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LETTER

Dual behavior of gold nanoparticles, as generators *and* scavengers for free radicals

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Literature data available on the interaction of stable free radicals with gold nanoparticles (Au NPs) suggested the adsorption of stable-free radicals on the nanoparticles surface, and the possibility of exchange interaction between the unpaired electron from the free radicals and the conduction-band electrons of the metal [1, 2]. Au NPs, as well as gold salts, are able to catalyze different processes, like oxidation, C–C bond formation, additions, alkylations, etc. [3, 4]. Exchange reactions (the most convenient method to prepare functionalized nanoparticles) mechanism of the ligands involves also in the first step the formation of an organometallic reactive complex [5–7]. The mechanisms of such processes are still under consideration. Nonetheless, free radicals play a major role in the surface chemistry of metal nanoparticles.

Our previous work demonstrates that Au NPs may abstract a hydrogen or a halogen atom from different substrates, yielding the corresponding short-lived radicals [8, 9]. However, there is little information about the final products derived from the free radicals formed on or near the metal surface. Till now, literature data suggest that stable-free radicals may stay adsorbed on the nanoparticles surface [1], while the short-lived radicals may react with the nanoparticles (as in the thiol exchange reaction occurs [8]). Aryl radicals may act as well as stabilizers in the synthesis of metal NPs, via a metal–carbon bond formation [10]. Short-lived radicals are very reactive species, and they can stabilize in very different ways (dimerization, abstraction of different atoms, radical + radical reactions). The knowledge of the pathway followed by the radicals toward their final products may provide very useful information about catalysis by Au NPs.

Our first aim was to use Au NPs as catalyst at room temperature in an *Ullmann*-type reaction (a well-known coupling reaction, performed in harsh conditions, which uses copper as catalyst; the mechanism involves an organocopper compound and does not follow a radical pathway [11]), using the classical reactants aniline and iodobenzene.

First, we used the spin-trapping technique (see also supplementary data for more details) to test if, from aniline or from iodobenzene, phosphine-protected Au NPs [12] generate the corresponding short-lived radicals $C_6H_5NH^\bullet$ and $C_6H_5^\bullet$, in the same way as for previous substrates [8, 9]. As expected, our results showed (Fig. 1) that, from both reactions, the corresponding free radicals were formed and trapped by a spin-trap (DMPO). The hyperfine coupling constants of the EPR spectra are in full agreement with the literature data [13], and the EPR spectra can be very well simulated (see supplementary data). The amount of free radicals formed (measured by double integral of the spectra) was up to 12%, as previous data showed [8].

Using an equimolecular mixture of aniline and iodobenzene, we expected as well the formation of diphenylamine, in a radical + radical reaction (Scheme 1). Remarkably, no diphenylamine was found in the reaction mixture. An EPR spin-trapping test was also performed to check if the radicals are formed in the mixture of the two reactants, and the recorded spectra showed that a mixture

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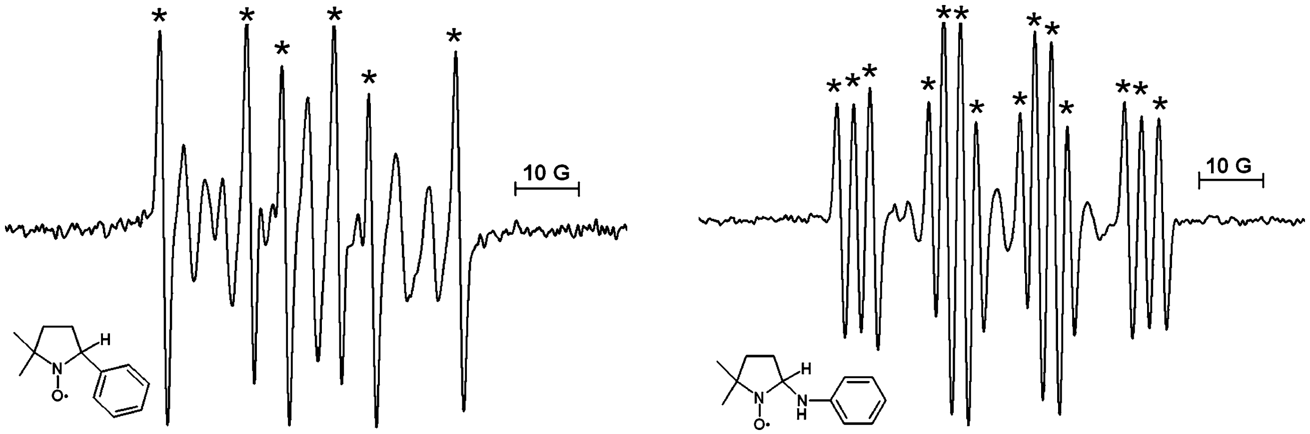
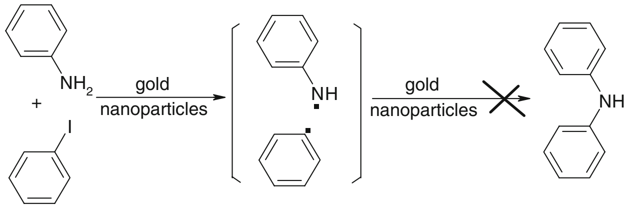


Fig. 1 EPR spectra of DMPO spin-adducts formed from iodobenzene (left, $a_N = 13.96$ G, $a_H = 19.54$ G) and from aniline (right, $a_N = 14.27$ G, $a_{H1} = 16.49$ G, $a_{N2} = 2.58$ G); the peaks corresponding to the spin-adducts are marked with asterisk



Scheme 1 Short-lived radicals are generated and trapped by Au NPs

of the corresponding short-lived radical is trapped by the DMPO spin-trap (see supplementary data).

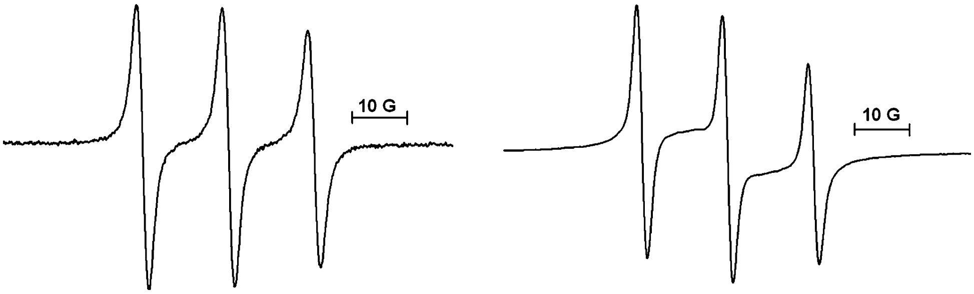
Moreover, monitoring the reaction by GC, besides the un-reacted starting materials, biphenyl, and triphenylphosphine were found. The biphenyl amount formed (1%) by dimerization does not count for the overall amount of short-lived radicals formed in the first step (up to 12% [8]), meaning that they follow a major different pathway. Regarding the presence of the free triphenylphosphine, this suggested the possibility that the reactive radicals replace the existing ligands, as was also showed for the thiol radicals formed in an exchange reaction [8]. The absence of diphenylamine may be thus explained by the scavenging activity of the Au NPs toward the short-lived radicals.

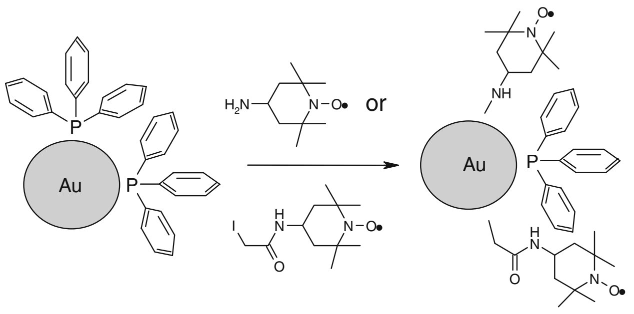
This scavenging activity for free radicals may be easily monitored by EPR, if suitable probes are used, like 4-aminotempo or 4-iodoacetamidotempo-free radicals; the advantage of those probes is due to the presence in the same molecule of a stable-free radical moiety of a nitroxide type, and of an amino- or iodo-group, from which a short-lived radical can be easily formed [9].

Our experiments involving Au NPs and 4-aminotempo or 4-iodoacetamidotempo showed several quite interesting features: (i) addition of the spin-probe to a solution of Au NPs (in a ratio of 1:1) led to the decreasing of the third line in the EPR spectrum (Fig. 2, left); (ii) large addition of the spin-probe (ratio 100:1) showed that a high amount of the nitroxide moiety is bonded to the nanoparticles (Fig. 2, right); (iii) after 'pre-poisoning' (see supporting information for experimental details) the Au NPs by reacting them with aniline or iodobenzene, they become inert toward further radical reaction with 4-aminotempo, but they kept their reactivity toward 4-iodoacetamidotempo. The decreasing in the third line (Fig. 2) clearly indicates that the spin-probe is attached to the nanoparticles, and hence the tumbling of the spin probe is hindered [14]. Spin–spin interaction (a broad line superposing the triplet) it is also noticed in the case of large addition of the spin-probes to Au NPs (Fig. 2, right).

All these facts emphasize that the spin-probes are irreversibly attached to the gold surface; the mechanism

Fig. 2 EPR spectra of 4-aminotempo in the presence of phosphine-protected Au NPs, at different ratio: left, ratio 1:1; right, ratio 100:1





Scheme 2 Radical exchange reaction with reactive spin-probes

involves in the first stage the generation of the corresponding short-lived radicals (Scheme 1), which subsequently are scavenged by the Au NPs (Scheme 2).

The presence of air (oxygen) seems also to be necessary in the generation of the short-radicals, ligands exchange, or in the catalytic processes of Au NPs [4–9, 15]. The initial formation of an active catalyst, from the adsorption of oxygen on the gold surface, yielding a superoxide-type species, was proposed before [8]. These species act probably as oxidants in the H-abstracting process, which in the first step generate the radicals. In the second step, the radicals are scavenged by the Au NPs, rather then reacting with the solvent or dimerizing. The I-abstraction probably occurs initially via an electron-transfer process (no air is necessarily, so the active site remains active further [9]).

The proposed mechanism (generation and scavenging of short-lived radicals) might be even more complicated, taking into consideration that that gold chlorides as well as Au NPs are able to trap in situ formed radicals, yielding stable organogold intermediates [16]. These kinds of intermediates react further with the Au NPs, removing the surface ligands, in an exchange type reaction [5–7]. Reactive radicals may reduce also Au^{3+} to Au NPs [17]. Halide ions were proved also to act as oxidants in the presence of air for thiol protected Au NPs [18]. As we mentioned before, after reaction, in all cases we noticed the presence of the free ligands triphenylphosphine.

Moreover, major changes were noticed by UV–Vis (the disappearance of the peak at 512 nm, the plasmon band of the Au NPs), and by TEM (differences in size and shape of the Au NPs) after the reaction of Au NPs with excess (100:1) spin-probes (Fig. 3) (if 1:1 ratio was used, no changes in TEM picture were noticed).

In conclusion, the dual behavior of gold nanoparticles has been proved, as generators and scavengers of short-lived-free radicals. These radicals are highly reactive species and their main way of stabilization is the reaction with the parent gold nanoparticles, rather their dimerization. At least two types of active sites are present on the surface of gold nanoparticles, as monitored by electron paramagnetic resonance spin-probe techniques.

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References

1. Zhang Z, Berg A, Levanon H, Fessenden RW, Meisel D (2003) J Am Chem Soc 125:7959
2. Harada G, Sakurai H, Matsushita MM, Izuoka A, Sugawara T (2002) Chem Lett 1030
3. Campbell CT (2004) Science 306:234
4. Tsunoyama H, Sakurai H, Ichikuni N, Negishi Y, Tsukuda T (2004) Langmuir 20:11293
5. Wang W, Murray RW (2005) Langmuir 21:7015
6. Guo R, Song Y, Wang G, Murray RW (2005) J Am Chem Soc 127:2572
7. Woehrle GH, Brown LO, Hutchison JE (2005) J Am Chem Soc 127:2172
8. Ionita P, Gilbert BC, Chechik V (2005) Angew Chem Int Ed 44:3720
9. Ionita P, Conte M, Gilbert BC, Chechik V (2007) Org Biomol Chem 5:3504
10. Mirkhalaf F, Paprotny J, Schiffrin DJ (2006) J Am Chem Soc 128:7400
11. Ullmann F (1904) Annalen 322:38
12. Weare WW, Reed SM, Warner MG, Hutchison JE (2000) J Am Chem Soc 122:12890
13. Buettner GR (1987) Free Radical Biol Med 3:259

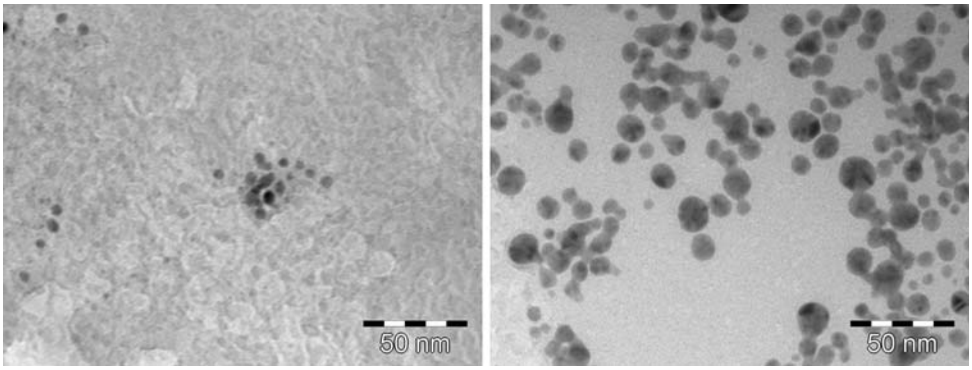

Fig. 3 TEM pictures of Au NPs before (up) and after (down) reaction with 4-aminotempo

14. Ghica C, Ionita P (2007) J Mater Sci 42:10058. doi:10.1007/s10853-007-1980-4
15. Hutchison JE, Postlethwaite TA, Murray RW (1993) Langmuir 9:3277
16. Aprile C, Boronat M, Ferrer B, Corma A, Garcia H (2006) J Am Chem Soc 128:8388
17. McGilvray KL, Decan MR, Wang D, Scaiano JC (2006) J Am Chem Soc 128:15980
18. Dasog M, Scott RWJ (2007) Langmuir 23:3381