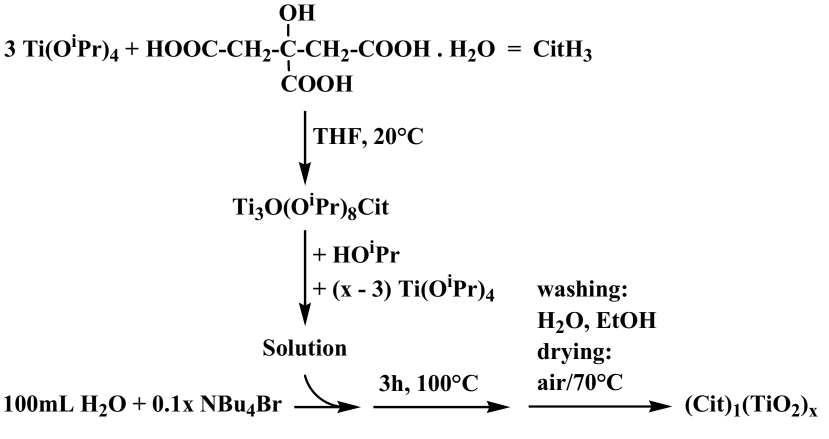
Electronic Supplementary Information (ESI)

MATERIALS

Characterization of the heteroleptic titanium precursor $Ti_3O(O^iPr)_8(OOC\text{-}CH_2\text{-}C(OH)(COO)\text{-}CH_2\text{-}COOH)$:
^1H NMR ($CDCl_3$, ppm, 20°C): 1.12-1.51 (48 H, overlap of doublets); 2.53 (1 H, d, ^2J =17.9Hz); 2.71 (1 H, d, ^2J =17.9Hz); 3.20 (1 H, d, ^2J =16.8Hz); 3.34 (1 H, d, ^2J =16.8Hz); 4.49 (2H, sept, ^3J = 5.9Hz); 4.58-5.19(5H, overlap of septuplets); 5.30 (1H, sept, ^3J = 5.9Hz).
FT-IR (Nujol, cm^{-1}): 3411 m (νO-H); 1705 s (νCOOH); 1585 s (ν_{as} COO); 1548 sh, 1527 s, 1455 s (ν_s COO), 681 m; 616 s, 563 m, 530 w, 486 m, 459 sh (νM-O).
Elemental Analysis calculated for $C_{30}H_{62}O_{16}Ti_3$ (found): %C : 43.72 (43.85); %H : 7.51 (7.55).

Reference WGC Au/TiO_2 catalyst: The Au/TiO_2 catalyst (type A, lot. no. Au-TiO_2 #02-05, sample no. 53) was purchased from the World Gold Council (WGC) [Gold reference catalysts, Gold Bull. 36 (2003) 24]. It is manufactured by Süd-Chemie Catalysts (Japan) under the supervision of M. Haruta, and characterized by S. Tsubota and coworkers. Its preparation followed a deposition– precipitation protocol developed by M. Haruta and coworkers [M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, J. Catal. 144 (1993) 175.2]. The powder catalyst contains 1.4±0.1 wt% of gold, as checked by inductively coupled plasma (ICP) chemical analysis. The average particle diameter of the fresh catalyst is 3.7±1.5 nm, as analyzed by transmission electron microscopy. The Degussa P25 titania support (50 ± 15 m^2g^{-1}) is a mixture of anatase (75 ± 5 wt%) and rutile (25±5 wt%) crystallites with mean particle diameter 25 nm and 40 nm respectively.

Optimised synthesis of 0.2wt.%$Au/(Cit)_1(TiO_2)_{20}$
An aqueous solution of $HAuCl_4$ is added to an aqueous suspension of $(Cit)_1(TiO_2)_{20}$ and the resulting suspension is heated to reflux during 30min. Then, the pinkish solid is centrifuged, washed with water and ethanol and finally dried at 70°C overnight. After 3h at 350°C under air, the resulting Au/TiO_2 has a gold loading of 0.2w %.



Scheme 1S Synthesis of the $(Cit)_1(TiO_2)_x$ hybrid nanoparticles via low temperature hydrolysis of the heteroleptic Ti alkoxide-citrate precursor; the Ti/Cit molar ratio (x) has been varied from 20 to 125

CHARACTERIZATION TECHNIQUES AND PROTOCOLS USED

X-ray diffraction (XRD): The XRD patterns are collected using Cu $K_{\alpha1+\alpha2}$ radiations (λ = 1.54184 Å) over a 2θ range of 3–80° at a rate of 0.028 s^{-1} on a Bruker (Siemens) D5005 diffractometer. The average size of the titania crystallites is calculated according to the Scherrer equation.

Fourier Transformed Infrared spectroscopy (FT-IR): FT-IR spectra were recorded on a Perkin-Elmer Paragon 500 spectrometer. The precursor was emulsified in nujol between two KBr pellets and the powders from the hydrolysis were pelletized with KBr.

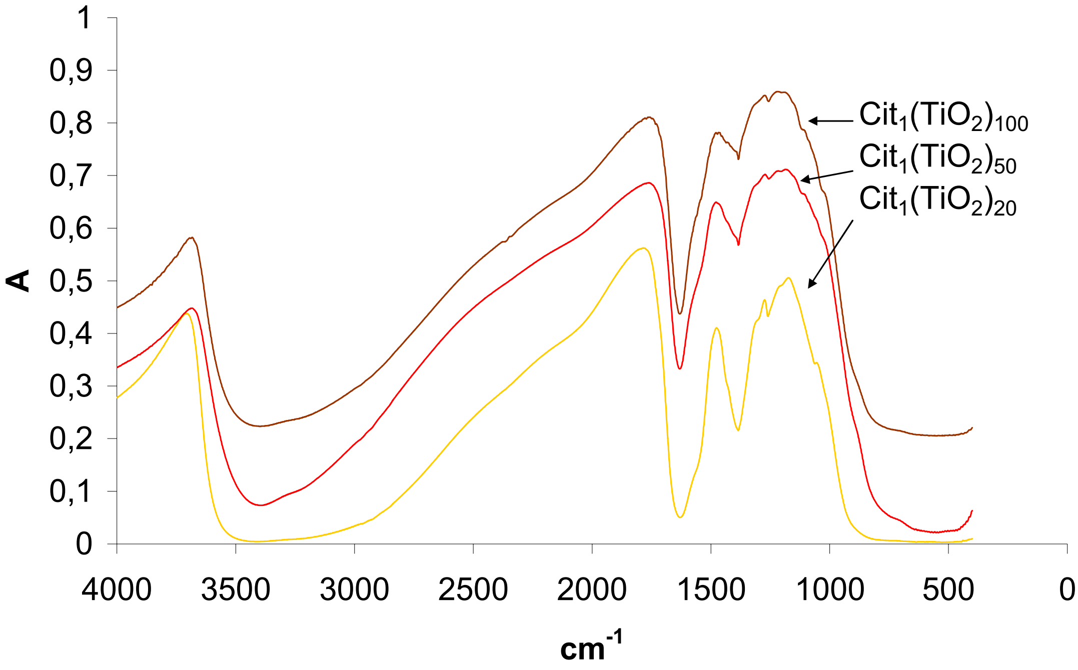


Fig.1S : FTIR spectra of the as-prepared $(Cit)_1(TiO_2)_x$ support with x = 20, 50 or 100

MS-coupled thermogravimetric/differential thermal analyses (MS-TG–DTA) are carried out on a Setaram Instrumentation SETSYS Evolution-1200 apparatus fitted with a Pfeiffer Omnistar 2006 mass spectrometer (1-200 uma). Samples are heated in flowing air (50 cm^3 min^{-1}) from 20 to 600°C at 10° min^{-1}.

Iso-electric points (IEP) of the hybrid titanias are determined by zeta potential measurements, using a Malvern Nano ZS. Suspensions were prepared under sonication with each powder using aqueous solutions set at pH from 2 to 9.

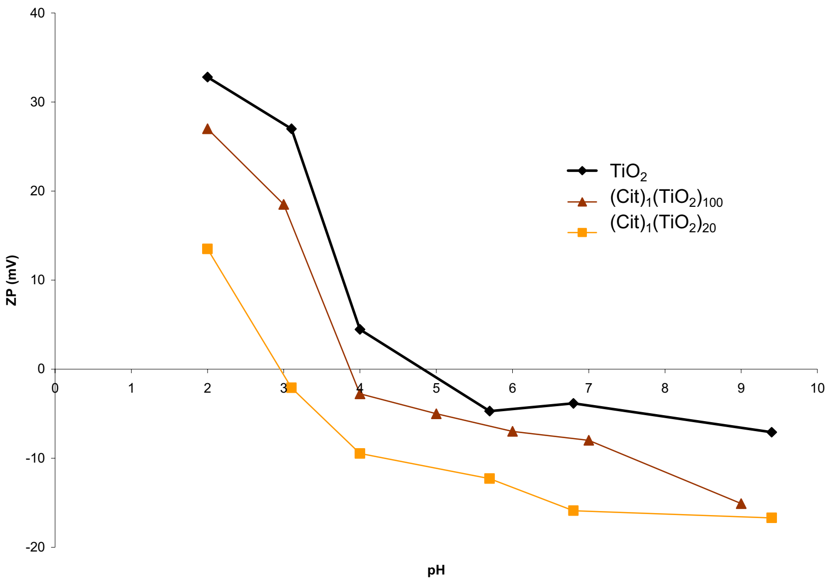


Fig. 2S: ZP (zeta potential in mV) as a function of pH spectra of the as-prepared $(Cit)_1(TiO_2)_{20}$ support and simple TiO_2

BET surface areas are determined on N_2 adsorption/desorption isotherms collected at liquid nitrogen temperature using a Micromeretics ASAP 2010 apparatus. Before the measurement, ~80 mg of the hybrid titania powder is dehydrated under vacuum at 100°C overnight.

UV–vis diffuse reflectance spectroscopy: UV–vis analyses of the powder samples are performed on a PerkinElmer Lambda 35 UV– vis spectrometer equipped with a Labsphere RSA-PE-20 diffuse reflectance accessory. UV spectra are recorded in the range 190–1100 nm with a scan speed of 240 nm min^{-1} and a slit width of 2 nm. The incident beam is 8° off axis from the sample holder in order to eliminate specular reflection.

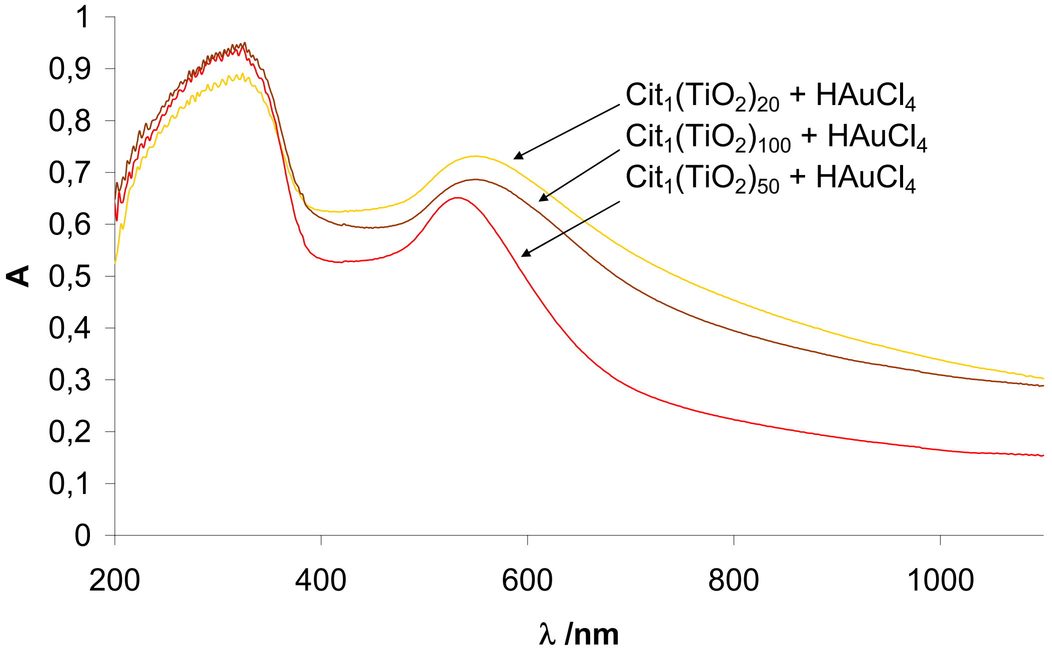


Fig. 3S: UV–vis spectra of the as-prepared $Au/(Cit)_1(TiO_2)_x$ using $HAuCl_4$ with x = 20, 50 or 100

X-ray photoelectron spectroscopy (XPS) experiments are carried out on a Kratos Axis Ultra DLD spectrometer using monochromated Al Ka X-rays (1486.6 eV, 150 W), a pass energy of 40 eV, a hybrid lens mode and an indium sample holder in ultra-high vacuum ($P < 10^{-9}$ mbar). The analyzed surface area is 700 mm × 300 mm. Charge neutralization is required for all samples. The peaks (O 1s, Au 4f, Ti 2p) are referenced to the Ti 2p band at 458.8 eV in TiO_2. Shirley background subtraction and peak decomposition using Gaussian–Lorentzian products are performed with the Vision 2.2.6 Kratos processing program. A degree of asymmetry is added to fit the Au 4f peaks.

	Atomic ratio		$E_{binding}$ Au $4f_{7/2}$ (eV)
	Au/Ti	C/Ti	
as-prepared $HAuCl_4$ + $Cit_1(TiO_2)_{100}$	4.7 10^{-3}	1.02	83.7
350°C-calcinated $HAuCl_4$ + $Cit_1(TiO_2)_{100}$	4.2 10^{-3}	0.76	83.3

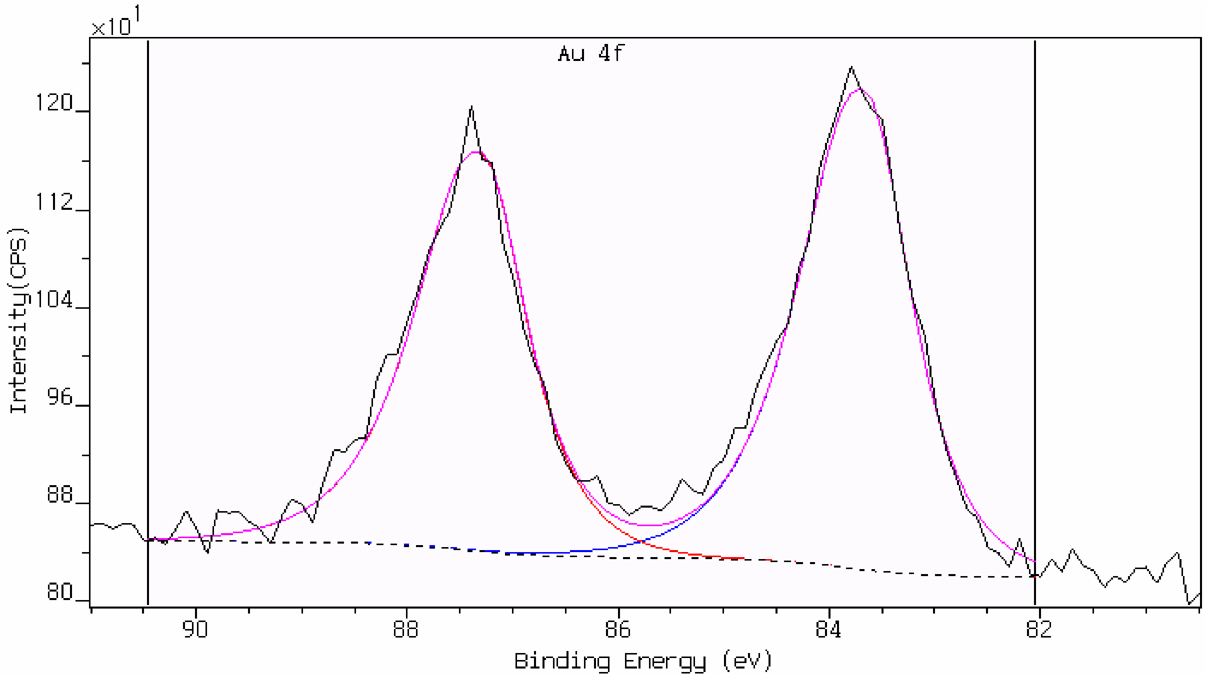


Fig.4S : XPS spectrum of Au $4f_{7/2}$ of the as-prepared $HAuCl_4$ + $Cit_1(TiO_2)_{100}$

Chemical analyses of the samples are carried out in-house by inductively coupled plasma optical emission spectroscopy (ICP-OES Activa from HORIBAJobin Yvon) to determine the gold loadings.

Transmission electron microscopy (TEM) is performed on a JEOL 2010 LaB6 microscope operating at 200 kV. Size distributions are obtained on bright field images.

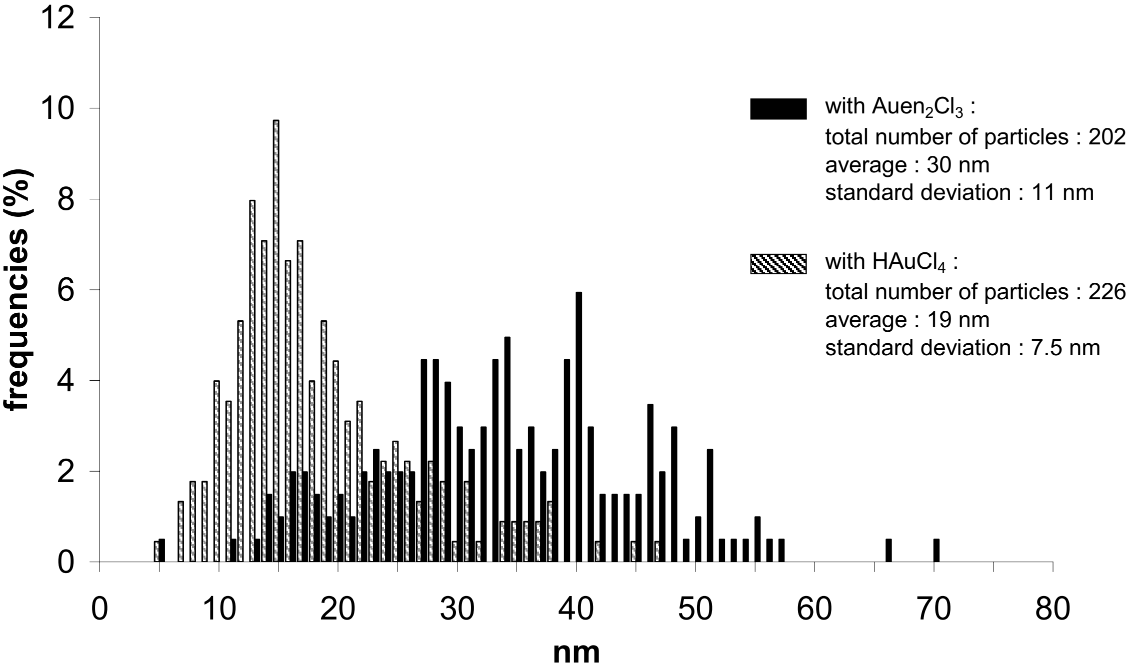


Fig.5S : Particle size distribution histogram of the 350°C-calcinated Au/(Cit)$_1$(TiO$_2$)$_{20}$ with each gold precursor

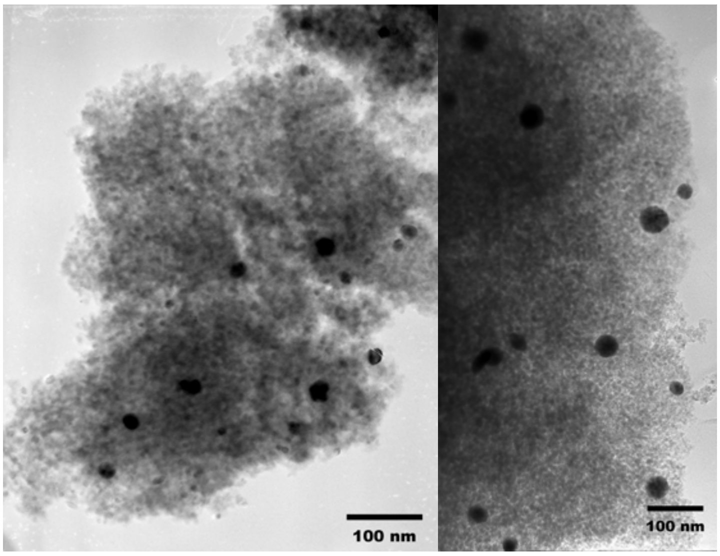


Fig.6S : TEM image of 350°C-calcinated Au/(Cit)$_1$(TiO$_2$)$_{20}$ with HAuCl$_4$ (left) and Au(en)$_2$Cl$_3$ (right)

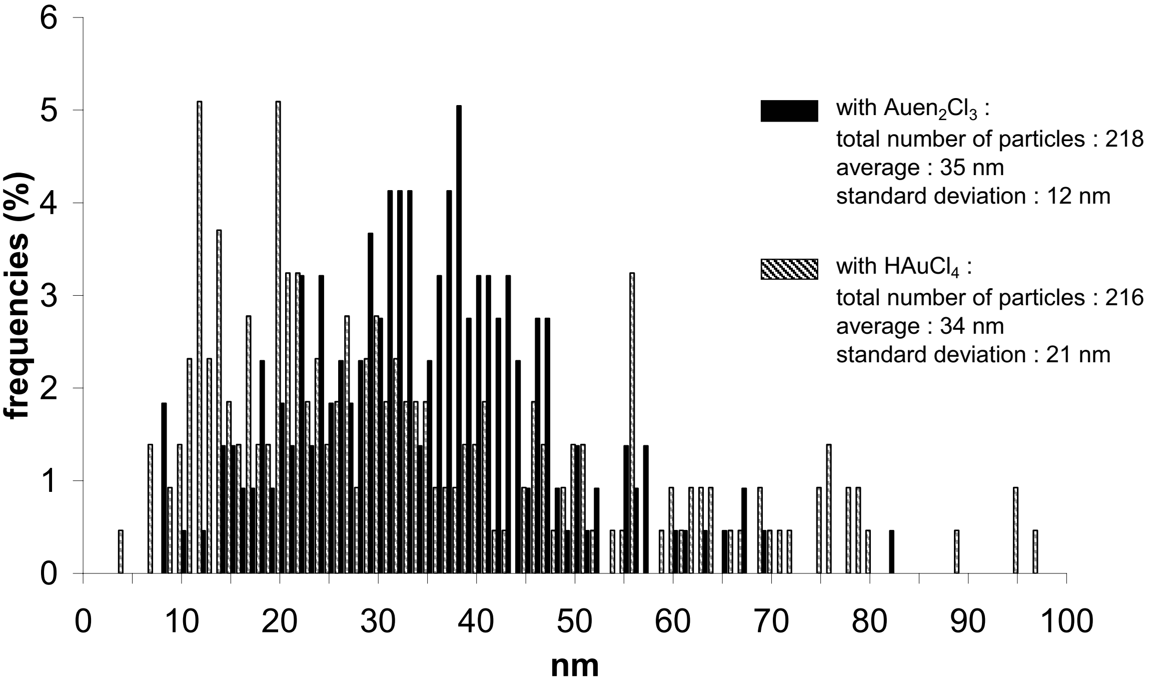


Fig.7S : Particle size distribution histogram of the 350°C-calcinated $Au/(Cit)_1(TiO_2)_{50}$ with each gold precursor

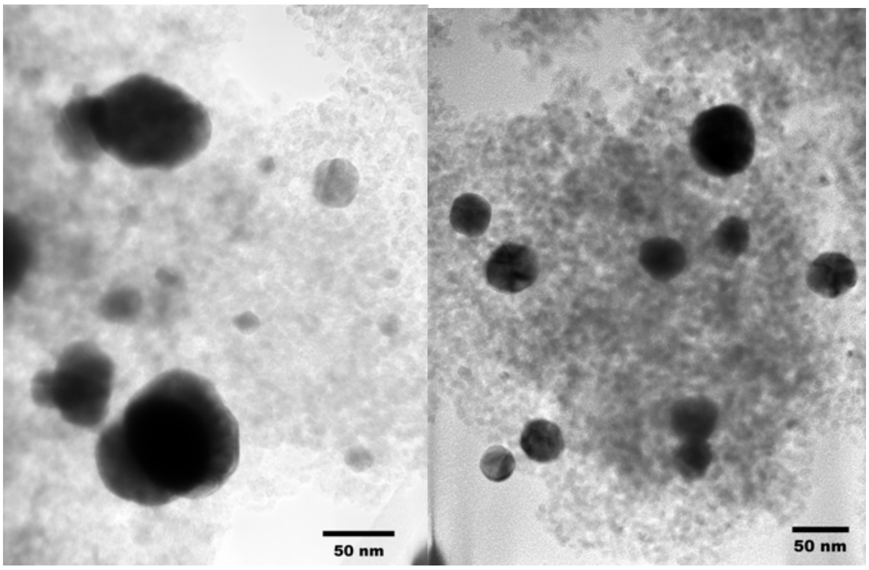


Fig.8S : TEM image of 350°C-calcinated $Au/(Cit)_1(TiO_2)_{50}$ with $HAuCl_4$ (left) and $Au(en)_2Cl_3$ (right)

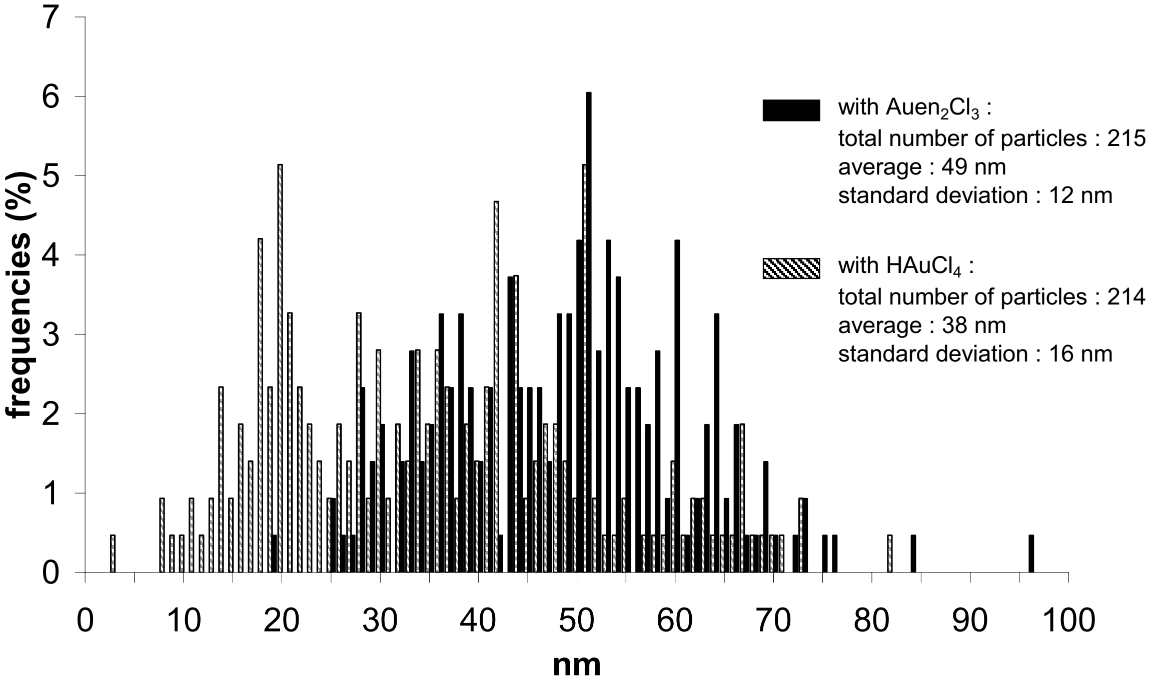


Fig.8S : Particle size distribution histogram of the 350°C-calcinated Au/$(Cit)_1(TiO_2)_{100}$ with each gold precursor

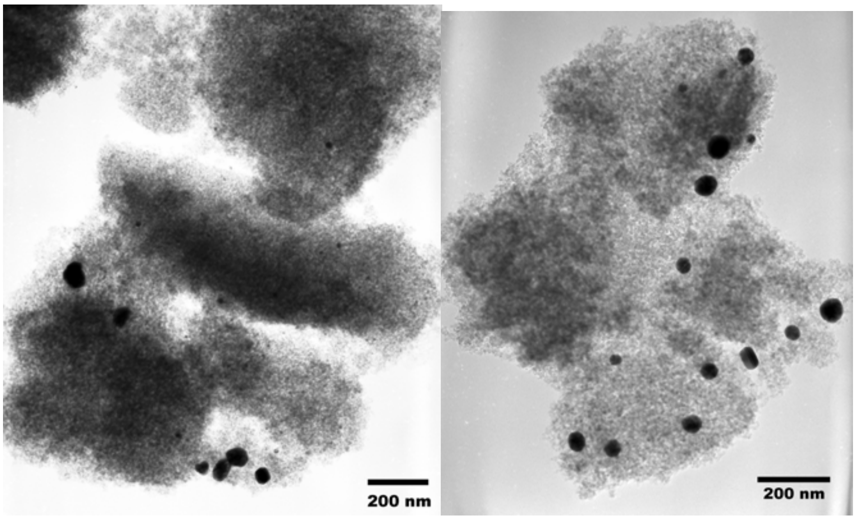


Fig.9S : TEM image of 350°C-calcinated Au/$(Cit)_1(TiO_2)_{100}$ with $HAuCl_4$ (left) and $Au(en)_2Cl_3$ (right)

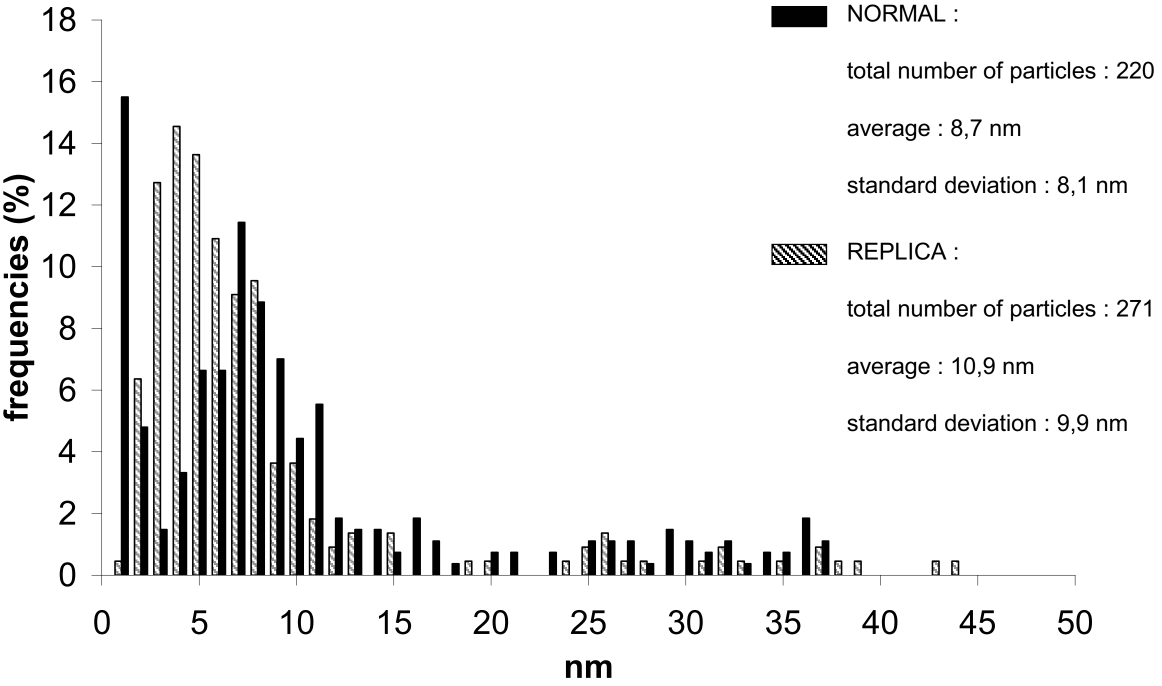


Fig.10S : Particle size distribution histogram of 350°C-calcinated 0.2wt.%Au/$(Cit)_1(TiO_2)_{20}$ and its replica which was prepared as follow: the sample is pre deposited on an amorphous carbon film and the support (TiO_2) is dissolved by H_2O + acetone + HF, the resulting carbon film contains only the gold particles.

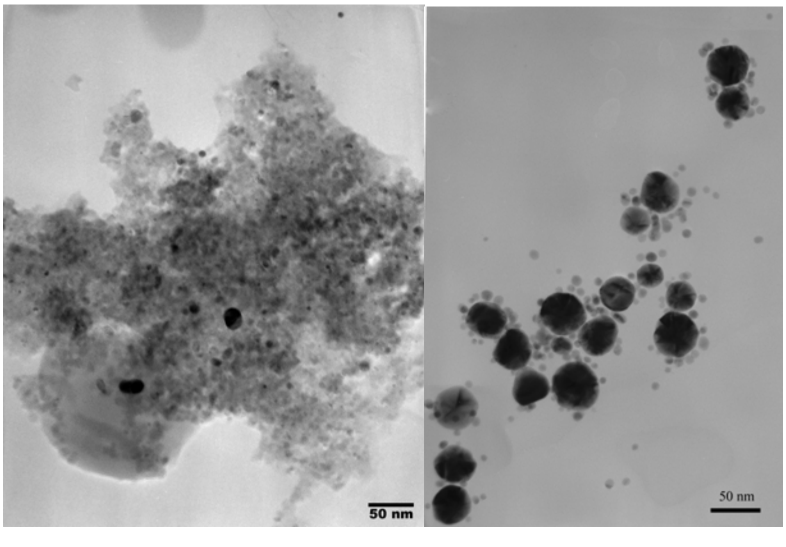
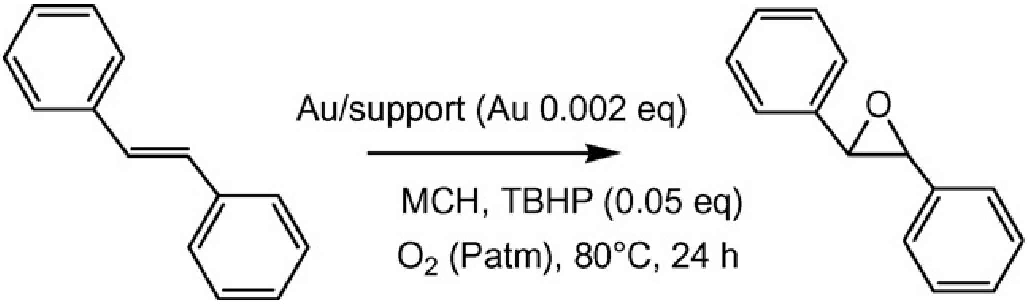


Fig.11S : TEM image of 350°C-calcinated 0.2wt.%Au/$(Cit)_1(TiO_2)_{20}$ (left) and its replica (right)

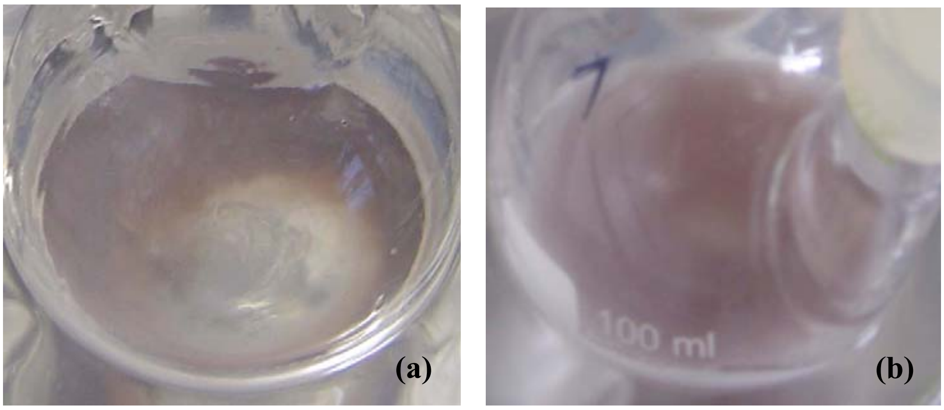
CATALYTIC EVALUATIONS

Aerobic stilbene epoxidation

The liquid phase catalytic tests are carried out in magnetically stirred (900 rpm) glass batch reactors held at 80°C for 24 h in air at atmospheric pressure. The reaction mixtures consist of substrate (*trans*-stilbene, 96%, 186 mg /1 mmol), solvent (methylcyclohexane, MCH, 99%, 20 mL / 155 mmol), catalyst (2.1 ± 0.1 mmol Au) and *tert*-butylhydroperoxide (70% TBHP in H_2O, 7 μl / 0.05 mmol). The reaction products are identified and quantified by HPLC (Perkin-Elmer Series 200 lc pump, autosampler and UV–vis detector set at 250 nm, reverse phase C-18 column Brownlee, ValueLineSpheri-5 C18, 220 mm × 4.6 mm, acetonitrile/water as eluent at 1 cm^3 min^{-1}). HPLC calibration is carried out using *trans*-stilbene oxide (epoxide, 99%, Acros Organics). Conversion (%) is defined as [[(initial concentration of tS) × (final concentration of tS)]/(initial concentration of tS) × 100]; yield of epoxide (%) is defined as [(final concentration of epoxide)/(initial concentration of tS) × 100]; selectivity to epoxide (%) is defined as [(final concentration of epoxide)/[(initial concentration of tS) × (final concentration of tS)] × 100]. It is noted that *trans*-stilbene oxide (the epoxide) is the main product of the reaction. Only traces of benzil and benzaldehyde are detected. The remaining *trans*-stilbene conversion is accounted for by the formation of HPLC-undetectable total oxidation products, such as carbon dioxide [see ref 13 in the text: P. Lignier, F. Morfin, L. Piccolo, J.-L. Rousset and V. Caps, Catal. Today, 2007, 122, 284.] (Scheme 1).



Scheme 2S. Reaction conditions for the epoxidation of trans-stilbene over gold catalysts (from ref 6 in the text: P. Lignier, M. Comotti, F. Schüth, J.-L. Rousset and V. Caps, Catal. Today, 2008, doi:10.1016/j.cattod.2008.04.032)



Pictures 1S: Aerobic stilbene epoxidation: Dispersion in the epoxidation reaction of (a) the reference WGC Au/TiO_2 catalyst and (b) the 350°C heated $Au/(Cit)_1(TiO_2)_{20}$

CO oxidation (in the presence or in the absence of hydrogen)

Reactions are carried out in a continuous flow fixed bed reactor at atmospheric pressure and variable temperature. The catalysts are placed in a quartz tube reactor located in a ceramic furnace. They are diluted in γ-alumina (Condea Puralox SCFa215, 215 m^2/g, which is inert under all reaction conditions used) in order to ensure similar gold content (0.16 mg) in the catalytic beds and similar bed lengths (13 mm). The reactant gases are mixed with mass flow controllers (Brooks Instrument) and sent through the reactor at a total flow rate of 50 $mLmin^{-1}$ corresponding to a gas hourly space velocity (GHSV) of ~3000 h^{-1}. The in-let gas mixtures consist in 2% CO / 2% O_2 for CO oxidation, 2% CO / 2% O_2 / 48% H_2 for the PROX reaction (preferential oxidation of CO in H_2), balanced in helium. The outlet gases are analyzed with online VARIAN-Micro GC (CP2003) equipped with a TCD detector. Two columns are used in parallel: a Molsieve 5Å column (Ar as carrier gas) to quantify H_2, O_2 and CO and a poraPLOT Q column (He as carrier gas) to quantify CO_2. The catalysts are heated from ambient to 280°C with a heating rate of $1°min^{-1}$ and cooled down at the same rate. The reaction temperature is controlled by a thermocouple located inside the catalytic bed. Two reaction cycles (heating up to 280°C and down) are performed. Results obtained in the second heating step, corresponding to stabilized activity, are used for discussion.

Turnover frequencies (s^{-1}) are defined as the number of mole of CO converted per number of mole of surface gold atom per second; they are determined as follows:

$TOF = (y_{CO,in} * X_{CO} * V_{gas}*196.95)/(m_{Au}*d)$

Where

m_{Au} is the mass of Au in the catalytic bed in g

V_{gas} is the total molar flow rate in mol s^{-1} (= 50/(60*22400) = 3.72 * 10^{-5} mol s^{-1})

X_{CO} the conversion of CO

$y_{CO,in}$ is the mole fraction of CO in the in-let gas mixture (2%)

196.95 is the molecular weight of gold

d is the dispersion of the gold particles (0.16 for the hybrid $0.2\%Au/(Cit)_1(TiO_2)_{20}$ catalyst and 0.35 for the WGC Au/TiO_2 reference catalyst)