Supporting Information

Anchoring PdAg alloys on self-crosslinked carbon dots as efficient catalyst for formic acid dehydrogenation under ambient conditions

Zhenluo Yuan[a], Ouyang Liu[a], Shuyan Guan[a], Xianyun Liu[a], Linyan Bian[a], Qiuming Peng[b], Shumin Han[b], Yanping Fan[a, c,]*, Baozhong Liu[a, c,]*

[a]College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454003, P. R. China

[b]State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, P. R. China

[c]Henan Key Laboratory of Coal Green Conversion, Henan Polytechnic University, Jiaozuo 454003, P. R. China

*Corresponding Author: fanyanping@hpu.edu.cn, bzliu@hpu.edu.cn

Preparation of catalysts

Preparation of CDs support: Nitrogen-doped carbon dots derived from citric acid (CA) and ethylenediamine (ED) were prepared by hydrothermal method. Briefly, the appropriate amount of citric acid and ethylenediamine were dissolved in 140 mL of deionized water with vigorous stirring until a clear solution was obtained. Subsequently, the solution was transferred into a 200 mL Teflon lined stainless steel autoclave, and then heated to 473 K and maintained for 5 h in an oven. After the hydrothermal process, the suspension was on dialysis for 12 h using a 500 Da membrane until the clear brown-black solution was obtained. The product of carbon dots was obtained after the freeze-drying, and it was denoted as CDs.

Characterization of catalysts

X-ray diffraction (XRD) analysis was performed using a SmartLab Rigaku equipped with Cu-Kα radiation (40 kV, 40 mA). The XRD profiles were recorded at the range of 10-85° with a rate of 10°/min. X-ray photoelectron spectra (XPS) were performed on a Thermo SCIENTIFIC ESCALAB 250Xi spectrometer with a monochromatic Al Kα X-ray source (hv = 1486.6 eV) and the binding energy was calibrated by referencing the C1s peak (284.8 eV) to reduce the sample charge effect. The morphologies of materials were studied using a transmission electron microscope (TEM, JEOL JEM-2100F, Japan). Fourier-transform infrared spectroscopy (FTIR) was performed on an IR Spectrometer Bucks HP9 2FX.

Dehydrogenation reaction of formic acid

The dehydrogenation of FA was carried out in a two-neck round bottom flask, and

the effluent was collected by the water displacement method. Typically, a two-necked round bottom flask was charged with 5 mL of water and 0.046 mmol of catalyst. One of the necks was served to add the 1.7 mL of FA aqueous solution (1 mol/L) via a funnel. The catalytic dehydrogenation process starts when the FA aqueous solution was poured into the flask. The reaction was carried out under the air environment in a closed system with magnetic stirring, and the reaction temperature was regulated using a thermostatic water bath. The reaction was conducted at a temperature of 298 K in general. An inverted gas burette (100 mL) filled with water was used to measure the volume of effluent. Using the equation below, the TOF values were calculated based on the molar of Pd atoms in the relevant catalyst at the initial 10 min of the dehydrogenation process.

$$TOF_{initial} = \frac{P_0 V}{RT n_{Pd} t}$$

Where, P_0 is the atmospheric pressure (101325 Pa), V is the volume of generated gases (H_2-CO_2) at the initial 10 mL of reaction, R is the molar gas constant, T is room temperature of 298 K, n_{Pd} is the mole of Pd in the catalyst, and t is the time corresponding to hydrogen volume of 10 mL.

Table S1 The content of Ru and Ni elements were obtained by ICP-OES.

Sample	Pd content	Ag content
Pd_1-CDs	10.12 %	-
$Pd_{0.95}Ag_{0.05}$-CDs	9.55 %	0.45%
$Pd_{0.90}Ag_{0.1}$-CDs	9.02 %	0.99%
$Pd_{0.8}Ag_{0.2}$-CDs	8.11%	1.99%
$Pd_{0.6}Ag_{0.4}$-CDs	6.02%	3.99%
$Pd_{0.4}Ag_{0.6}$-CDs	3.99%	6.06%
$Pd_{0.2}Ag_{0.8}$-CDs	2.01%	7.99%

Table S2: Catalytic activity of various catalysts for FA dehydrogenation (TOF values taken directly from related references)

Catalyst	Reagent	Temp. (K)	$TOF_{initial}$	Average	Ref.
AgPd@Pd	FA	300	70	-	S1
$AgPd@Pd/TiO_2$	FA	300	200	-	S2
$AuPd/TiO_2(L)$-400	FA	298	373	-	S3
$AuPd/TiO_2$	FA	298	294	-	S4
$Pd-NH_2/MIL-125$	FA/SF=9.8/7.9	305	214	3.1	S5
$Pd@SiO_2$	FA/SF=3:1	365	70	20-35	S6
$Pd-N-SiO_2$	FA/SF=9/1	358	115	-	S7
Pd/MSC-30	FA/SF=1/1	298	750	2.3	S8
Pd@CN	FA	288	71	2.5	S9
PdNPs/ XC-72R	FA/SF=1/1	303	1678	1.4	S10
Pd@CN900K	FA/SF=1/3	298	1963	1.1±0.2	S11
Pd/CE-CDs-III	FA	298	256	1.94±0.16	S12
$Pd_{0.9}Ag_{0.1}/CDs$	FA	298	619	1.14	This work

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