Supporting Information

Ultrasonic-assisted oxidation of Cellulose to Oxalic acid over gold nanoparticles supported on iron-oxide

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1. Image of Ultrasonic batch reactor used in this work



Figure S1. Image of ultrasound batch reactor used in this work.

2. Calibration curves of identified products at optimised conditions (External



calibrations)

Figure S2a. Calibration curve of formic acid



Figure S2b. Calibration curve of oxalic acid



Figure S2c. Calibration curve of glucuronic acid



Figure 2Sd. Calibration curve of gluconic acid.

3. HPLC profiles of crude reaction product and standard products



Figure S3. HLPC graphs of reaction products and standard products

4. Analysis of reaction products by high resolution mass chromatography (HR-LCMS negative mode analysis)

High resolution mass chromatography was performed on the crude reaction product after lyophilisation to confirm the products formed and observed with HPLC. According to the National Institute of Standards and Technology, US Department of Commerce, the actual mass of oxalic acid is 90.0349 g/mol, mass of oxalic found [M+1] = 89.9856 m/z. Actual mass of gluconic acid is 196.1553 g/mol, mass of gluconic acid found is [M+1] = 196.0454 m/z. Actual mass of 2-keto-gluconic acid is 194.1390 g/mol, mass of 2-keto-gluconic acid found is [M+1] = 194.0349 m/z



Figure S4. HR-MS of crude reaction product.



5. ¹³C NMR analysis of reaction product and standard products

Figure S5. ¹³C NMR analysis of crude reaction product and standard samples. Solvents (a) DMSO (b) D_2O (c) D_2O

6. Product yields for the Au/Fe₂O₃ catalyzed sonochemical oxidation of substrates

но он он	он))) Au-Fe ₂ O ₃ ►	HO Oxalic acid	HO Glu	OH O H OH H H OH H	OH O H OH H OH 2-dehydro-Gluconic	OH O OH OH		o formic acid
Substrate	Gas	Reaction	Conversion	Oxalic	Gluconic	2-keto-	Glucuronic	Formic	Acetic
	atmosphere	time (h)	(%)	acid	acid	gluconic	acid	acid	acid
						acid			
		1	25.2	4.5	3.8	5.8	-	0.7	0
Cellobiose	Argon	2	40	6.0	26	13	-	2.8	0
		4	52	28.3	8.6	1.1	-	4.6	0
Fructose	Oxygen	1	62	0	8.1	47.3	0	2.5	0
		2	5	2	1	2	0	0	0
		4	12	5	3	4	0	0	0
Cellulose	Argon	8	20	10	6	3	0	0	0
		10	36	18	10	0	0	6	0
Reactions condition: 0.200g of substrate, 15 mL H ₂ O, 0.15 MPa of gas, 0.025g of Au/Fe ₂ O ₃									

Table S1 Product yields for the Au/Fe₂O₃ catalyzed sonochemical oxidation of cellulose.

7. Size Exclusion Chromatographic analysis of water-soluble oligomers obtained after

ultrasound irradiation of cellulose under oxygen pressure.



Figure S6. Size exclusion chromatography (SEC) analysis of the soluble fractions recovered after ultrasound irradiation of cellulose.

8. Hydrogen-peroxide quantification using UV visible spectrophotometer

The H_2O_2 concentration in the solution was measured using a UV visible spectrophotometer (ThermoFisher Evolution 60S).

Principle

H2O2 reacts with TiO^{2+} to form a yellow-orange complex Ti(IV)-H₂O₂. The absorption spectrum of this complex shows a maximum absorption wavelength at 412 nm.

Calibration curve

$TiOSO_4$ solution 0.02 M in H_2SO_4 0.5M

Typically, 0.552 g of titanium oxysulfate (TiOSO₄) are dissolved in water and then 2.8 mL of $H_2SO_4(18 \text{ M})$ are added. The solution was then diluted with water to a final volume of 100 mL.

Standard solutions of H_2O_2

The hydrogen peroxide solutions were prepared from a commercial H_2O_2 solution (35%w) at concentrations between 0 and 0.005 M.

For the calibration curve, the analysis was performed by mixing the same volume of the $TiOSO_4$ solution and hydrogen peroxide solution (0.5 mL) (in order to obtain a dilution by 2 of the H_2O_2 solution). The absorbance was measured at 412 nm. The calibration curve is shown in Figure S7.



Figure S7. Hydrogen peroxide calibration curve

Quantification of hydrogen peroxide in solution

Reaction samples are taken directly in the solution from the ultrasound reactor and mixed with the titanium oxysulfate solution in 1/1 v/v (the same conditions as the standards solutions). The absorbance is measured at the same wavelength as the one used for the calibration.

9. Characterization of Au-Fe₂O₃ Catalyst



Figure S8. XRD analysis of Au-Fe₂O₃ catalyst

10. Relative atomic percentages of elements estimated by XPS analysis

Table S2.	Elemental	atomic	percentages	determined	using XPS	analysis
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Element	Au-Fe ₂ O ₃
Fe 2p	41.7
O 1s	51.6
Au 4f	0.9
C 1s	5.8
Total	100

11. Computational details.

All first-principle calculations are performed based on periodic boundary conditions and planewave pseudopotential implementation of DFT using the Vienna ab-initio simulation package (VASP) developed at the Fakultät für Physik of the Universität Wien.^{1, 2} Projector augmented wave (PAW) method³ employed with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁴ are used to describe the interaction between valence electrons and ions with a plane wave cut-off energy of 450 eV. For DFT calculations on Fe₂O₃ and CuO systems, the Generalized Gradient Approximation (GGA) and the Hubbard correction U = 4.3 eV and U =4.5 eV within the GGA+U scheme were used to correct the electron delocalization that occurs in strongly correlated systems such as transition metal oxides, respectively.⁵⁻⁷ All calculations involving Fe₂O₃ and CuO structures were performed using spin-polarization setup with the antiferromagnetic ordering, and the Grimme's D3 approach was included to correct the longrange dispersion interactions.⁸ Bulk lattice parameters of Fe₂O₃ and CuO were optimized using the $10 \times 10 \times 4$ and $15 \times 15 \times 15$ k-points grid. The optimized lattice parameters for Fe₂O₃ within this GGA+U scheme are a = b = 5.0429 (5.031) Å; c = 13.7852 (13.765) Å, with values in parentheses are reported experimental data.9, 10 The optimized lattice parameters for CuO are a = 4.4487 Å; b = 3.6776 Å; c = 5.1925 Å, β = 95.67°. Surfaces of Fe₂O₃ was modeled using the structure of $p(1 \times 3)$ slab of Fe₂O₃ (0001) surface with oxygen termination (Figure S1). Surfaces of CuO was modeled using the structure of $p(1 \times 1)$ slab of CuO(111) surface as was reported in earlier studies.^{5, 11} We used a k-points sampling of $4 \times 2 \times 1$ and $4 \times 4 \times 1$ for integration over the Brillouin zone in reciprocal space for all systems of Fe₂O₃ (0001) and CuO(111) structures (including the Au nanowire and Au overlayers which are mentioned in the main text and will be described more details in Figure S9).



Figure S9. a) Model of Fe_2O_3 (0001) with oxygen termination; b) Model of monolayer of Au(111) film on Fe_2O_3 (0001) support; c) Extended model of Au nanowire on Fe_2O_3 (0001) support. Au, Fe, and O are shown in yellow, purple, and red, respectively. The supercell in Figure S8a and S8b are marked by black lines.

To provide the comprehension understanding on the role of interfacial sites between Au nanoparticle and Fe_2O_3 (0001) support in generating the active oxygen species (O*, OH* and OOH*), we also evaluated the formations of those species on pure gold catalyst using the p(3×3) slab of Au (111) surface with 4 layers, and the 5×5×1 k-points grid was used for calculations on pure Au (111) model. For both Fe_2O_3 (0001) and Au (111) systems, the vacuum thickness of 20 Å above the topmost layer was employed to avoid interactions between repeted slabs.⁵ Geometries were fully relaxed using the conjugate-gradient algorithm until the energy changes by less than 0.1 kJ/mol. Transition states were located using the Climbing-Nudged Elastic Band (Cl-NEB) method,¹² and frequency calculations confirmed the nature of the transition states with only one imaginary vibrational frequency.

12. Models of Au/Fe₂O₃ and Au/CuO interface

The model of $p(1\times3)$ slab of Fe_2O_3 (0001) surface with oxygen termination is presented in Figure S9a. This model includes 6 layers of Fe atoms and 7 layers of O atoms, which was reported in literature as the most stable exposure surface of Fe_2O_3 under the reaction conditions

applied in this study.¹³⁻¹⁵ To create model of overlayer Au (111) films on Fe₂O₃ (0001), we used the Atomic Simulation Environment package¹⁶ to build a first monolayer of Au with one-to-one matching between Au atoms and surface oxygens of Fe₂O₃ (0001) (Figure S9b). After building the model of monolayer Au(111) film on Fe₂O₃, the bilayer and trilayer of Au films were created based on the bulk fcc structure of Au. Finally, the model of Au nanowire on Fe₂O₃ support was created by trimming 3 continuous rows of the trilayer Au(111) films/Fe₂O₃, and that structure was subsequently fully optimized.

To create model of overlayer Au (111) films on CuO (111), we used the Atomic Simulation Environment package¹⁶ to build a first monolayer of Au via two steps: first, two Au atoms are added on the one-to-one matching with the under-coordinated surface oxygen's of CuO (111) (called O_3 site). Since there are only two under-coordinated surface oxygens on CuO(111) surface, two other Au atoms are created to form the (111) registry of Au overlayers on CuO.

13. Charge density plots for for Au(111) overlayer films on Fe₂O₃ support with different overlayer thicknesses

Using the Atomic Simulation Environment package,¹⁶ we managed to build models of Au(111) films on Fe_2O_3 with low strains (+1.2%) to avoid spurious errors caused by geometric reconstructions. The structure of mono, bi- and tri- Au layer on Fe_2O_3 is shown in **Figure S10a**, **b**; **Figure S10d**, **e** and **Figure S10g**, **h**, respectively.

Figure S10. (a) top view, (b) side view, and (c) charge density difference plot for mono-layer Au (111)/Fe₂O₃. (d) top view, (e) side view, and (f) charge density difference plot for bi-layer Au (111)/Fe₂O₃. (g) top view, (h) side view, and (k) charge density difference plot for tri-layer Au (111)/Fe₂O₃. In the charge density difference plots, regions with depleted electron density (excess electron density) are shown in blue (green). Au, Fe, and O are shown in yellow, purple, and red, respectively. The supercell is marked by black lines.

For the monolayer of Au film supported on Fe_2O_3 , it could be visualized in the charge density difference plot shown in **Figure S10c** that the charge depletion regions (presented in blue color) are localized in the Au overlayer, consistent with the positive charges implemented on those Au atoms as is mentioned in the main text. The electron densities are accumulated at the interfacial oxygen atoms of the Fe_2O_3 support (green color regions), reflecting the charge transfer direction from Au to Fe_2O_3 . The charge density difference plots in **Figure S10f**, **k** for the bi-layer and tri-layer Au films supported on Fe_2O_3 , respectively, show that the charge transfers between Au and Fe_2O_3 in those structures are also majorly confined at the first Au layer directly at the interface.

14. Adsorption of species on Au(111)

We propose that atomic oxygen could be formed on Au(111) either via the direct dissociation of O₂ or via the two step decomposition of H₂O₂ into OOH*/OH*. From the data presented in Figure 8 of the main text, it could be seen that O_2 adsorbs weakly on Au(111) surface via the van der Waals interaction with the binding energy of -0.12 eV, consistent with earlier studies.¹⁷⁻ ¹⁹ The weak interaction of O₂ with Au(111) surface results in the high barrier of 1.85 eV for O₂ activation on Au(111) as was reported by Zhang et al.²⁰ Therefore the formation of atomic oxygen on Au(111) surface is both thermodynamically and kinetically unfavourable. Instead of being directly dissociated, O2 can be activated by H*, forming the OOH* intermediate. However, H* adsorbs weakly on the Au(111) surface, consistent with earlier studies stated that the adsorbed H* on Au(111) is even less stable than H_2 gas form.²¹ This observation suggests that once H^* is formed from H_2O by the ultrasound irradiation, it could not participate in the activation of O₂ on pure Au(111) surface. Therefore the activation of O₂ either via the direct dissociation of O₂ or via the formation of OOH* to generate active oxygen O* on Au(111) all not feasible. Similarly, all other possible intermediates during the decomposition of H₂O₂ (OH*, OOH*, H₂O or H₂O₂) also bound weakly to Au(111) surface and therefore the formation of atomic oxygen via the H₂O₂ decomposition pathway on Au(111) also not thermodynamically feasible.

15. Adhesion energy of Au on CuO

The computed adhesion energy of a monolayer Au(111) film on CuO is -3.02 eV (Table S3). At the interface between Au monolayer film and CuO support, the charge is transferred from Au over-layer to the support, resulting in the positive charge of +0.13 for Au atoms (Table S3). For the bilayer and tri-layer of Au films supported on CuO, the computed adhesion energies become stronger with the computed values of -3.37 and -3.47 eV, respectively (Table S3). It is important to mention that the differential adhesion energy (energy to adhere one more Au layer on existing overlayer of Au/CuO) of the bilayer (-3.72 eV) and tri layer (-3.76 eV) are very close to the adhesion energy of Au film on pure Au(111) (-3.78 eV, Table 2 of the main text), suggesting that the Au atoms in the 2^{nd} and 3^{rd} layer above the interface with CuO might have the chemical properties similar to surface metallic Au atoms of pure Au(111). Only the Au atoms in the 1^{st} atomic layer above CuO support gain the positive charge for all those overlayer models of Au films (Table S3), indicating that the interaction of CuO and Au is mainly occurred at the interface, similar to the observation on Au/Fe₂O₃ systems.

Tabl	e S3. Adhesion	energy and B	ader charge for .	Au overlayer film	s on CuO support.
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Systems	Average/Differential adhesion energy (eV)	Bader charge of Au atoms ^a
1 Au layer on CuO	-3.02	0.13
2 Au layers on CuO	-3.37/-3.72	0.17
3 Au layers on CuO	-3.47/-3.76	0.18

^aBader charge is presented only for Au atoms in atomic layer directly at the interface with CuO

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