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Nitrogen functional carbon nanotubes supported bimetallic PtNi nanoparticles for hydrogen generation from hydrous hydrazine

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1. Materials

Hydrazine monohydrate ($H_2NNH_2 \cdot H_2O$, Aladdin reagent Co., Ltd, >98%), nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Sinopharm Chemical Reagent Co., Ltd, >98%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd, >96%), potassium permanganate ($KMnO_4$, Sinopharm Chemical Reagent Co., Ltd, ⩾99.5%), graphite power (Sinopharm Chemical Reagent Co., Ltd, ⩾99.85%), hydrogen peroxide (H_2O_2, Sinopharm Chemical Reagent Co., Ltd, ⩾30%), phosphoric acid (H_3PO_4, Sinopharm Chemical Reagent Co., Ltd, AR), sulfuric acid (H_2SO_4, Sinopharm Chemical Reagent Co., Ltd, 95~98%), vulcanic-72 carbon (Cabot corporation, ≥97 %), multi-walled carbon nanotube (Shandong Dazhan nano materials Co., Ltd, 97%) were used without further purification. De-ionized water with a specific resistance of 18.2 MΩ·cm was obtained by reversed osmosis followed by ion exchange and filtration.

2. Synthesis of N-MWCNTs

1.0 g MWCNTs were mixed with 1.5 g urea, which was transferred to a ceramic crucible and heat treatment in a muffle furnace at 300 ^{o}C for two hours. (ACS Catal. 2017, 7, 2720−2724) After cooling to room temperature, the mixture was washed with DI water and ethanol for three times. The product was obtained after drying in an oven at 60 ^{o}C overnight. After that, 1.0 g as-prepared sample was mixed with 2.0 g urea again, and then heat-treated at 175 ^{o}C for 4 hours. The final N-MWCNTs samples were collected by centrifuging and washed with DI water three times and then dried in an oven at 60 ^{o}C.

3. Catalytic measurement:

An aqueous suspension (4 mL) containing the as-prepared catalysts was placed in a two-neck round-bottom flask (30 mL), which was placed in a water bath under an ambient atmosphere. The reaction started when 2 mmol of hydrazine monohydrate was injected into the mixture using a syringe. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas. The gas released during the reaction was measured volumetrically. The molar ratios of metal/N_2H_4•H_2O were theoretically fixed at 0.025 for all the catalytic reactions.

4. Durability testing of the catalysts:

For testing the durability of PtNi/N-MWCNTs catalysts, 2 mmol of N_2H_4•H_2O was subsequently added into the reaction flask after the completion of the first-run decomposition of N_2H_4•H_2O. Such test cycles of the catalyst for the decomposition of N_2H_4•H_2O were carried out for 5 runs at 50 °C by adding N_2H_4•H_2O.

5. Calculation of turnover frequency (TOF)

The TOF reported here is an apparent TOF value based on the number of Ni and Pt atoms in the catalyst, which is calculated from the equation as follow:

$$TOF = 2P_0V / (3RTn_{NiPt}t) \quad (1)$$

Where P_0 is the atmospheric pressure (101325 Pa), V is the final generated volume of H_2/N_2 gas, R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the room temperature (298 K), n_{NiPt} is the total mole number of Ni and Pt atoms in catalyst and *t* is the completion time of the reaction in hour.

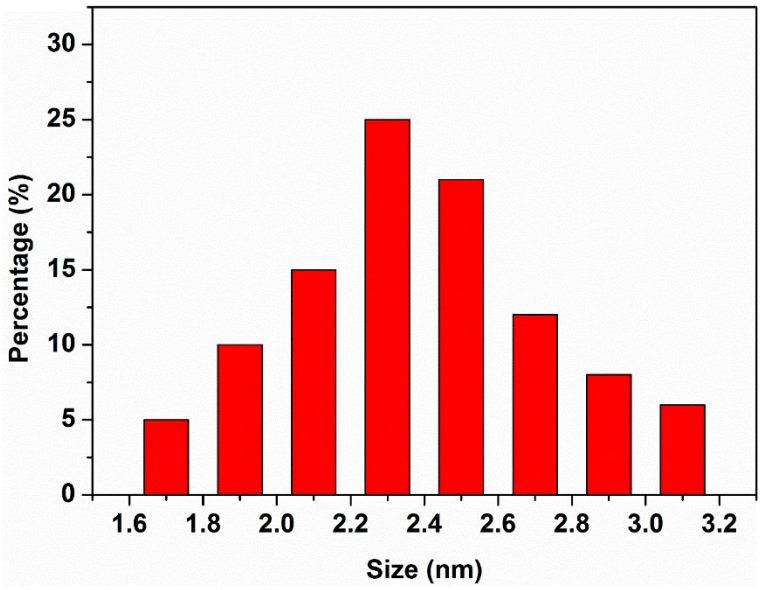

Figure S1. The particle size distribution of PtNi in PtNi/N-MWCNTs.

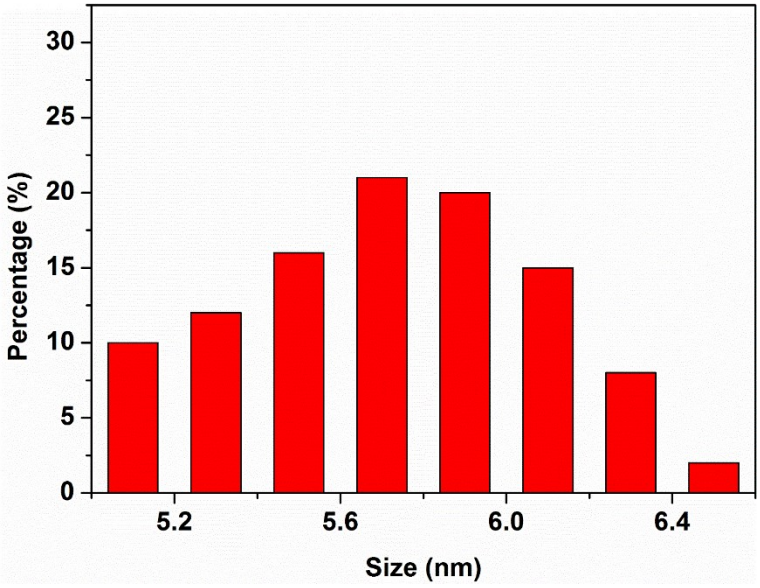

Figure S2. The particle size distribution of PtNi in PtNi/MWCNTs.

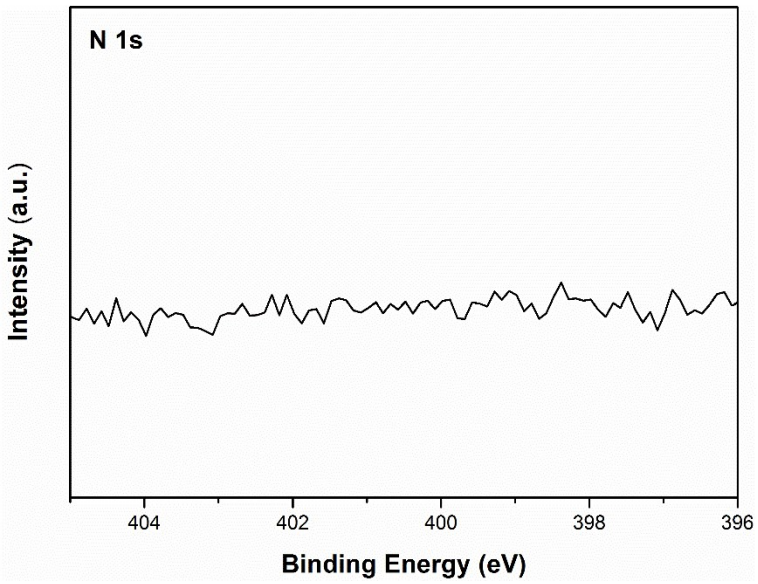

Figure S3. XPS spectrum of N 1s in PtNi/MWCNTs.

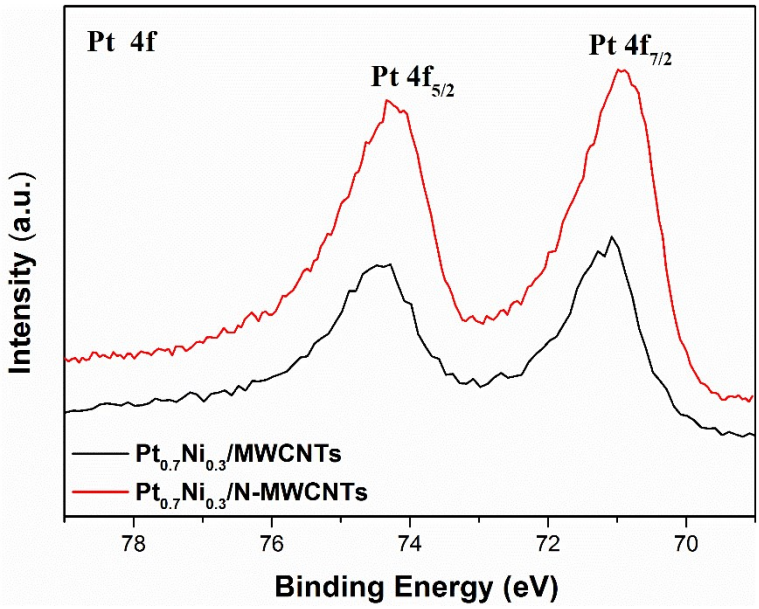

Figure S4. XPS spectrum of Pt 4f in PtNi/N-MWCNTs and PtNi/MWCNTs.

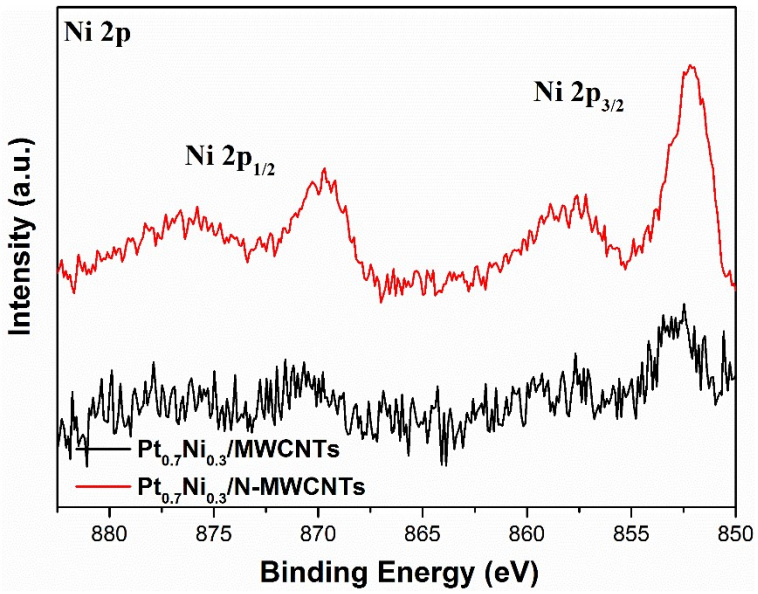

Figure S5. XPS spectrum of Ni 2p in PtNi/N-MWCNTs and PtNi/MWCNTs.

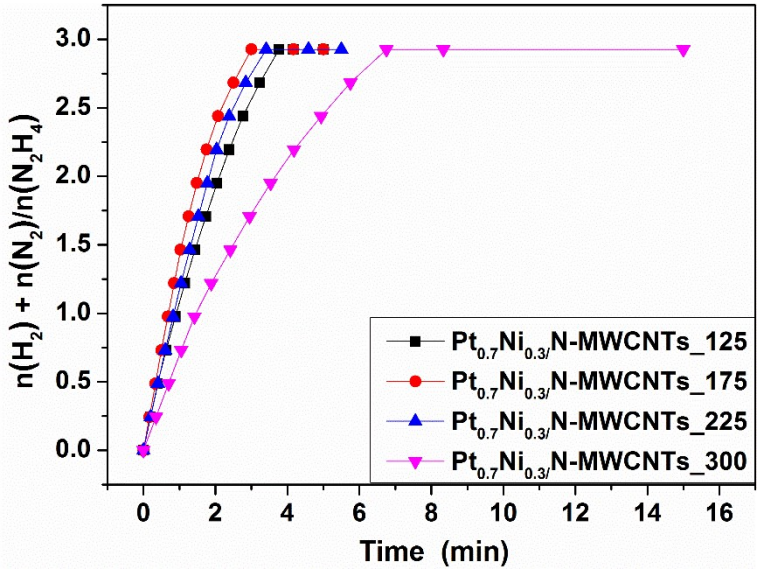

Figure S6. Time-course plots for the generated N_2+H_2 from catalytic hydrazine decomposition over $Pt_{0.7}Ni_{0.3}$/N-MWCNTs nitridated different temperatures.

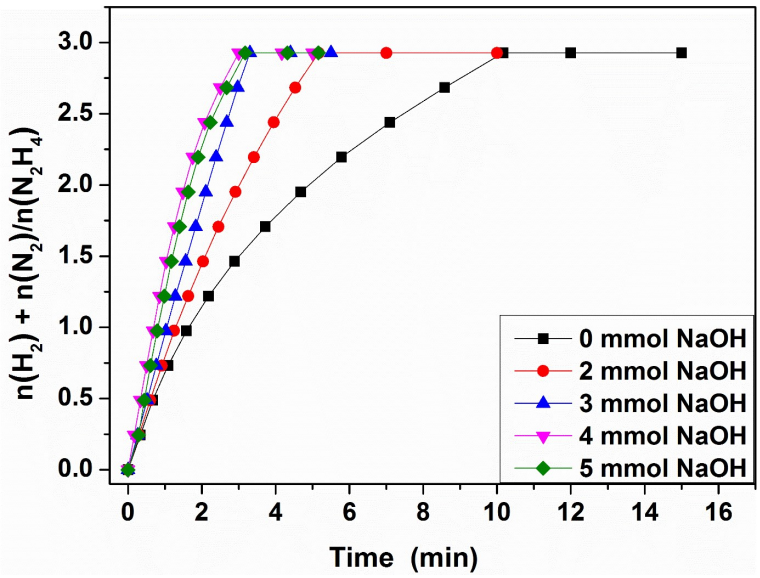

Figure S7. Time-course plots for the generated N_2+H_2 from catalytic hydrazine decomposition over $Pt_{0.7}Ni_{0.3}$/N-MWCNTs in various NaOH amounts.

Table S1 Catalytic activities of different catalysts for $N_2H_4 \cdot H_2O$ decomposition

Catalyst	Solvent	Temp. (°C)	Selectivity H_2 for (100 %)	TOF (h^{-1})[a]	Ref.
$Pt_{0.7}Ni_{0.3}$/N-MWCNTs	Aqueous NaOH	50	100	1595	This work
$Ni_{0.6}Pt_{0.4}$/g-C_3N_4 NPs	Aqueous NaOH	50	100	2194[b]	[1]
$Pt_{0.5}Ni_{0.5}$/NGNs-850	Aqueous NaOH	50	100	2116[b]	[2]
$Ni_{0.4}Pt_{0.6}$/CNTs	Aqueous NaOH	50	100	1725[b]	[3]
Pt_4Ni_6/NC	Aqueous NaOH	50	100	1602[b]	[4]
$Rh_{55}Ni_{45}$/Ce(OH)	Aqueous NaOH	50	100	395[b]	[5]
$Rh_{34}Ni_{66}$@ZIF-8	Aqueous NaOH	50	100	140	[6]
$(Ni_3Pt_7)_{0.5}$-$(MnO_x)_{0.5}$ /NPC-900	Aqueous NaOH	50	100	706[b]	[7]
Pt_3Ni_2	Aqueous NaOH	50	100	290[b]	[8]
PtNi/CeO_2	Aqueous NaOH	50	100	286[b]	[9]
Ni_3Pt_7/BNG-1000	Aqueous NaOH	30	100	199.4	[10]
$Ni_{0.9}Pt_{0.05}Rh_{0.05}$/$La_2O_3$	Aqueous NaOH	25	100	45.9	[11]
$Ni_{0.9}Pt_{0.1}$/Ce_2O_3	Aqueous NaOH	25	100	28.1	[12]
$Ni_{0.58}Pt_{0.42}$/graphene	Aqueous NaOH	30	100	434	[13]
$Ni_{0.9}Pt_{0.1}$/MIL-101	Aqueous NaOH	30	100	140	[14]
$Ni_{0.8}Pt_{0.2}$/MIL-101-NH_2	Aqueous NaOH	50	100	676	[15]

[a] TOF values were calculated using the amount of released gas and the completion time of reaction in hour, [b] Initial TOF values were calculated at the initial stages of the catalytic reactions.

Table S2 Elemental analyses for the samples

Catalyst	N content
$Pt_{0.7}Ni_{0.3}$/N-MWCNTs_125	2.72%
$Pt_{0.7}Ni_{0.3}$/N-MWCNTs_175	3.25%
$Pt_{0.7}Ni_{0.3}$/N-MWCNTs_225	4.59%
$Pt_{0.7}Ni_{0.3}$/N-MWCNTs_300	9.28%

Notes and references

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