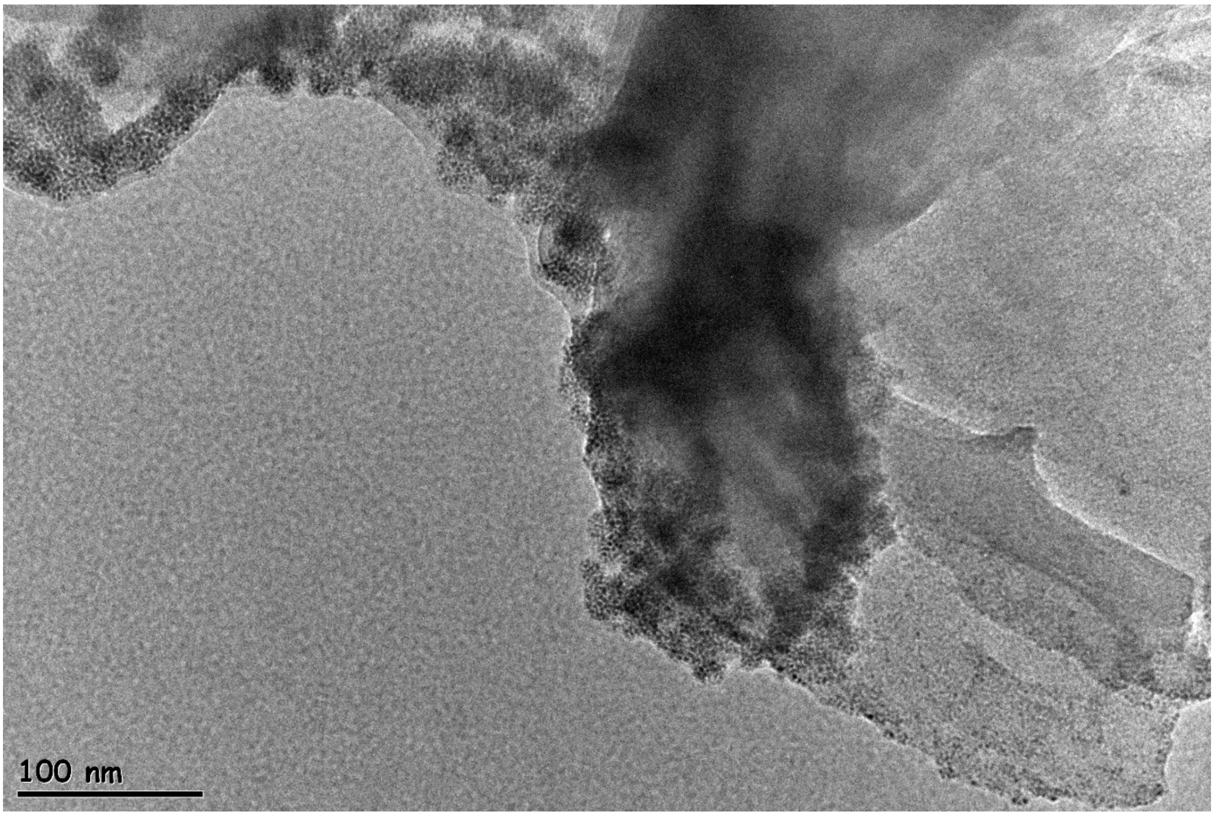

Figure S6. BFTEM image of $Pd_{0.58}Au_{0.22}Ni_{0.20}$/f-GNS nanocatalyst prepared by the conventional impregnation reduction technique.

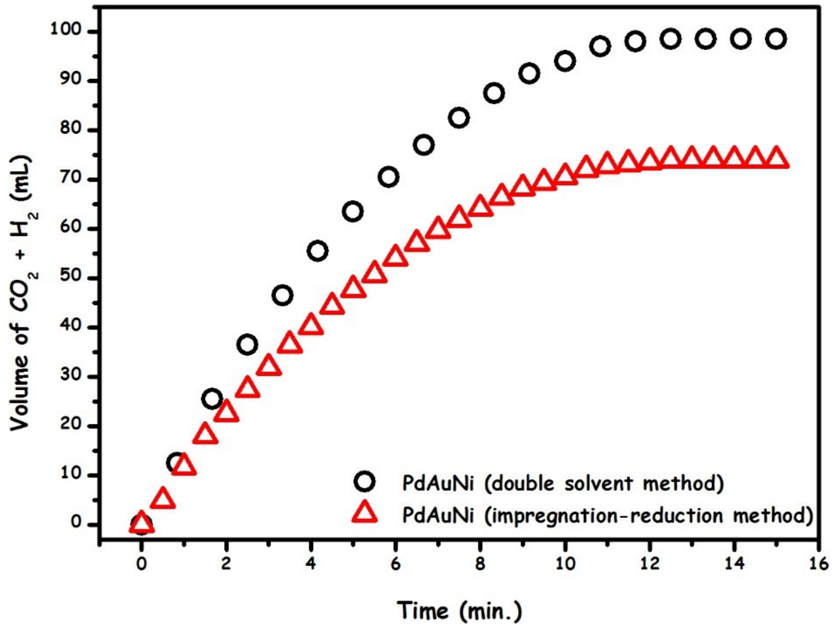

Figure S7. The volume of generated gas (H_2+CO_2) versus time graphs for the dehydrogenation of aqueous FA solution (0.22 M) at room temperature in the presence of $Pd_{0.60}Au_{0.20}Ni_{0.20}$/f-GNS (prepared by double solvent method) and $Pd_{0.58}Au_{0.22}Ni_{0.20}$/f-GNS (prepared by impregnation-reduction method) (in all n_{metal} = 20 μmol).

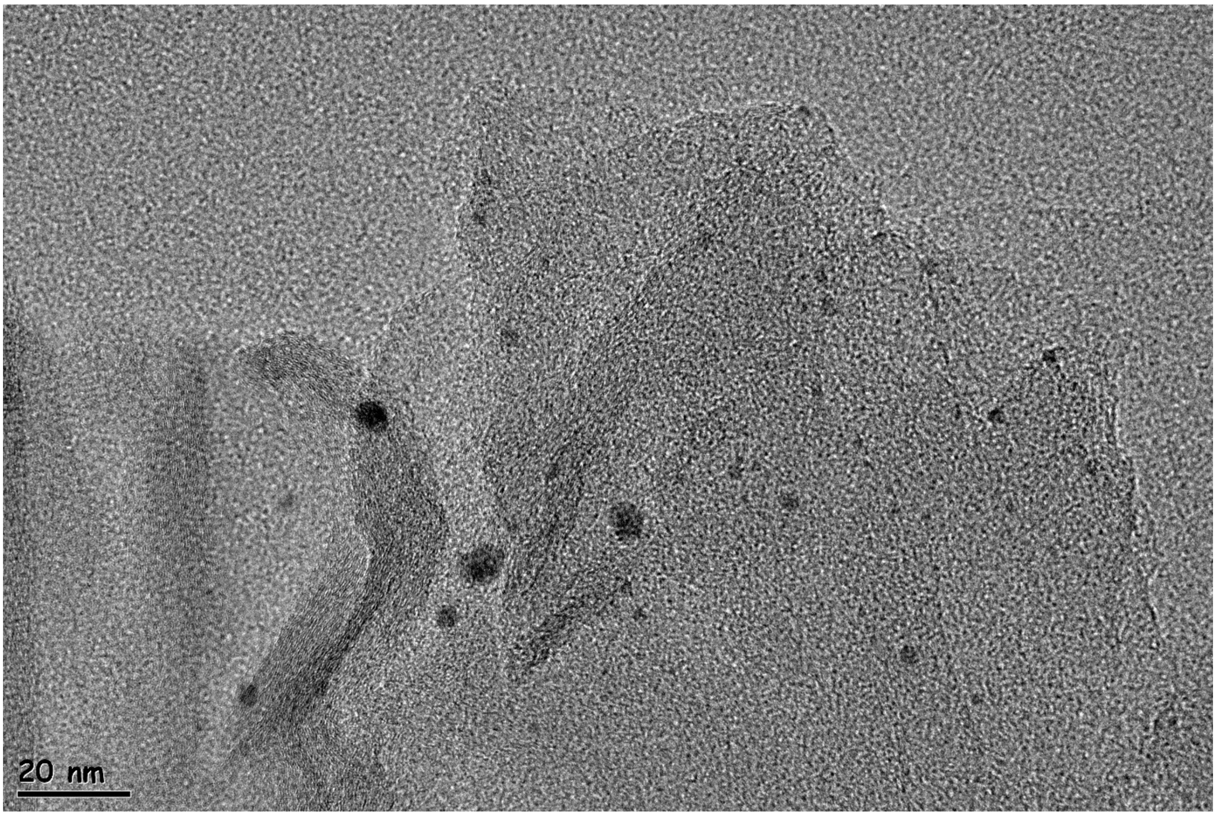

Figure S8. BFTEM image of $Pd_{0.60}Au_{0.20}Ni_{0.20}$/f-GNS nanocatalyst harvested after 10^{th} catalytic recycle from additive-free dehydrogenation of aqueous FA solution (0.22 M) at room temperature.

Calculation of TOF Values

TOF values were calculated by considering the region where 20 % conversion is achieved (*Angew. Chem. Int. Ed*. **2013**, 52, 4406). For example TOF value at room temperature was calculated as given below.

- 0.22 M FA in 10.0 mL solution corresponds to 2.2 mmol FA and according to stoichiometry ($HCOOH \rightarrow H_2 + CO_2$) 2.2×10^{-3} mole FA generates 4.4×10^{-3} mole gas at complete conversion,
- At complete conversion 4.4×10^{-3} mole (CO_2+H_2) gas generation yields 98.7 mL gas production,
- We considered the region where 20 % of conversion is reached, so ~ 20 mL gas should be produced at 20 % conversion,
- From Figure 5 in the presence of 20 μmol catalyst at 25 °C, 21.5 mL gas generated at 80 sec (0.0133 h),
- Initial TOF = $[1/2\times[(21.5\ mL/22400\ mL.mol^{-1})]/[(20\times10^{-6}\ mol)\times(0.022\ h)]$ initial TOF was found to be ~ 1090 mol H_2.mol metal^{-1}.h^{-1} . As given in the equation, this value was found by considering only the amount of H_2 not CO_2+H_2 (this is the reason why the equation given above is multiplied with ½)

Calculation of Lower-Limit Total Turnover Number (TTON)

1st recycle: 2.2 mmol H_2 (100 % conversion)

2nd recycle: 2.2 mmol H_2 (100 % conversion)

3rd recycle: 2.2 mmol H_2 (100 % conversion)

4th recycle: 2.178 mmol H_2 (99 % conversion)

5th recycle: 2.118 mmol H_2 (96 % conversion)

6th recycle: 2.118 mmol H_2 (96 % conversion)

7th recycle: 2.030 mmol H_2 (92 % conversion)

8th recycle: 2.030 mmol H_2 (92 % conversion)

9th recycle: 2.030 mmol H_2 (92 % conversion)

10th recycle: 2.030 mmol H_2 (92 % conversion)

After 10 recycle total amount of evolved H_2 = 21.134 mmol

TTON = mole of product/mole of catalyst

TTON = 21.134 mmol H_2/0.02 mmol metal

TTON = 1057 mmol H_2/0.02 mmol metal

Table S1. Comparison of the catalytic performance data in terms of conversion and activity for PdAuNi/f-GNS nanocatalyst with the prior best heterogeneous catalyst systems reported for the dehydrogenation of aqueous FA solution in the absence of any additives (references cited here refer those given in the main manuscript).

Entry	Catalyst	Temperature (°C)	[FA]/[catalyst]	Conversion (%)	Activity (TOF)	Reference
1	Ag@Pd NPs	20	50	36	63	22
2	AgPd NPs	20	50	10	72	22
3	Ag@Pd/C	20	50	44	96	22
4	PdAuCo/C	25	50	91	37	23
5	AuPd	25	50	28	41	45(a)
6	AgPd	25	100	52	102	24(a)
7	Ag/AgPd	25	100	92	316	24(b)
8	PdAg	60	50	99	419	24(c)
7	PdAuCr/N-SiO_2	35	75	92	1280	27
8	PdAu-MnO_x/Graphene-ZIF-8	25	50	94	180	25
9	PdAg-MnO_x/N-SiO_2	25	90	99	330	26
10	PdAu-MnO_x/N-SiO_2	25	80	92	785	28
11	Pd/N-KIE-8	25	50	97	281	33(a)
12	Pd/NH_2-KIE-6	25	140	96	746	33(b)
13	Ag@Pd/N-GCNT	25	75	95	413	34
14	Pd@N-SBA-15	25	90	94	355	35
15	AuPd/N-CNS	25	75	94	527	36
16	Pd@TB-POP	50	71	98	1344	37
17	NiPd@NH_2-N-rGO	25	50	99	954	38
22	PdAuNi/f-GNS	25	110	>99	1090	this study
23	PdAuNi/f-GNS	35	110	>99	2590	this study
24	PdAuNi/f-GNS	65	110	>99	16840	this study