Electronic Supplementary Material (ESI) for ChemComm.

Supplementary information for

The role of surface chemistry of functionalized carbon nanotubes for immobilizing gold nanoparticles

Jingjie Luo,[a] Hua Wei,[a] Yuefeng Liu,[b,]* Di Zhang,[a,c] Bingsen Zhang,[a] Wei Chu,[c] Cuong Pham-Huu,[d] Dangsheng Su[a,b,]*

[a] Shenyang National Laboratory for Materials Science (SYNL), Institute of Metal Research, Chinese Academy of Science, 72 Wenhua Road, 110016 Shenyang, China.

[b] Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, 116023 Dalian, China.

[c] School of Chemical Engineering, Sichuan University, Chengdu 610065, China.

[d] Institute of Chemical and Processes for Energy, Environmental and Health (ICPEES), UMR 7515 CNRS-University of Strasbourg, 25, rue Becquerel, 67087 Strasbourg cedex 08, France.

*Corresponding author. E-mail: yuefeng.liu@dicp.ac.cn (YF Liu); dssu@dicp.ac.cn (DS Su).

Materials and Methods

Sample preparation

The initial CNT were supplied by Shandong Dazhan Nano Materials Co, Ltd, which was used after washed by concentrated HCl solution at room temperature for 12 h. Chloroauric acid ($HAuCl_4 \cdot 4H_2O$), concentrated HCl (AR, 36.0-38.0%), EtOH, and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. Iron(II) acetate and PVA (87.0-89.0% hydrolyzed, M.W. approx. 31,000-50,000) were purchased from Acros Organics. Benzylamine (98+%) were bought from Alfa Aesar.

1. Ozone functionalized CNT

Pristine CNT (CNT, 500 mg or 3g) was placed into an upright reactor. The sample was then treated at 40 ^{o}C with the O_3/O_2 gas mixture with water vapor (vapor generated at 40 ^{o}C or 80 ^{o}C) for 60 min. The functionalized CNT was labeled as oCNT and oCNT-HO, respectively. Ozone was produced from pure O_2 gas with a flow rate of 500 mL/min by an ozone generator (SW-002-2g, Qin Dao Vest Industry Electronic Purification Equipment Co. Ltd., China) with a production rate of 3 g/h when using oxygen as the source.

2. Au colloid

The gold colloid solution was prepared from $HAuCl_4$ solution (10^{-3} mol/L) reduced by $NaBH_4$ in the presence of PVA. Certain amounts of $HAuCl_4$ solution and PVA (0.5 wt%) was added together into a 250 ml beaker with the weight ratio of PVA and Au as 5:1. After stirring at 750 r/min for 20 min, the $NaBH_4$ solution (molar ratio of $NaBH_4$:Au=5:1) was then injected into the mixed liquid rapidly. The color of the solution changed from light yellow to wine-red suggesting the successful reduction of $HAuCl_4$ to AuNPs.

3. FeO_x/oCNT

The carbon nanotubes supported 5 wt% FeO_x sample was synthesized by sonication-assisted impregnation method. First of all, the iron acetate (II) was used as precursor and dissolved in ethanol. Appropriate amount of nano-carbon support was added subsequently into the solution under stirring for 0.5 h. The sonication was then used for further dispersing the iron species for 0.5 h. The sample in powder form after dried at 80 ^{o}C over night was finally thermally treated in air at 350 ^{o}C for 3 h. The as-received sample was labeled as FeO_x/oCNT.

4. Supported 1.5 wt% AuNPs by colloidal immobilization method

Supported AuNPs (supports including CNT, oCNT, oCNT-HO, FeO_x/oCNT, and SiC) were synthesized by using colloid immobilization method. 1 g support powder were added into the fresh gold colloid under stirring. The mixture solution was aged for 16 h for the complete deposition of colloidal AuNPs (except the SiC as support that was unable to totally capture the AuNPs from colloid). The samples were then washed and filtered with distilled water, and then dried at 60 ^{o}C in air. The samples were finally calcined in air at 300 ^{o}C for 3 h and denoted by Au/CNT, Au/oCNT, Au/oCNT-HO, Au/FeO_x/oCNT and Au/SiC, respectively.

Characterization

Ultraviolet spectra (UV–vis) were performed on an UVIKON 933 Double Beam UV–vis spectrophotometer in the range of 350–800 nm by using a quartz cuvette. **Transmission electron microscopy** (TEM) was performed on a FEI Tecnai G2 F20 microscope equipped with high angle annular dark field (HAADF) and energy dispersive X-ray analysis (EDAX) detectors under 200 keV. The statistical results of the size distribution were based on more than 200 particles for each sample. **Raman spectra** were recorded using a 532 nm laser source and were normalized with respect to the G-band intensity. **X-ray photoelectron spectra** (XPS) were recorded on an ESCALAB 250 spectrometer with an Al Kα (1486.6 eV, 15mA) X-ray source. **Zeta potential** of different support materials were measured by using a Malvern zeta meter (Zetasizer 2000). The pH value of the CNTs solution was adjusted from 12.0 to 1.0 by adding 0.1 mol/l NaOH or HCl solution to the glass beaker at room temperature. **Temperature programmed desorption-mass spectrometry** (TPD-MS) experiments were performed under He atmosphere with the blowing rate of 40 ml/min. 30 mg sample was added into the vertically positioned reaction tube. The temperature was raised to 900 ^{o}C (10 ^{o}C/min^{-1}) and kept for 20 min before the sample was cooled down to room temperature. The resulting gases were analyzed on-line by MS (Pfeiffer-Balzer Omnistar). The m/z signals of 28 (CO) and 44 (CO_2) were monitored with an time interval of 0.1 s. The Au loading levels were determined by inductively coupled plasma atomic emission spectroscopy (ICPAES) using an PerkinElmer ICP-OES 7300DV. The real gold loading of Au/CNT and Au/oCNT were 1.63 wt.% and 1.83 wt.%, respectively. The slightly higher loading than the theoretical value (1.5 wt.%) may be due to the consumption of carbon fragments during thermal treatment.

Oxidative coupling of benzylamine to imine

The CNT and oCNT as well as their supported AuNPs were tested for oxidative self-coupling of benzylamine under base-free and solvent-free conditions. Typically, the experiments were performed in 10 ml round-bottom flask containing the benzylamine (7.5 mmol) and catalysts (20 mg). The flask was vacuumed and purged with oxygen (99.9%) three times before it was finally connected with oxygen balloon. The reaction mixture was stirred under atmosphere at 100 °C for 10 hours. The constant solution (1 mL) after removing catalyst was diluted 100 times by CH_3CN and 80 mg toluene was added as internal standard. The solution after reaction was determined by a gas chromatograph (Agilent 7890) equipped with a flame ionization detector (FID) and an HP-5 capillary column and confirmed by ^{1}H NMR. The TOF based on gold nanoparticles (h^{-1}) was calculated by [Converted molar quantity of amine by Au sites/molar quantity of gold], by assuming that the amine converted on Au sites was the total conversion of amine minus amine conversion based on pure carbon support.

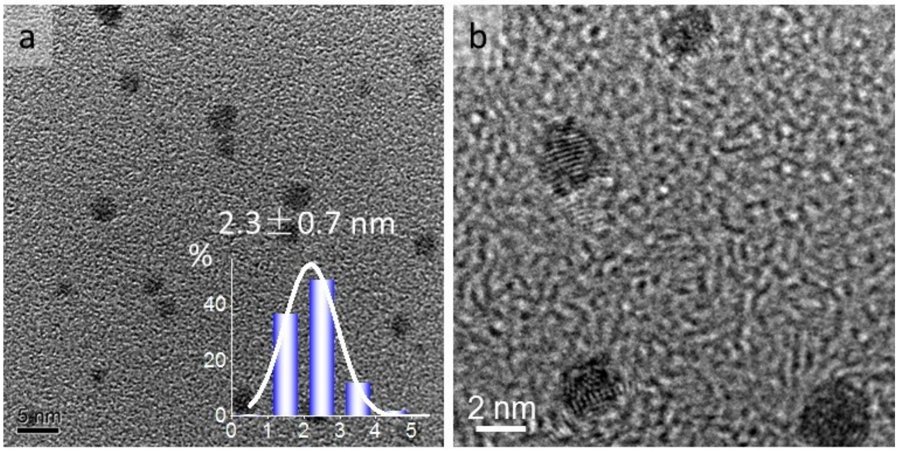


Figure S1. TEM images of the well-formed small gold nanoparticles in the as-synthesized gold colloid.

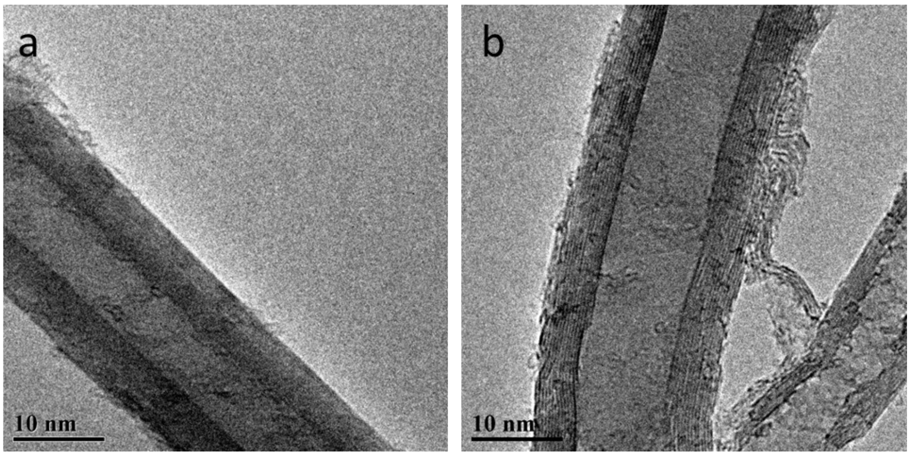


Figure S2. TEM of a) CNT and ozone functionalized b) oCNT with broken side walls and defects.

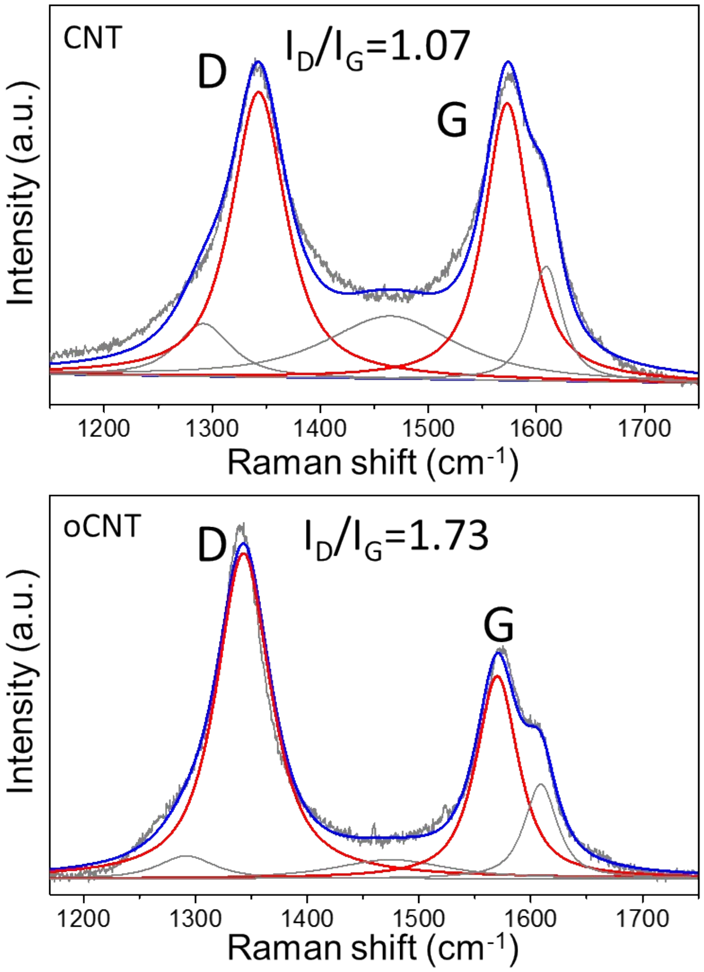


Figure S3. Raman spectra of CNT (up) and ozone functionalized oCNT (down).

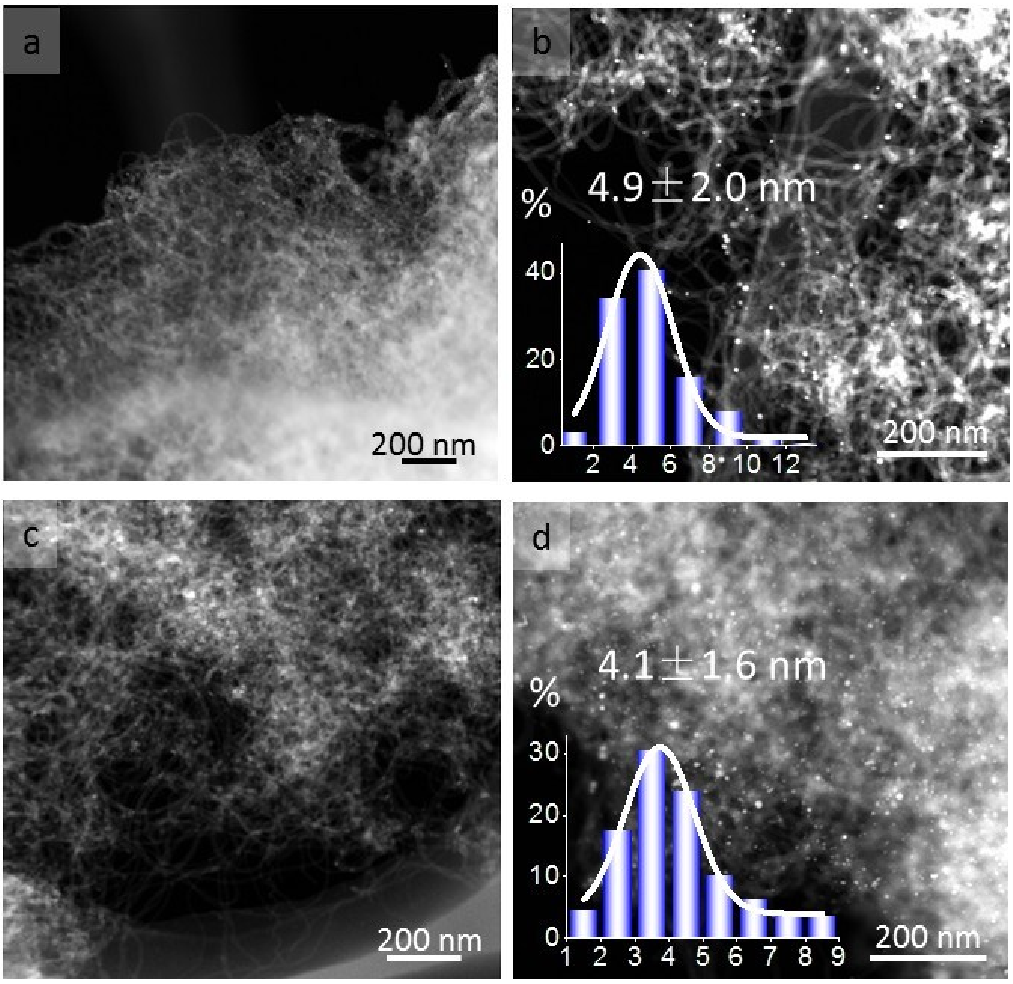


Figure S4. HAADF-STEM images of CNT and oCNT supported colloidal gold nanoparticles. a) Freshly synthesized Au/CNT after washing and drying. b) Au/CNT calcined in air at 300 °C for 3 h. c) Freshly synthesized Au/oCNT after washing and drying. d) Au/oCNT calcined in air at 300 °C for 3 h.

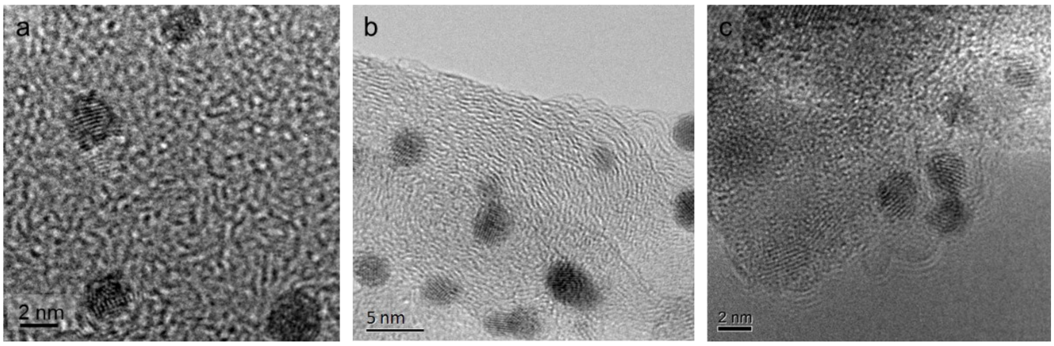


Figure S5. TEM images of initial gold colloid (a); SiC supported fresh gold colloid before calcination (b) and oCNT supported fresh gold colloid before calcination (c).

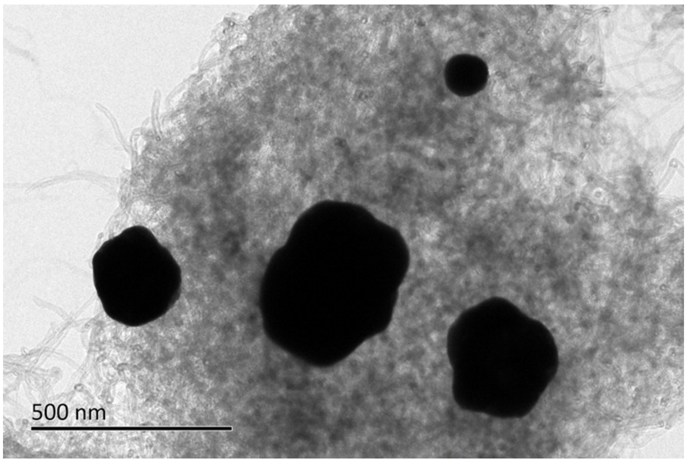


Figure S6. TEM image of Au/oCNT-IMP prepared by impregnation method.

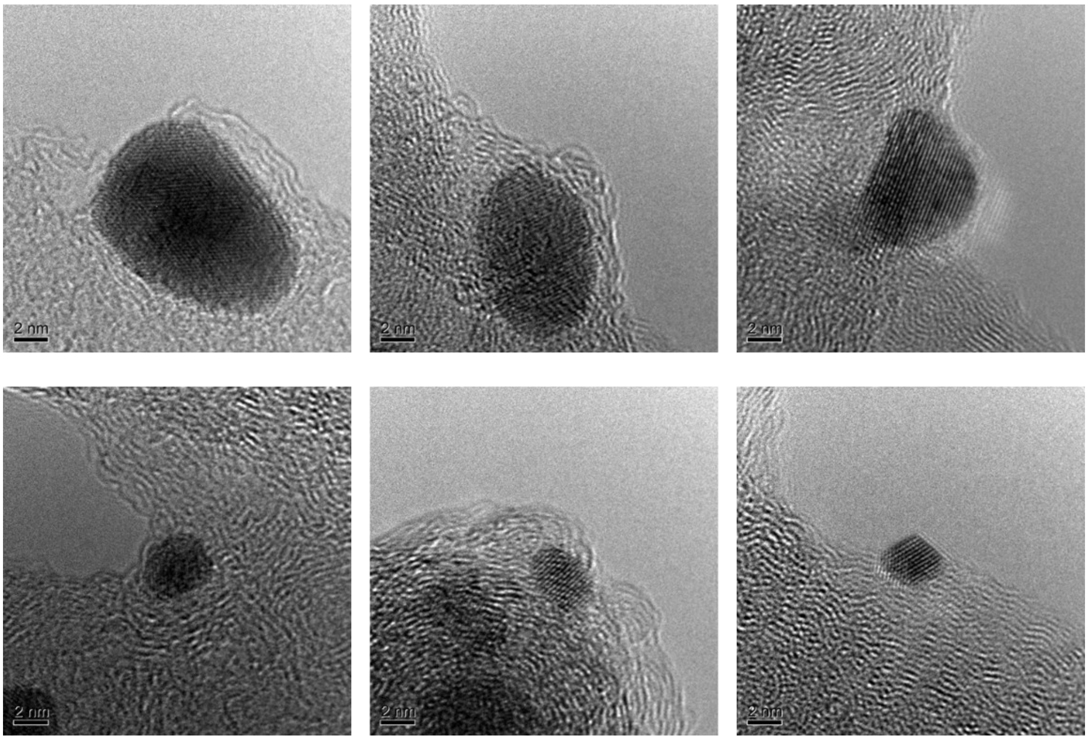


Figure S7. HR-TEM images of the Au/oCNTs sample. The images displaying gold nanoparticles partially surrounded by carbon layer due to the existence of Au-C interaction.

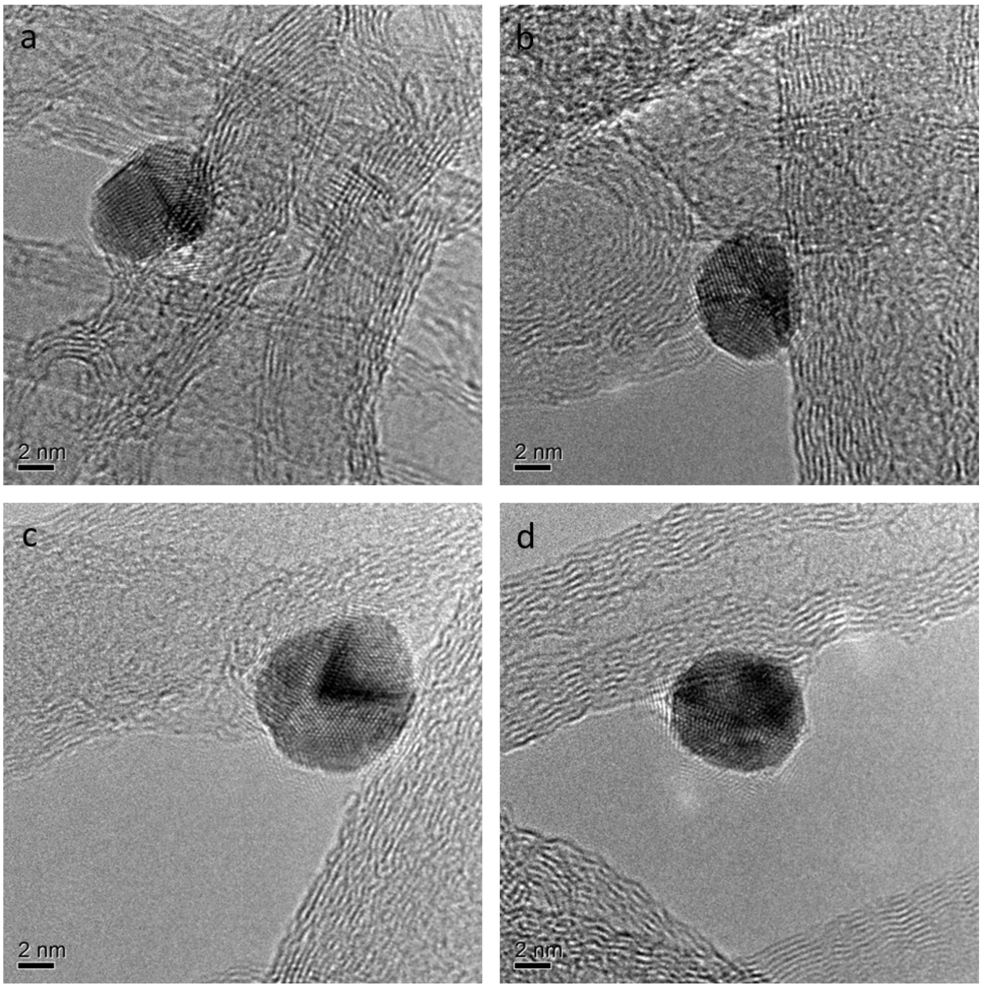


Figure S8. HR-TEM images of the Au/CNT sample. Different from the Au/oCNT sample, gold nanoparticles partially encapsulated by carbon layer was not observed in this sample.

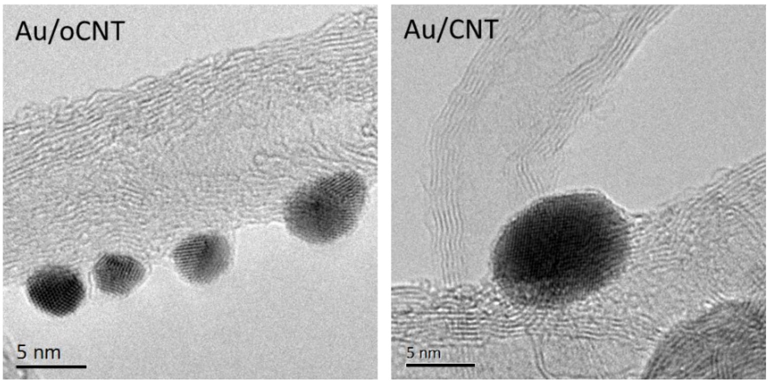


Figure S9. TEM images of Au NPs supported on oCNT and CNTs before thermal treatment at 300 ^{o}C.

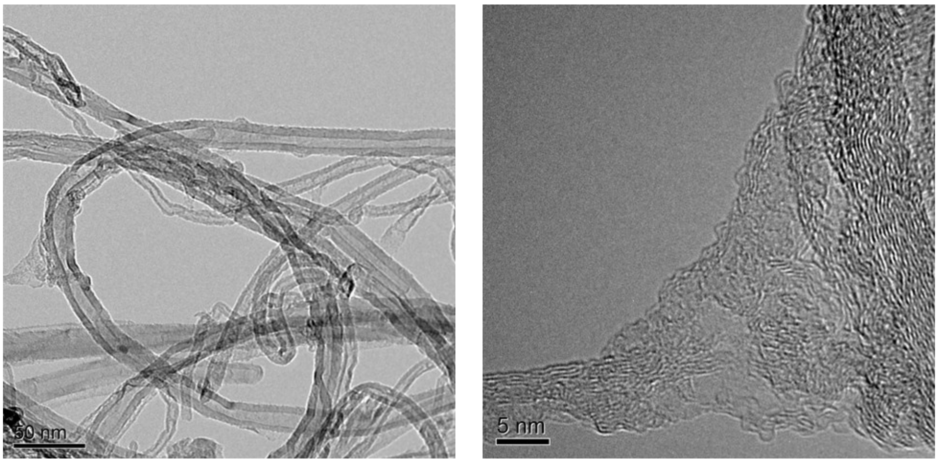


Figure S10. TEM images of oCNT-HO functionalized by vigorous ozone treatment.

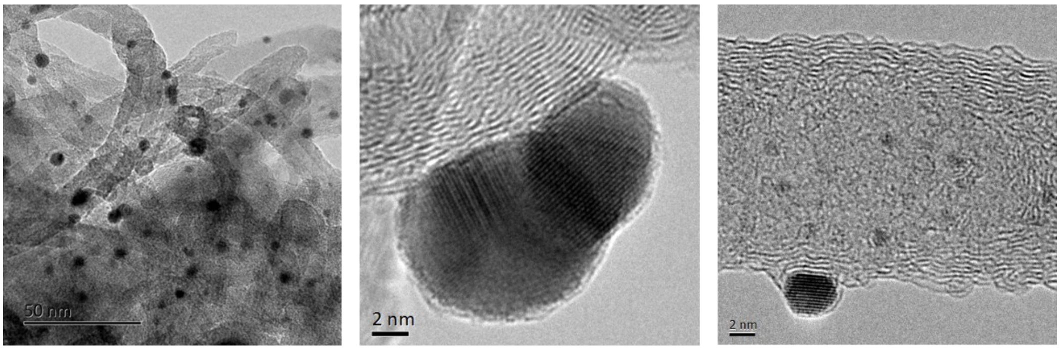


Figure S11. TEM images of the Au/oCNT-HO sample.

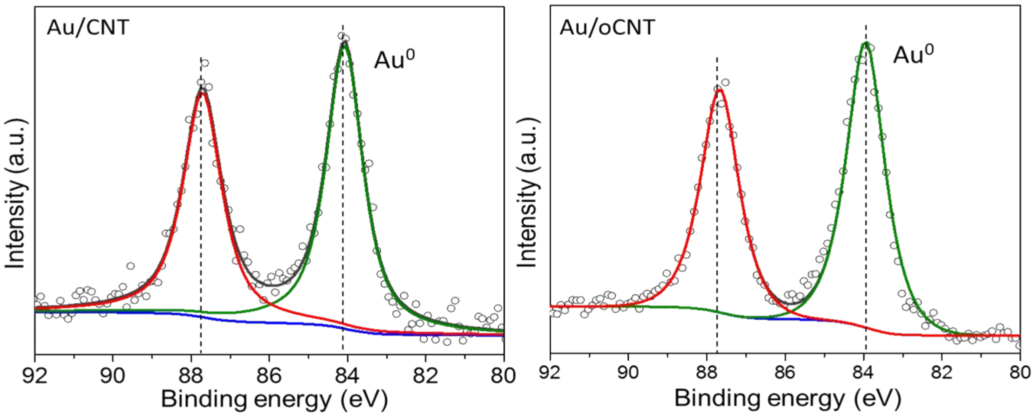


Figure S12. XPS spectra of Au 4f region over Au/CNT and Au/oCNT samples.

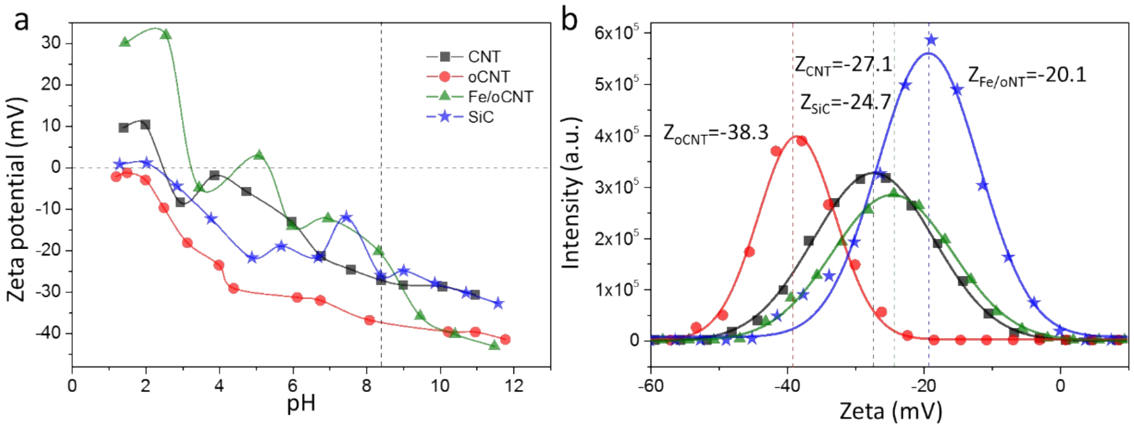


Figure S13. a) Zeta potential varying along with pH value of different materials. b) Zeta potentials of different supports under pH value of 8.4 (pH value of initial gold colloid).

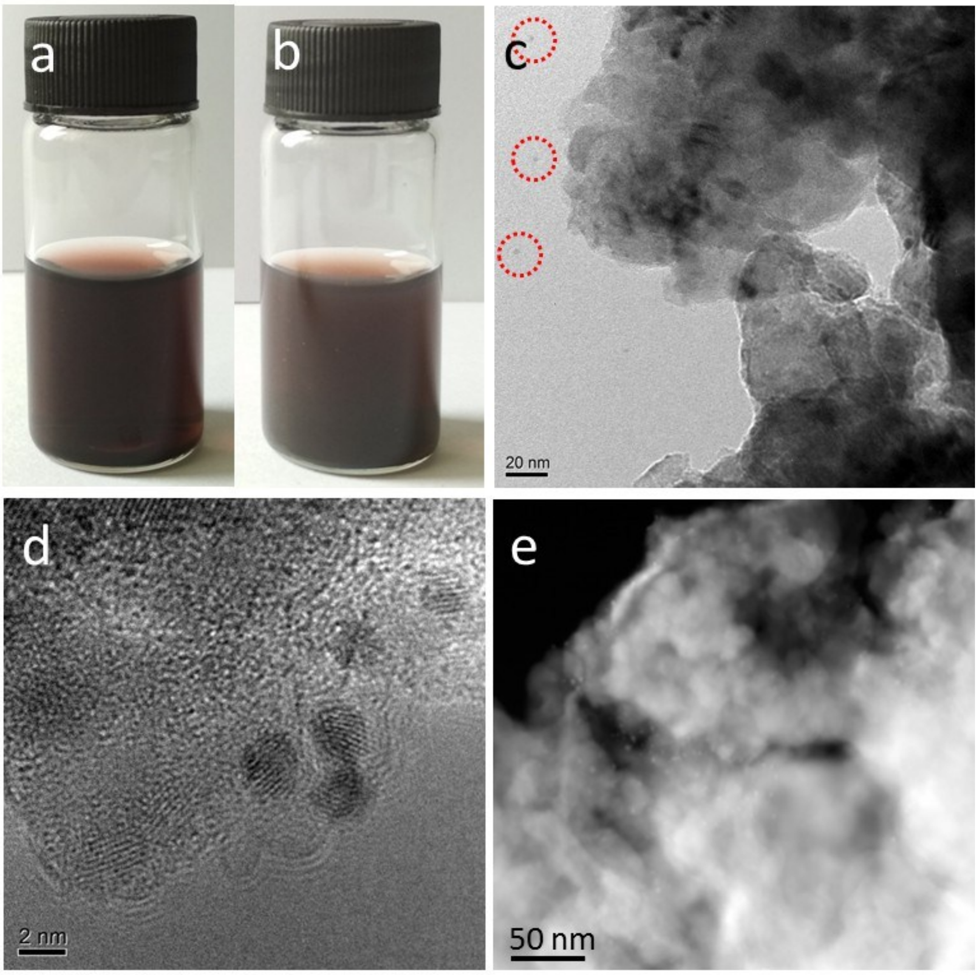


Figure S14. a) Digital photo of Au colloid. b) Digital photo of SiC in Au colloid after 16 h. The thick wine-red color of the supernatant liquid suggested the uneasy anchoring of gold nanoparticles by SiC material. c) TEM images of scattered gold nanoparticles around SiC support, d) Gold nanoparticles moving towards each other, e) HADDF-STEM image of freshly prepared Au/SiC sample only after extraction from the colloid solution with CNT impregnation after 16 h.

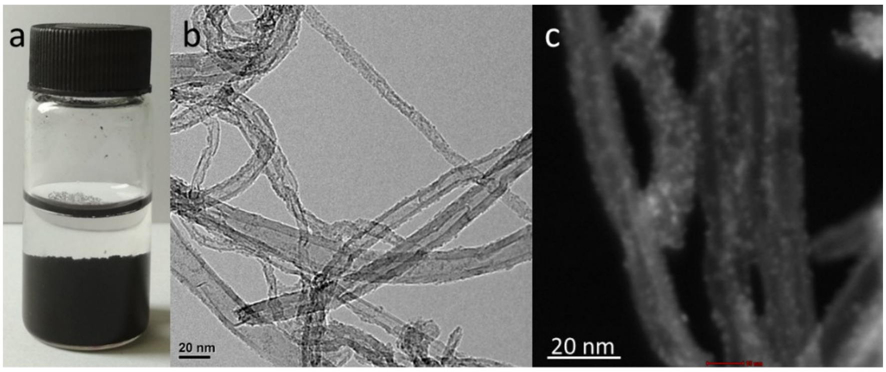


Figure S15. a) Digital photo of FeO$_x$/oCNT within Au colloid. b-c) TEM and HAADF-STEM images of FeO$_x$/oCNT.

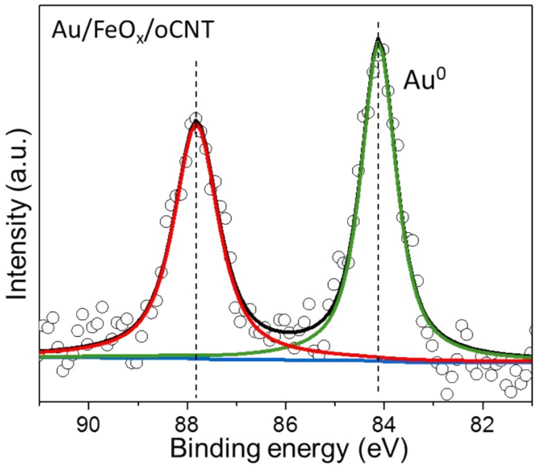


Figure S16. XPS spectrum in Au 4f region of the Au/FeO$_x$/oCNT sample.

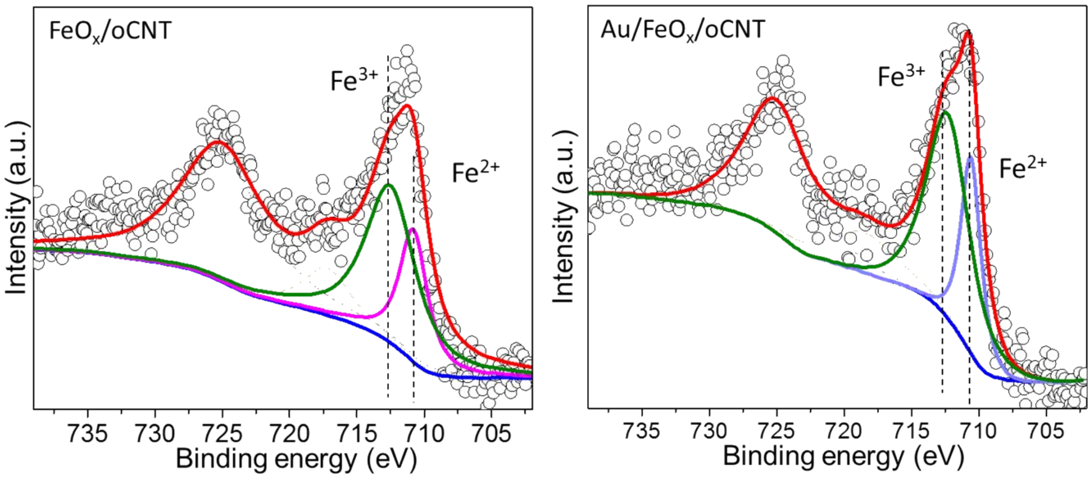


Figure S17. XPS spectra in the Fe 2p region of FeO$_x$/oCNT and Au/FeO$_x$/oCNT.

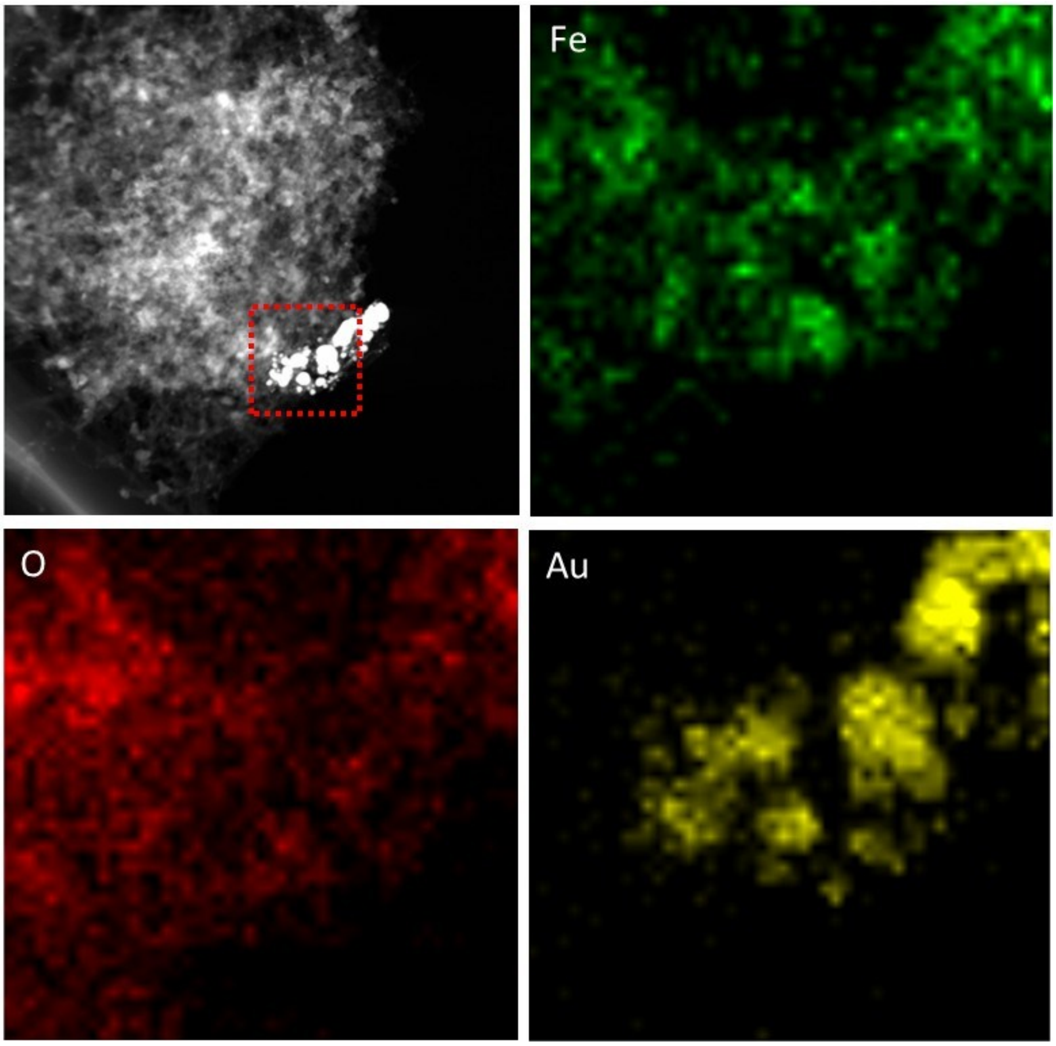


Figure S18. HADDF-STEM elemental mapping of the Au/FeO$_x$/oCNT smple.

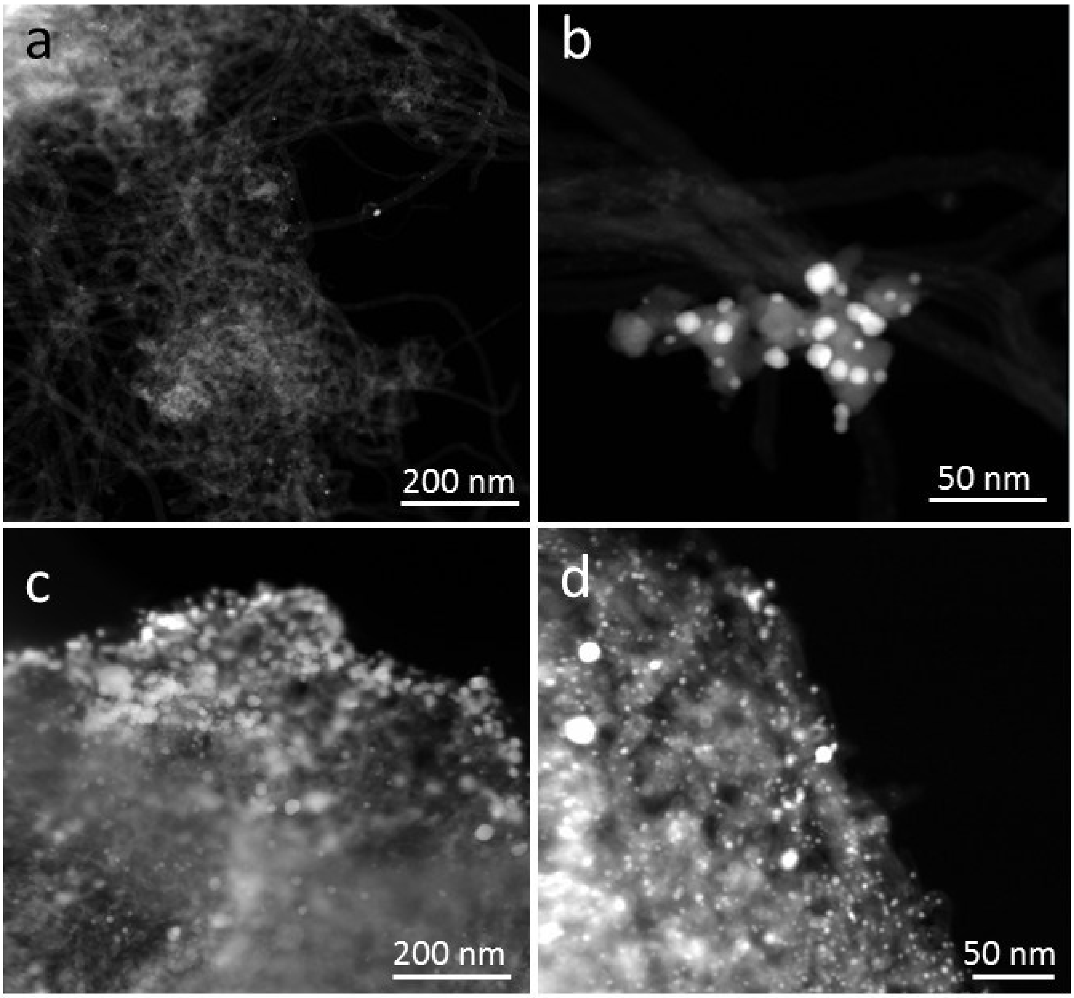


Figure S19. HADDF-STEM images of Au/FeO$_x$/oCNT. a) Overview of the sample. b) Small amounts of gold aggregates locating on bulk FeO$_x$. c-d) Sintered gold particles on the margin of FeO$_x$/oCNT.

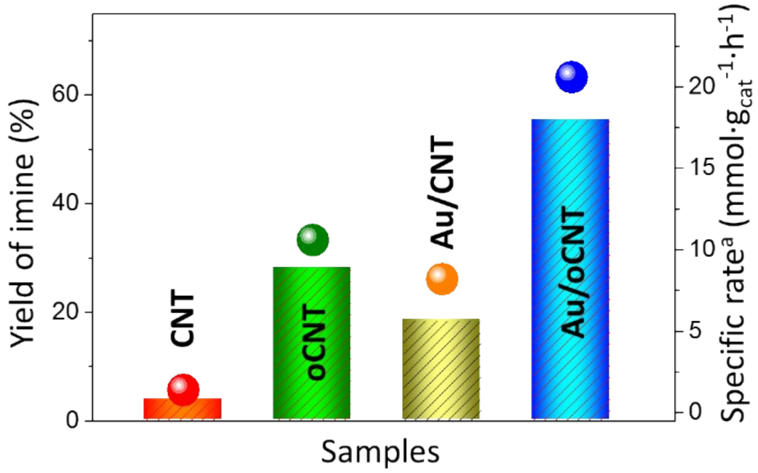


Figure S20. Yields of imine from oxidative coupling of benzylamine over different samples. [a] Specific rate based on per gram of catalyst. Reaction conditions: 20 mg Catalyst, 7.5 mmol benzylamine, Au/substrate mol ratio: 0.02%, reaction without any base or solvent at 100 °C for 10 h using O_2 balloon.

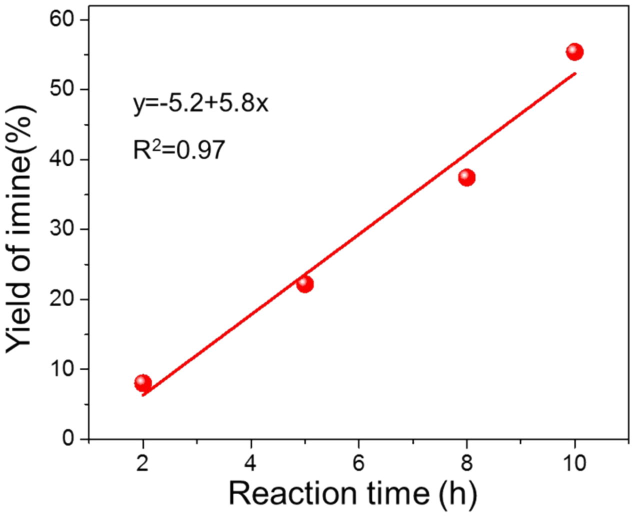


Figure S21. Yield of imine as a function of reaction time catalyzed by Au/oCNT. Reaction conditions: 20 mg Catalyst, 7.5 mmol benzylamine, Au/substrate mol ratio: 0.02%, reaction without any base or solvent at 100 °C for 2-10 h using O_2 balloon.

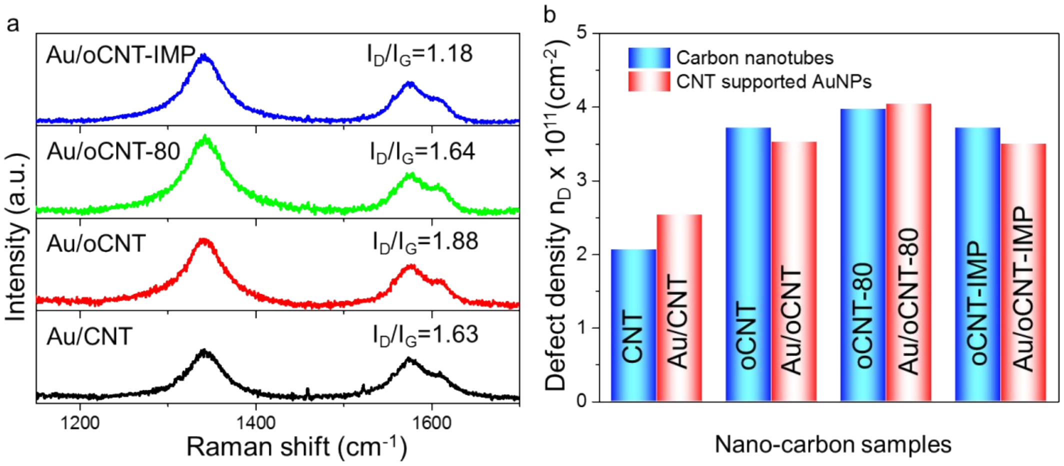


Figure S22. (a) Raman spectra of CNT before and after functionalization supported AuNPs, and (b) the surface defect density of different CNTs and their supported AuNPs by colloid method and impregnation method. Reaction conditions: 20 mg Catalyst, 7.5 mmol benzylamine, Au/substrate mol ratio: 0.02%, reaction without any base or solvent at 100 ^oC for 10 h using O_2 balloon.

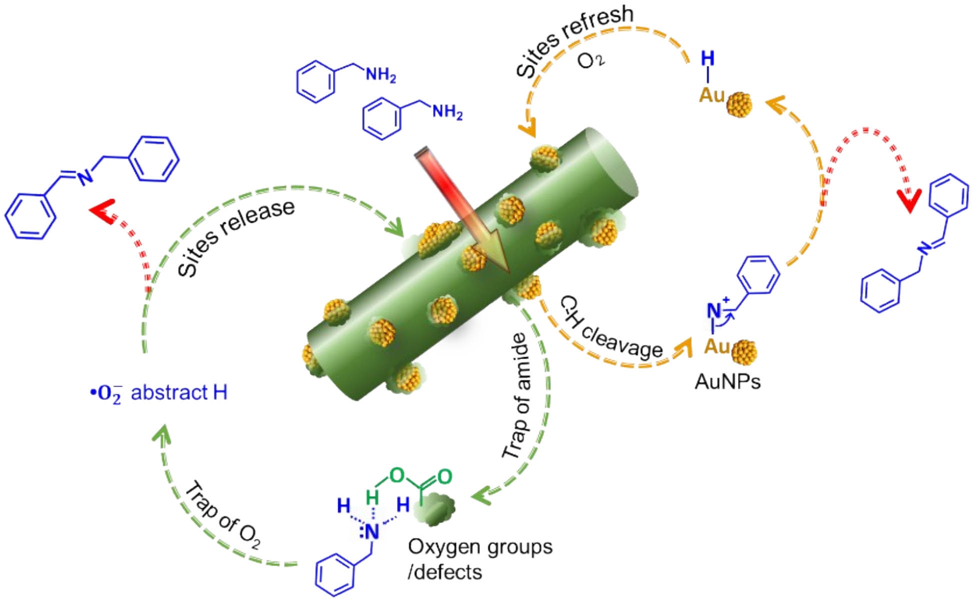


Figure S23. Schematic representation of the double active sites and their functions for the reaction.

Both the AuNPs and the surface chemistry of oCNT were evidenced to be synergistically responsible for the coupling reaction. The reported possible functions of different active sites can be summarized as above based on pioneers' researches. Su et al.[1] suggested that the benzylamine was easily captured by the surface carboxylic groups, where the trapped oxygen molecules facilitated the abstract of H atoms. The benzylamine was connected with the surface of carbonous material by H bond of –COOH group and unpaired electron was generated, which facilitated the activation of O_2 molecules as $\bullet O_2^-$. Further oxidation of the captured benzylamine and the extraction of H were fulfilled then by such $\bullet O_2^-$ species. The carbonous material will be refreshed by releasing the produced imine. Whilst for gold catalyzed coupling oxidation of benzylamine, the mechanism was reported to be different. So et al.[2] confirmed the capacity of AuNPs for the cleavage of C-H bond, which was viewed as a rate-determining step for this reaction. Benzylamine was more likely to be directed transformed into imine and released the Au atom connecting with H. The bonded H was further removed as H_2O by oxidation and gave the refreshed Au sites for next cycles. By the way, Donoeva et al.[3] also suggested that the active sites was around the periphery of AuNPs (Au-support interface) in the Au-graphite system. In this current work, it is believed that the strong interaction between Au and carbon synergistically enhanced the catalytic performances, emphasizing the design of catalysts for these double-active sites reactions.

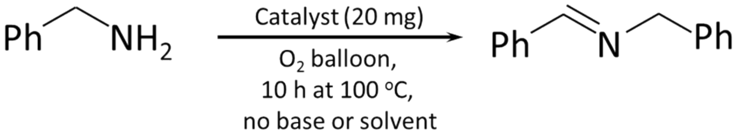
Reference

1. C. Su, M. Acik, K. Takai, et al. *Nat. Commun.*, 2012, **3**, 1298-1306.
2. M.-H. So, Y. Liu, C.-M. Ho, et al. *Chem. - Asian J.* 2009, **4**, 1551-1561.
3. B. Donoeva, N. Masoud and P. E. de Jongh, *Acs Catal.*, 2017, **7**, 4581-4591.

Table S1 Surface oxygen species from XPS spectra in O1s region.

Sample	Surface O species (O/Ototal%)			O at.%	O/C
	O=C	O-C=O	O-H		
CNT	0.3	47.6	52.1	3.1	0.032
oCNT	12.5	49.1	38.4	6.2	0.066
Au/CNT	6.1	43.1	50.8	3.5	0.036
Au/oCNT	22.6	42.5	34.9	7.5	0.081
FeO_x/oCNT	17.5	65.2	17.3	6.6	0.071

Table S2 Reaction conditions and yield of imine on oxidative self-coupling of benzylamine.



Sample	Conv. (%)	Select. (%)	Yield (%)[a]	Specific rate[b] ($mmol \cdot g_{cat}^{-1} \cdot h^{-1}$)	TOF[c] (h^{-1})
Blank test	0	0	0	n.a.[d]	n.a.
CNT	3.9	> 99.0	3.9	1.4	n.a.
oCNT	28.4	> 99.0	28.1	10.6	n.a.
Au/CNT[d]	18.7	> 99.0	18.5	8.2	78.1
Au/oCNT[d]	56.0	> 99.0	55.4	20.6	109.3

[a] Determined by GC using methylbenzene as an internal standard and calculated based on. [b] Specific rate based on per gram of catalyst. [c] Turnover frequency (TOF) values based on per mol of gold (equal to [(mol of amine conversion based on Au)/(mol of gold × h)], normalized by total amount of Au in the catalyst. The amine conversion based on Au was assumed by amine conversion based on Au/C-support minus amine conversion from pure C-support. The real gold loading of Au/CNT and Au/oCNT were 1.63 wt.% and 1.83 wt.%, respectively. The higher Au loading than the theoretical value of 1.5 wt.% may be caused by the removal of surface carbon fragments during thermal treatment. [d] 20 mg Catalyst, 7.5 mmol benzylamine, Au/substrate mol ratio: 0.02%, reaction without any base or solvent at 100 °C for 10 h using O_2 balloon.