

Gold on Diamond Nanoparticles as a Highly Efficient Fenton Catalyst

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Dedicated to Professor Carmen Nájera on the occasion of her 60th birthday

The Fenton reaction consists of the generation of highly aggressive hydroxyl radicals from hydrogen peroxide and is widely used to degrade organic pollutants. Due to its general applicability, the Fenton reaction is employed in water and soil disinfection/remediation and for removal of non-biodegradable chemicals. The main limitation of the Fenton reaction is the consumption of stoichiometric amounts of transition metals, mostly iron. There is considerable incentive in developing a catalytic Fenton process using exclusively hydrogen peroxide and a catalyst. Herein we report that gold nanoparticles grafted on nanoparticulate diamond catalyze the formation of hydroxyl radicals from hydrogen peroxide with at least 79 % efficiency and reach a turnover number of 321 000, many orders of magnitude higher than any currently available catalysts. This extraordinary activity is derived directly from the nanometric diameters of gold and diamond (“nanojewels”) and from the remarkable inertness of the diamond surface.

The Fenton reaction, in which highly aggressive hydroxyl radicals ($\text{HO}^\bullet$) are generated from H_2O_2 by reduction with Fe^{II} , Cu^{II} , or other transition metal salts, is a general process that can be used for the degradation/mineralization of recalcitrant organic pollutants as well as for disinfection.^[1–4] In spite of the wide applicability of the Fenton reaction for decomposing almost any organic compound, its widespread use for pollution abatement and disinfection is limited by the need for stoichiometric amounts of Fe^{II} or other transition metals. Most of the efforts to transform the Fenton reaction from a stoichiometric to a catalytic process have met with failure or at best can produce $\text{HO}^\bullet$ with remarkably low efficiency.^[5] For instance, the photo-Fenton process requires transparency of the solution (a prerequisite not frequently fulfilled in polluted waters or soils) and consumes “expensive” photons as stoichiometric reagents. A large number of iron-containing solids such as iron-exchanged zeolites and montmorillonites have also been reported as heterogeneous Fenton catalysts,^[6] but their use typically requires very large excesses of H_2O_2 (about 500 equiv) to achieve a moderate level of $\text{HO}^\bullet$ generation and they are remarkably inefficient. Here we describe a new type of Fenton catalyst based on gold nanoparticles deposited on nanoparticulate diamond (npD)

that is at least four orders of magnitude more efficient than the solid catalysts reported so far.

Although supported Au catalysts have been frequently used for in situ H_2O_2 generation, none of these studies reported the generation of $\text{OH}^\bullet$ radicals, the key intermediate of the Fenton reaction.^[7,8] In the only related precedent to this work Au nanoparticles supported on hydroxyapatite were used as a Fenton catalyst to decompose phenol at 70 °C by using 416 equiv of H_2O_2 , whereby the system was particularly active below pH 4.^[9] H_2O_2 is an expensive commodity, the price of which can be twice that of phenol, and its excess must be greatly reduced. In addition, heating the aqueous phase to 70 °C consumes considerable energy, and operation at room temperature is preferable.

Following most of the previous work on Fenton reactions, we also selected the transformation of phenol into catechol and hydroquinone as model reaction. Observation of these isomeric dihydroxybenzenes in quasistoichiometric amounts with respect to H_2O_2 consumption provides strong support for the operation of a highly selective Fenton-like decomposition of H_2O_2 . At high phenol conversions, observation of secondary decomposition products derived from the reaction of primary dihydroxybenzenes is also expected. The series of catalysts that were tested in the preliminary study of the catalytic activity towards the Fenton reaction is summarized in Table 1. The preparation procedure for these noble metal catalysts and relevant characterization data are provided in the Supporting Information. Importantly, preliminary tests have shown that some of the catalysts used, such as Au/ CeO_2 , Au/ TiO_2 , and Au/C, exhibit very high catalytic activity for

Table 1: Catalytic activity for Fenton reaction of supported gold catalysts. Reaction conditions: 100 mg L^{-1} phenol (1.06 mM), 200 mg L^{-1} H_2O_2 (5.88 mM), room temperature, 0.0025 mM metal, pH 4, $t = 24$ h.

Entry	Catalyst	Size ^[a]	Phenol degrad. [%]	H_2O_2 decomp. [%]	Leaching [%]
1	Au/ CeO_2 (1.0 %)	5	7	88	0.8
2	Au/ Fe_2O_3 (1.5 %)	4	3	8	0.7
3	Au/ TiO_2 (1.5 %)	15	3	19	0.5
4	Au/C (0.8 %)	10	7	14	5.8
5	Au/npD (< 1.0 %)	< 1	< 1	6	0.5
6	Au/ HO-npD (1.0 %)	< 1	93	48	0.7
7	npD	7	0	0	–
8	HO-npD	4.7	0	0	–

[a] Particle size in nanometers.

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aerobic oxidation of alcohols and amines, as reported in the literature.^[10–12] Thus, we tested catalysts that exhibit high activity for other gold-catalyzed reactions. For these initial assays the conditions selected were room temperature, pH 4, and an H_2O_2 /phenol molar ratio of 5.5. The small molar excess of H_2O_2 with respect to phenol used in these screening assays is noteworthy. Besides the disappearance of phenol, simultaneous H_2O_2 consumption was also determined. As can be seen in Table 1, most of the catalysts exhibit high activity for H_2O_2 decomposition without effecting simultaneous degradation of phenol due to the small excess of H_2O_2 . Actually only three catalysts (Table 1, entries 1, 4, and 6) have significant activity for phenol degradation. With the small H_2O_2 excess used, the best performing catalyst of the series is by far that in which gold nanoparticles were deposited on Fenton-treated diamond nanoparticles (Au/HO-npD; Table 1, entry 6), which is able to effect complete disappearance of phenol with only a moderate decomposition of H_2O_2 (2.9 equiv of H_2O_2 consumed for complete disappearance of phenol). A control experiment in the absence of H_2O_2 with bubbling O_2 showed that Au/HO-npD does not decompose phenol, and thus proves that H_2O_2 is needed.

Au/HO-npD is a material in which gold from HAuCl_4 has been supported by the conventional deposition/precipitation method^[13] on Fenton-treated diamond nanoparticles followed by hydrogen reduction at 300 °C. Nanoparticle diamond is a commercially available, inexpensive material obtained by explosive detonation.

Purification of commercial npD without altering the diamond crystal structure can be effected conveniently by Fenton treatment, which removes amorphous carbonaceous soot, deagglomerates the particles (see Figure S1 in the Supporting Information), and greatly increases the population of surface hydroxyl groups (hence, Fenton-treated npD is denoted as HO-npD).^[15] The presence of this high density of OH groups makes HO-npD a suitable support to anchor gold nanoparticles by deposition/precipitation, as is usual for nanoparticulate metal oxides.^[13] However, in contrast to the samples in which gold is supported on metal oxides, Au/HO-npD exhibits a remarkable Fenton activity with low spurious H_2O_2 consumption (Table 1). Importantly, controls using commercial npD, HO-npD without gold, or npD as gold support (Au/npD) exhibit no Fenton activity (Table 1, entries 5, 7, and 8), that is, the catalytic properties of Au/HO-npD are derived from the combination of gold nanoparticles and HO-npD.

To understand the origin of the remarkable activity of Au/HO-npD, this material was characterized by TEM. In gold catalysis the particle size plays an important role determining the activity.^[16–19,20] The TEM images of Au/HO-npD (Figure 1) show that the sample contains very small gold nanoparticles whose size is at the resolution limit of our electron microscope (2 nm). The size of gold particles in Au/HO-npD is significantly smaller than those estimated for Au/CeO₂ and Au/C, two of the most widely used gold catalysts (for particle size distribution of Au/HO-npD, see Figure S2 in the Supporting Information). This small particle size reflects impeded growth after nucleation of gold nanoparticles on the surface of HO-npD. This was confirmed by preparing a Au/

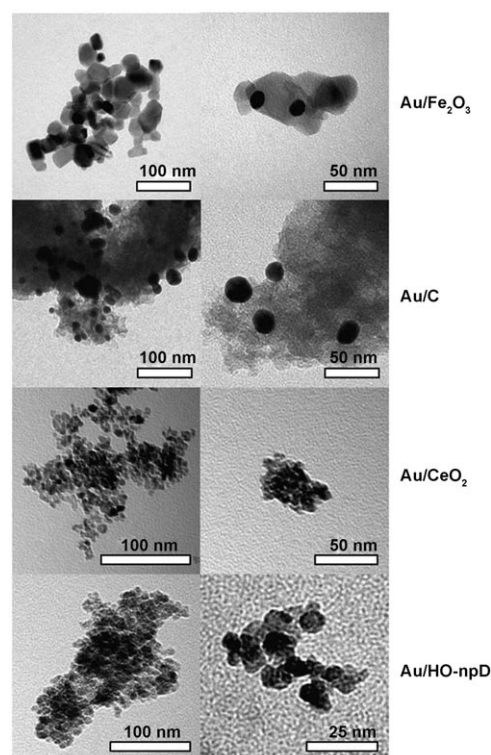


Figure 1. TEM images of some of the Fenton catalysts used in the present work.

HO-npD with larger particle size (Au/HO-npD_{cluster}) by performing the deposition–precipitation method at pH 7 (average particle size 10.8 nm, see Figure S3 in the Supporting Information) and observing that this material exhibits much lower catalytic activity due to its larger particle size (see Figure S4 in the Supporting Information). Moreover, if another HO-npD sample having about 50 % lower population of OH groups (HO-npD_{50%}, as determined by quantitative IR spectroscopy), obtained by milder Fenton treatment, is used as support, the corresponding sample contains much less gold (0.45 wt %) but has the same catalytic activity per gold atom. Thus, the catalytic activity of Au/HO-npD arises from a combination of small gold nanoparticles and a large population of surface OH groups in the support.

To establish the way in which these small gold nanoparticles interact and are stabilized on the surface of HO-npD, FTIR spectra of the samples before and after Au deposition were recorded (Figure 2). They show that Fenton treatment of commercial npD produces a remarkable increase in the population of surface hydroxyl groups. Importantly, deposition of gold nanoparticles considerably decreases the population of OH groups, that is, gold atoms are grafted to the HO-npD nanoparticles through these groups.

The Au_{4f} X-ray photoelectron spectrum of Au/HO-npD is coincident with previously reported spectra and exhibits peaks with binding energies at 84.0 and 87.7 eV (see Figure S5 in the Supporting Information).^[21] These data were interpreted by other authors as corresponding to a predominant population of Au⁰.^[21]

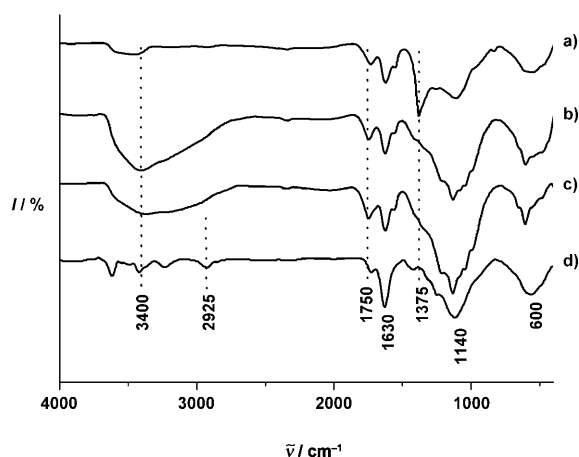


Figure 2. Room-temperature FTIR spectra of a) commercial npD, b) Fenton-treated HO-npD, c) HO-npD_{50%}, and d) Au/HO-npD for the same sample weight.

Diffuse-reflectance optical spectroscopy of the Au/HO-npD shows the surface plasmon band characteristic of Au nanoparticles at $\lambda_{\text{max}} = 530$ nm (Figure 3). This λ_{max} is blue-shifted with respect to the surface plasmon bands recorded for

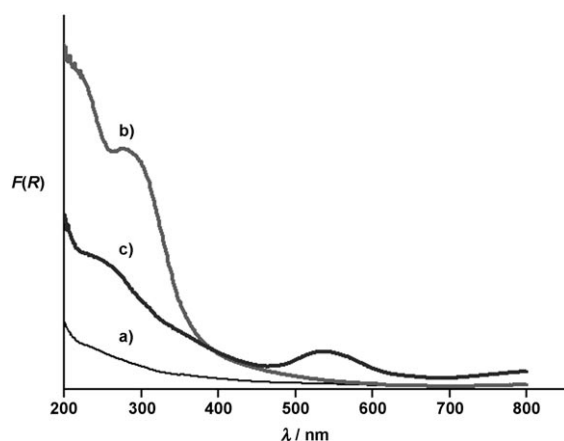


Figure 3. Diffuse-reflectance UV/Vis spectra of a) commercial npD, b) HO-npD, and c) Au/HO-npD.

Au nanoparticles supported on CeO₂ and on TiO₂, which appear around 565 nm (see Supporting Information, Figure S6). There are precedents in the literature in which variations of the position of the surface plasmon band were attributed to differences in the size of the gold particles, the dielectric constant of the support, and/or the Coulombic charge of the nanoparticles.^[15,22,23]

Heterogeneity of the process was demonstrated by performing the reaction under the usual conditions, filtering off the Au/HO-npD catalyst at 45% phenol conversion, and observing that no further phenol decomposition took place in the absence of the solid. The reusability of Au/HO-npD was tested by recovering the solid by filtration after a 24 h run, washing the solid with water at pH 10, and reusing it for a

consecutive run. Up to three consecutive uses were performed without observing any significant change in the temporal profiles of phenol or H₂O₂ disappearance.

Besides catalyst reuse, productivity of Au/HO-npD in terms of the amount of phenol that can be decomposed by a given amount of Au/HO-npD was addressed by performing an additional experiment in which a large excess of phenol (40 g L⁻¹) was contacted with Au/HO-npD (0.5 mg L⁻¹). These conditions are equivalent to 400 consecutive reuses of the catalyst under more dilute conditions. The results obtained show that working at room temperature with 5.5 equiv of H₂O₂ with respect to phenol, Au/HO-npD is able to decompose 25.6 g of phenol before becoming deactivated. At this time, the deactivated Au/HO-npD catalyst was regenerated by basic washing and reused for a second and then for a third run in such a large phenol excess. Regeneration was effective in recovering the activity of the deactivated catalyst to that of the fresh Au/HO-npD sample. The accumulated TON of the three cycles was 321 000 molecules of phenol degraded per Au atom of the catalyst. This TON is extraordinarily high and at least four orders of magnitude higher than those reported for other Fenton catalysts.^[5,9,24]

One feature of the Fenton reaction is its remarkable dependence on solution pH. In the case of Au/HO-npD we observed that Au/HO-npD became abruptly inefficient for pH values above 5. By determining the point of zero potential^[25] of suspended Au/HO-npD, it was established that the influence of the solution pH on the catalytic performance of Au/HO-npD corresponds to the change of positive colloid charge (pH < 5) to negative colloid charge (pH > 5). The solution pH also influences the percentage of gold leached from the solid to the solution. In the presence of H₂O₂ significant gold leaching occurs and can even amount to 47% of the total gold supported on Au/HO-npD when the solution pH is < 3, while at pH > 3 the percentage of leached gold is very low (see Table 1).

The data presented above suggests that Au/HO-npD is an efficient Fenton catalyst. To firmly support that Fenton chemistry is operative (i.e., generation of free HO[•]) we studied the primary products derived from phenol under conditions in which a large phenol excess with respect to H₂O₂ is used. Under these H₂O₂-deficient conditions phenol is converted into hydroquinone and catechol with a selectivity of 79% of the phenol disappearance. Furthermore, H₂O₂ consumption under these conditions is also quasistoichiometric (Table 2) with respect to the degraded phenol (1.1 equiv of converted H₂O₂/1 equiv of disappeared phenol). Importantly, under these conditions the initial reaction rates for H₂O₂ and phenol disappearance are coincident. These data indicate that one equivalent of H₂O₂ must give one equivalent of free HO[•] that can degrade one equivalent of phenol to dihydroxybenzenes with a selectivity of at least 79%. This stoichiometric relationship is observed when an excess of phenol with respect to H₂O₂ (1:0.5) is used. If the amount of H₂O₂ is increased, deviations from this theoretical stoichiometry are gradually observed due to the occurrence of secondary reactions.

Intermediacy of HO[•] was additionally supported by quenching the reaction with mannitol and DMSO, two well-

Table 2: Phenol disappearance and *ortho/para*-dihydroxybenzene (DHB) formation as a function of the initial H₂O₂/phenol molar ratio. Reaction conditions: 100 mg L⁻¹ phenol (1.06 mM), pH 4, room temperature, 0.0025 mM Au.

H ₂ O ₂ /PhOH molar ratio	PhOH degraded [mM]	Cat. [mM]	HQ [mM]	Selectivity of phenol to DHB [%]	Consumed H ₂ O ₂ /PhOH [mol/mol]
0.5:1	0.28	0.14	0.08	79	1.1
1:1	0.53	0.22	0.14	65	1.2
1:2	0.80	0.22	0.13	46	2.1
1:5.5	0.99	0.24	0.15	42	2.8

established HO• quenchers.^[26,27] Moreover, EPR with phenyl *N*-tert-butyl nitron as spin trap provided firm spectroscopic evidence for generation of HO• by recording the spectrum of the corresponding adduct (see Figures S7 and S8 in the Supporting Information).^[28]

We performed a kinetic study on the disappearance of H₂O₂ promoted by Au/HO-npD in the absence of phenol (Figure 4). While blank controls determined that at ambient

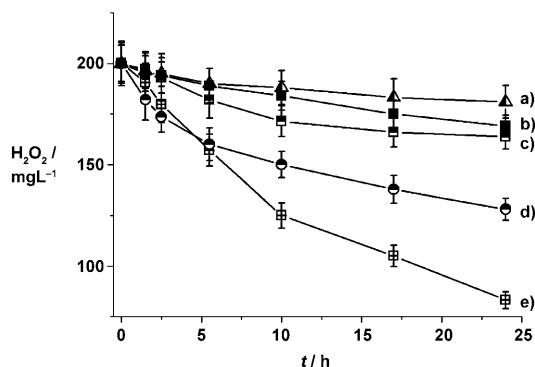


Figure 4. Activity of supported Au catalysts for H₂O₂ decomposition in the absence of phenol. a) Au/Fe₂O₃, b) Au/HO-npD, c) Au/TiO₂, d) Au/C, and e) Au/CeO₂. Reaction conditions: H₂O₂ 200 mg L⁻¹ (5.88 mM), pH 4, room temperature, metal 0.0025 mM.

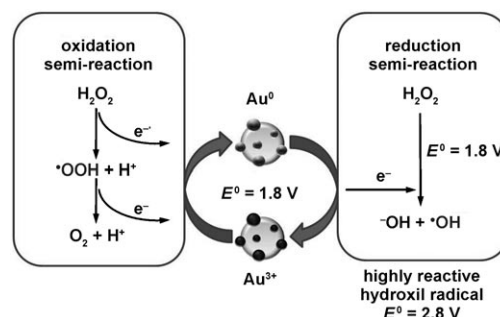
temperature H₂O₂ concentration is constant in the absence of catalysts, on addition of Au/HO-npD, H₂O₂ decomposes forming O₂ in stoichiometric amounts according to Equation (1). Importantly, the rate of H₂O₂ disappearance in the presence of Au/HO-npD is higher in the presence of phenol (0.131 mm h⁻¹) than when it is absent (0.056 mm h⁻¹).



Considering the information about H₂O₂ decomposition in the absence of phenol (low activity) and the catalytic phenol degradation, it can be concluded that Au/HO-npD is an extremely selective catalyst to promote Fenton chemistry with minor spurious H₂O₂ decomposition to O₂. This may be due to the fact that HO• in Au/HO-npD is not surface-bound and is present mostly as a free radical in solution. Probably, the inert nature of the diamond surface and Fenton pretreat-

ment of npD are responsible for the low affinity of the support for HO• radicals.

From the above data, the mechanism shown in Scheme 1 can be proposed for catalytic generation of HO• radicals promoted by Au/HO-npD. It involves a swing between positive and neutral gold states. Thus, gold acts as an electron



Scheme 1. Proposed mechanism for phenol degradation with Au/HO-npD and H₂O₂.

relay from the oxidation to the reduction semi-reaction. Reduction of H₂O₂ will give HO•, characteristic of Fenton chemistry. Based on the high catalytic activity, this HO• is not bound to gold or to the support, but free in the solution phase. When phenol is present, it is this species that undergoes oxidation by Au³⁺, since no O₂ evolution is observed under these conditions and the stoichiometry of H₂O₂ and phenol consumption approaches 1:1. When phenol is absent, H₂O₂ takes over the role of oxidizing and reducing agent, and is decomposed with formation of O₂ as reaction product. The standard redox potential of the Au³⁺/Au couple is compatible with the proposed mechanism (see values in Scheme 1).

In conclusion, a catalyst based on nanometrically dimensioned gold and diamond is highly active, selective (min. 79%), stable, and reusable for promotion of Fenton chemistry at room temperature with a quasistoichiometric amount of hydrogen peroxide. The key feature of our system is the use of inert, surface-functionalized diamond nanoparticles as supports.

Experimental Section

Au/HO-npD preparation: Au/HO-npD was obtained from commercial diamond nanoparticles (Aldrich) previously treated with H₂O₂ and FeSO₄·7H₂O in sulfuric acid (see Supporting Information). Au was deposited on HO-npD from HAuCl₄·3H₂O (800 mg) in 160 mL of deionized water brought to pH 10 by addition of 0.1M aqueous NaOH solution. Once the pH value was stable, the solution was added to colloidal HO-npD (4.0 g) in H₂O (50 mL). After adjusting the pH to 10 (0.1M NaOH), the slurry was vigorously stirred for 18 h at room temperature. Au/HO-npD was then dispersed in distilled water and excess HAuCl₄ removed by performing five consecutive centrifugation–redispersion cycles with Milli-Q water. Au/HO-npD was dried under vacuum at room temperature for 1 h. Then 150 mg of Au/HO-npD were placed in a quartz reactor and submitted to H₂ reduction at 300 °C for 6 h. The total Au content of Au/HO-npD was 1 wt %, as determined by chemical analysis. This catalyst is commercially available at argane.diamond@gmail.com.

Catalytic tests: 100 mL of Milli-Q water containing 100 mg L^{-1} (1.06 mM) of phenol and 200 mg L^{-1} (5.88 mM) of H_2O_2 was placed in an Erlenmeyer flask. The initial pH value was adjusted to the required value, the corresponding catalyst (H_2O_2 to metal molar ratio: 2318:1) added, and the suspension stirred in the dark. The conversion with time was determined by analyzing aliquots (2 mL, filtered through $0.2 \mu\text{m}$ Nylon filter) on a reverse-phase Kromasil-C18 column with $\text{H}_2\text{O}/\text{MeOH}/\text{acetic acid}$ (69:30:1) as eluent under isocratic conditions and a UV detector (monitoring wavelength 254 nm). The residual H_2O_2 was determined by tenfold dilution of the reaction mixture and using $\text{K}_2(\text{TiO})(\text{C}_2\text{O}_4)_2$ (Aldrich) in $\text{H}_2\text{SO}_4/\text{HNO}_3$ for colorimetric titration monitoring at 420 nm.

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