

Electronic Supplementary Information (ESI†)

Single component gold on protonated titanate nanotubes for surface-charge-mediated, additive-free dehydrogenation of formic acid into hydrogen

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Experimental section

Catalyst synthesis:

(1) synthesis of protonated titania nanotubes was by a modification of the previously reported method. TiO_2 (P-25) nanoparticles were placed into a beaker (50 mL). Using a syringe, we added 10 M sodium hydroxide solution (60 mL). The mixture was left stirring for 12 h. The resultant white slurry was transferred to a Teflon vessel which was then placed into a sealed autoclave and put in an oven at 150 °C for 72 h. After cooling to room temperature, the precipitated powders were filtrated and washed with 0.1 M aqueous HCl solutions and Milli-Q water, until the filtrate reached $\text{pH} = 7$. This resulting sample was protonated titania nanotubes and denoted as TiNTs.

(2) In a typical synthesis of AuNPs, 100 mg of AuPPh_3Cl was mixed with 400 μL of dodecanethiol in 20 mL of benzene to form a clear solution, to which 84 mg of NaBH_4 was then added in one portion. The mixture was heated with stirring at 55 °C for 7 h before the reaction system was cooled to room temperature. AuNPs were precipitated out from the reaction mixture as black solid powders by addition of 20 mL of ethanol. The precipitate was separated by centrifuge, washed with ethanol. Finally, the precipitate was dried naturally. Monodispersed AuNPs (3.3 ± 0.3 nm) pack in hexagonal arrays with particle-to-particle distance of 5.3 nm. The effective size of the AuNPs, defined as gold core plus ligand

shell, is estimated to be equal to particle-to-particle distance (i.e. 5.3 nm).

AgNPs: 110 mg AgCF_3COO was mixed with 250 μL of dodecanethiol in 50 mL of benzene to form a clear solution under a flow of H_2/Ar (5 v/v%) gas, to which 435 mg of borane-tert-butylamine complex (BTBC) was added in one portion. The mixture was heated with stirring at 55 °C for 2 h before the reaction system was cooled to room temperature. AgNPs were precipitated out from the reaction mixture as black solid powders by addition of 20 mL of ethanol. The precipitate was separated by centrifuge, washed with ethanol, and dried in H_2/Ar flow.

PtNPs: 100 mg $\text{Pt}(\text{acac})_2$ was dissolved in 30 mL oleylamine at 110 °C for 10 mins, then cooled to 100 °C. The mixture was heated to 140 °C and kept for 4 h after the addition of 2 mL oleylamine containing 200 mg BTBC as the reducing agent. After cooling to room temperature, PtNPs were precipitated from the mixture by addition of 60 mL anhydrous ethanol, and then collected by centrifuge and ethanol washing, and drying in vacuum (60 °C) overnight.

224 mg of palladium acetate (0.5 mmol) was mixed with 10 mmol of oleic amine under 50 °C with stirring to form a clear solution. Then 10 mmol of oleic acid was added, the mixture was kept at 50 °C for 1 h. Then 386 mg of BTBC dissolved in 2 ml CHCl_3 was added in one portion. The mixture was kept heat for another 1 h before it was cooled to room temperature. PdNPs was precipitated by addition of 15 ml of ethanol. The precipitant was separated by centrifuge, washed with ethanol. Finally, the

precipitate was dried in vacuum box over night before dissolving in organic solvent.

(3) AuNPs (and other MNPs) was loaded onto TiNTs by a colloid deposition method. Desired amount of AuNPs were dissolved in 25 ml of chloroform. To this solution, desired amount of TiNTs was added. After 30 min stirring, the solid product was centrifuged and dried in air. The AuNPs/TiNTs was calcined at different temperatures for 5 h (in air) to obtain the final catalysts.

Characterizations

(1) TEM images were recorded on a JEOL JEM-1230 operated at 100 kV.

HR-TEM and HAADF-STEM combined with EDS measurements were proceeded on FEI TITAN Cs-corrected ChemiSTEM equipped with an energy dispersive X-ray (EDX) spectroscope, operating at 200 kV.

(2) Wide-angle XRD patterns were recorded on a Bruker D8 diffractometer using CuK_α radiation.

(3) Inductively coupled plasma mass spectrometry (ICP-MS) was carried out in Agilent 7700 using the dissolving solution containing calculated AuNPs/TiNTs in nitric acid to determine the exact Au loading amount.

(4) XPS measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV)

chambers. All binding energies were referenced to the *C1s* peak at 284.8 eV of the surface adventitious carbon.

- (5) Nitrogen sorption analysis was carried out at 77 K using a Micrometrics TriStar 3000 system.
- (6) X-band EPR signals were recorded on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3511.39 G; sweep width, 100 G; microwave frequency, 9.86 G; modulation frequency, 100 kHz; power, 101 mW; conversion time, 10 msec. The solid EPR analysis was carried out by packing catalyst powders into a glass capillary tube, which was placed in the EPR chamber for testing. The location and the intensity of *g* factors were determined by Bruker's WINEPR program based on $h\nu = g\beta H$, where *h* is Planck's constant, *H* is the applied magnetic field, and β is the Bohr magneton. The spin trapping experiments were performed as follows: 5,5-Dimethyl-pyrroline-*N*-oxide (DMPO) spin-trapping reagent and other chemicals were purchased from Sigma-Aldrich Chemical Co. and used without further purification. Stock solutions of DMPO (0.8 M) in deaerated water were prepared under argon and stored in the dark at -20 °C. The stock DMPO solution was first diluted to 0.08 M with phosphate buffer solution (pH = 7.6) prior to the reaction with any solid substrate. The FA solution containing calculated catalyst and ice-cooled DMPO solution (0.08 M) was

quickly transferred into a glass capillary tube and tested by EPR spectroscopy at room temperature.

Catalysis: Catalytic H₂ production from FA solution was carried out with 20 mg of catalysts suspended in 5 mL of aqueous FA solution in a 55 mL Pyrex test tube under stirring (400 ± 10 rpm). A water bath was used to maintain the reaction temperature at 60 ± 0.5 °C. The residual O₂ in the test tube was eliminated by purging with high-purity N₂, and the tubes were finally sealed with silica gel stoppers. Gas volumes of 400 μL were extracted from the test tubes using a microliter syringe at regular intervals, and GC-TCD was employed for evaluating the gas evolution amount, including H₂, CO₂ and CO. The recycling experiment is carried as follows: after 6 h reaction (1 cycle), the test tube was opened and then purged with air for 5 min to remove residual H₂, and again sealed for the next cycle.

Table S1 Deuterated isotopic composition studies of the FA solution decomposition over AuNPs/TiNTs-300.

Entry	Reactants	H ₂ /6h	H/D
1	HCOOH+H ₂ O	24.9	–
2	DCOOD+H ₂ O	3.91	6.37
3	HCOOH+D ₂ O	6.34	3.93
4	DCOOD+D ₂ O	0.99	25.2

Reaction conditions: FA solution concentration: 0.2 M; reaction temperature: 60 °C.

Table S2 Catalytic performance and activation energy of AuNPs/TiNTs-x during HCOOH dehydrogenation.

Entry	Catalyst	TOF /h ⁻¹	Activation energy /kJ mol ⁻¹
1	AuNPs/TiNTs-100	0.78	–
2	AuNPs/TiNTs-200	82.1	105
3	AuNPs/TiNTs-300	100.3	108
4	AuNPs/TiNTs-400	14.7	112
5	AuNPs/TiNTs-500	15.2	115

Reaction conditions: FA solution concentration: 10 M; reaction temperature: 60 °C.

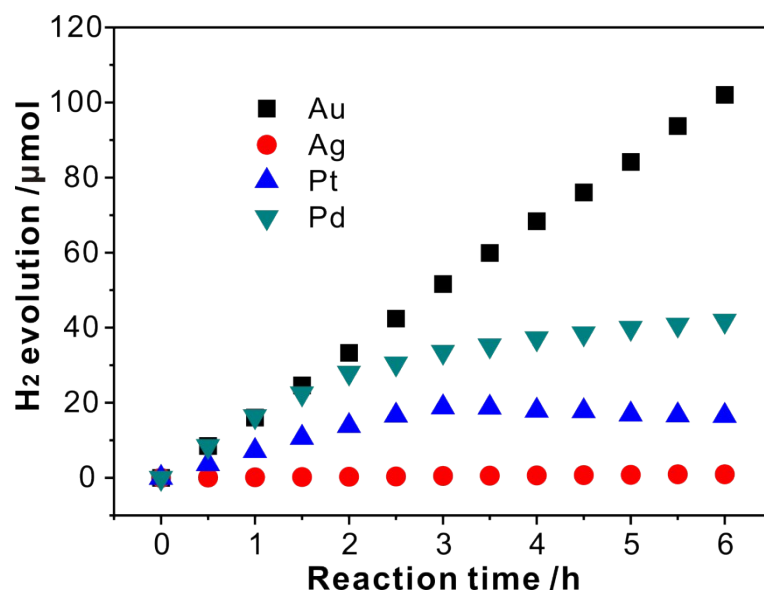


Fig. S1. Catalytic performance of MNPs/TiNTs (M = Au, Ag, Pt and Pd) for FA solution (1.0 M) decomposition into H₂ at 60 °C.

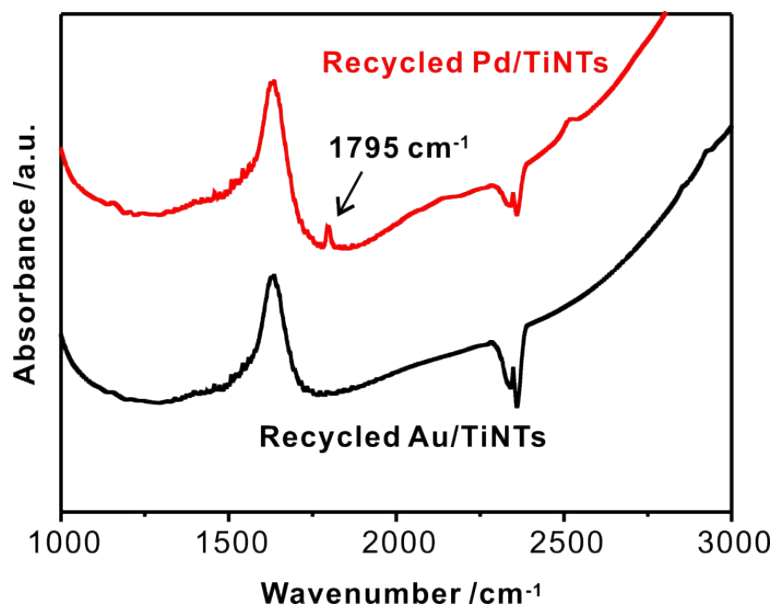


Fig. S2. FTIR spectra of recycled Au/TiNTs and Pd/TiNTs catalysts, where the 1795 cm⁻¹ peak corresponds to the adsorbed CO species of bridge type on Pd surface.

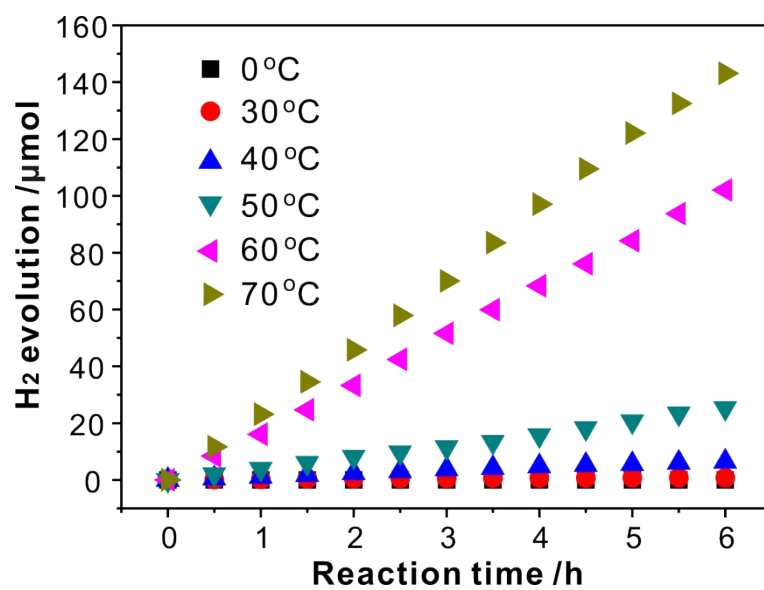


Fig. S3. Catalytic performance of AuNPs/TiNTs for FA solution (1.0 M) decomposition into H₂ at different temperatures.

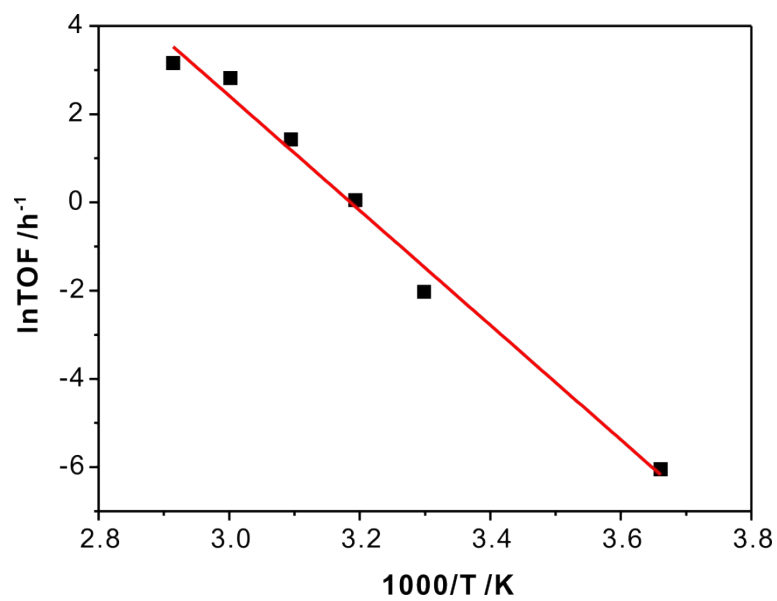


Fig. S4. Arrhenius plots for FA decomposition over AuNPs/TiNTs-300 catalyst at different reaction temperatures; the apparent activation energy of the reaction is calculated to be 108 kJ/mol.

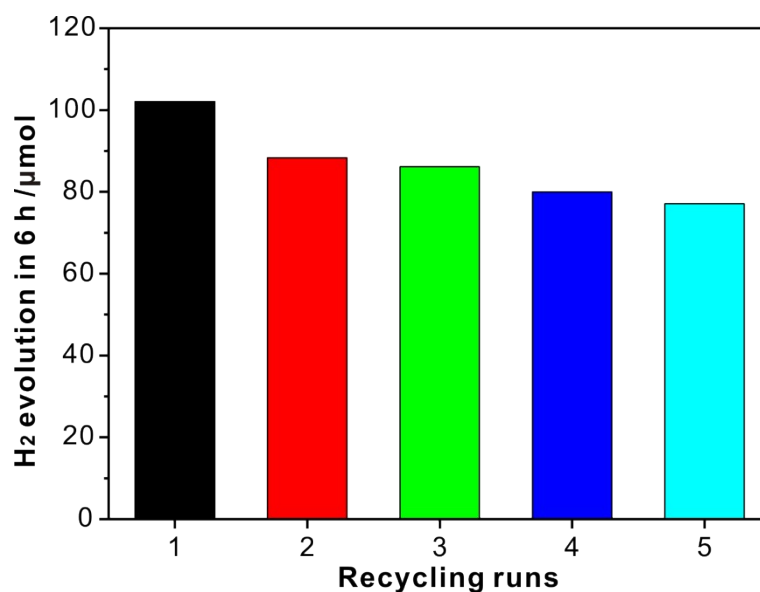


Fig. S5. Life cycle of AuNPs/TiNTs-300 on the decomposition of FA solution into H₂.

The stability is not very good, and we think there are two main reasons that potentially lead to the decrease of catalytic activity. One is the gradual growth of AuNPs during catalysis that reduces the surface area of catalytically active species, and the other is the surface contaminant by carbon deposition.