Sustainable Approaches for Polyaniline and Polypyrrole Synthesis

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Abstract: Among the conducting organic polymers (COPs), polyaniline (PANI) and polypyrrole (PPY) are the most investigated. Even though many efforts have been done to overcome the traditional synthetic methods typically based on the use of strong stoichiometric oxidants, the growing environmental sensitivity and the necessity of pure products, especially in medical and biological fields, make the COPs "green" synthesis a topic of the utmost importance. Herein, we report a brief overview of our results in the synthesis of PANI and PPY operating under mild conditions, using H_2O_2 and O_2 as the oxidants in the presence of different catalysts: colloidal Au nanoparticles (AuNPs), AuNPs/TiO_2, AuNPs/C, metallic Cu, Cu salts and Fe_3O_4 NPs.

Keywords: Catalysis, Conducting polymers, Green syntheses.

INTRODUCTION

As narrated by Nina Hall, the surprising story of conducting organic polymers (COPs) is the result of a fortuitous but fruitful collaboration among three extraordinary scientists from different disciplines and different continents: Hideki Shirakawa, a polymer chemist at the University of Tsukuba, Alan MacDiarmid, an inorganic chemist at the chemistry department at Pennsylvania, and Alan J. Heeger, a physicist at the University of California [1].

Their achievements were published in 1977 [2] but their genius was awarded with the Nobel Prize for Chemistry in 2000 "*for their discovery and development of conductive polymers*" [3].

Although polyacetylene was the first synthesized and characterized COPs, its high instability to air and difficulty of processing gradually reduced the interest in this material. Meanwhile, other two polymers caught the scientific community interest: polyaniline (PANI, Figure **1**) and polypyrrole (PPY, Figure **2**).

Depending on the oxidation and doping level, PANI can exist in different forms ranging from the fully reduced leucoemeraldine, to the half oxidized emeraldine, as well as the totally oxidized pernigraniline. The PANI backbone in its emeraldine form consists in an equal number of benzenoid and quinoid rings and amine and imine nitrogen atoms. Even though amine groups are more basic than imine ones, the doping process (protonation) preferentially occurs on these latter, because the resulting doped polymer (emeraldine salt, Figure **3**) is stabilized by resonance [4].

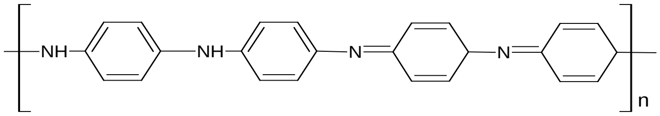

Figure 1: Polyaniline structure.

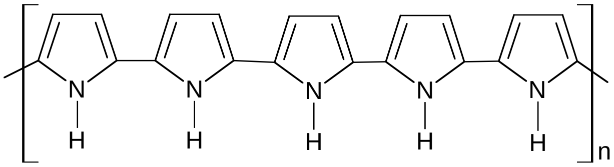

Figure 2: Polypyrrole structure.

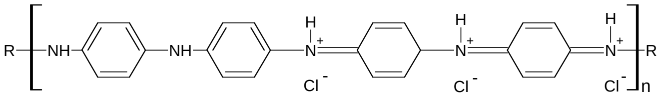

Figure 3: Emeraldine salt structure.

It was demonstrated that the doping process has a strong effect on the polymer conductivity, switching emeraldine from an insulator (about 10^{-11} S cm^{-1}) to a conductor (up to 10 S cm^{-1}) [4, 5].

If on the one hand PANI doping consists in a protonation reaction, on the other hand for PPY it consists in treating the polymer with either an electron donor or an electron acceptor, able to switch the polymer from its reduced insulating form (about 10^{-9} S cm^{-1}) to its oxidized conducting form (up to 100 S cm^{-1}) (Figure **4**) [6].

Thanks to their ease of synthesis, environmental stability, tunable conductivity and great versatility [7, 8] they can be applied in a wide spectrum of fields, ranging from electronic displays, [9] to electrode materials, [10] to molecular electronic circuit elements, [11] as well as sensors [12].

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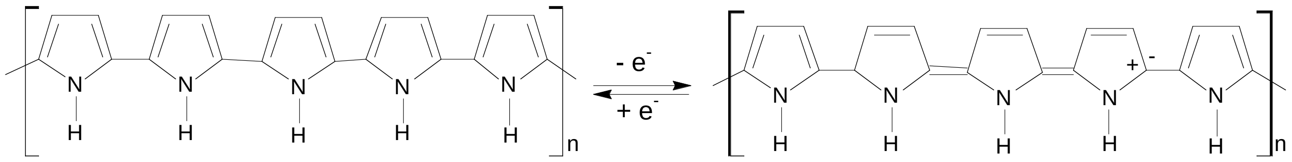

Figure 4: Polypirrole doping.

FROM CONVENTIONAL CHEMICAL SYNTHESIS TO SUSTAINABLE APPROACHES

Conventional chemical routes for polyaniline and polypyrrole preparations are waste-intensive. In fact, both PANI and PPY syntheses are often carried out at high temperature, in the presence of inorganic oxidants and toxic solvents [13]. Besides the chemical approaches, enzymatic and electrochemical methods have been proposed [14].

Whereas the use of enzymes is attractive but limited to small scale preparations, the electrochemical preparations are more interesting and industrially feasible.

However, despite all the drawbacks, the chemical polymerization is the oldest and still the most popular method employed to prepare PANI and PPY in bulk quantity. It is based on the oxidative coupling of monomers employing strong oxidants, as $(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, KIO_3 and metals in high oxidation states [15-18]. This approach is environmentally troublesome, owing to the formation of polluting co-products, *e.g*. ammonium sulfate in the case of APS, and heavy metals.

The growing interest in sustainable chemical processes and the necessity of producing high purity materials for specific applications have opened the way to the use of more eco-friendly reagents, hydrogen peroxide and molecular oxygen *in primis*, with the aid of a catalyst.

H_2O_2 is an appealing oxidant as its reduction product, H_2O, eliminates the problems related to polluting co-products and simplifies the post treatment of the polymeric materials. As far as the thermodynamic aspects are concerned, H_2O_2 shows a redox potential (1.77 V) high enough to polymerize aniline (ca. 1.46 V) [19] and pyrrole (1.2 V) [20] monomers. However, the polymerization reaction carried out by H_2O_2 is slow but can be accelerated by the use of proper catalysts [21-23].

Conversely, the lower redox potential of molecular oxygen (1.23 V) would suggest a thermodynamic barrier to the oxidative polymerization, especially for aniline.

However, the pioneering investigations of Toshima *et al*. allowed the synthesis of polyaniline and polypyrrole employing molecular oxygen in the presence of Cu-based catalysts [24]. The resulting material exhibited poor electroconductive properties probably related to the presence of branching and contamination by organic chlorine, along with carbonyl and hydroxyl derivatives. Further studies allowed to improve the PPY conductivity by replacing copper catalysts with soluble iron (III) [25].

Herein, we report our contribution to polyaniline and polypyrrole syntheses by innovative sustainable approaches with a particular focus on the catalytic aspects [26-30].

EXPERIMENTAL

The details about the experiments are available in the literature [26-28, 30].

RESULTS AND DISCUSSION

Gold Nanoparticles as Catalysts for Pyrrole and Aniline Oxidative Polymerization

Even though gold nanoparticles have been widely employed as catalysts in organic molecules Oxidetion, [31-33] their application in the aniline and pyrrole oxidative polymerization reactions has not been extensively investigated.

Inspired by our experience in the field of catalysis [31-32] recently we have focused our efforts on optimizing COPs environmentally friendly synthesis exploiting the catalytic activity of gold nanoparticles and our results are reported in the sections below.

Polypyrrole Synthesis

Although the metal-assisted pyrrole polymerization is a thermodynamically easier process than that of aniline, it has attracted less attention.

Our pioneering investigations, carried out in 2009, demonstrated that gold nanoparticles (AuNPs) are promising catalysts for pyrrole polymerization in the presence of both H_2O_2 and molecular oxygen/air as the oxidants [27].

Au NPs with a mean diameter of 3.6 nm were prepared as a colloidal dispersion in accordance with the literature [33].

As reported in Figure **5**, when the reaction was carried out under air at room temperature for three days polypyrrole was not produced. However, the colour of the reaction mixture turned dark gradually, indicating the presence of polymers characterized by low molecular weight (oligomers).

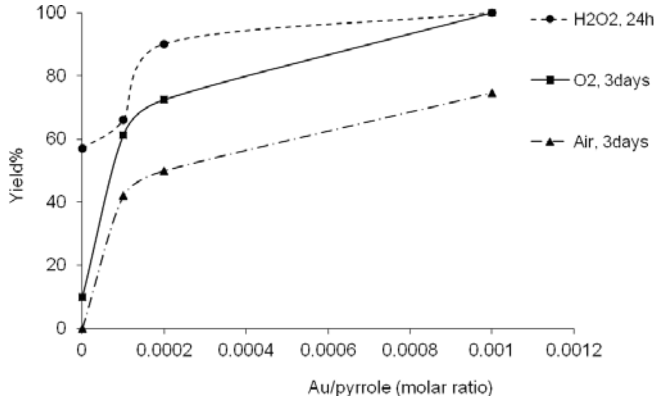

Figure 5: AuNPs catalytic effect on pyrrole polymerization using air, molecular oxygen and hydrogen peroxide as the oxidants.

Repeating the experiments using pure oxygen as the oxidant, in the absence of AuNPs a small amount of dark solid materials was obtained, thus demonstrating a modest auto-oxidation of pyrrole.

By adding colloidal gold to the pyrrole hydrochloride solution, a strong catalytic effect was observed, leading to achieve the polymeric material in 99% (under molecular oxygen) and 73% (under air) yield after 3 days.

Thanks to its higher oxidizing power, hydrogen peroxide was able to polymerize pyrrole also in the absence of AuNPs, thus producing the corresponding polymer in 57% yield after 1 day.

Similarly as the aerobic oxidation, adding colloidal AuNPs to the pyrrole solution allowed to increase the yield up to 99%.

The kinetics of polypyrrole formation was investigated during the pyrrole oxidative polymerization by molecular oxygen. The results show that the aerobic polymerization of pyrrole needs 8 h before a detectable amount of polymer is produced. Before this induction time, only oligomers are produced, as evidenced by the peculiar dark colour of the solution, afterwards polypyrrole yield increases by increasing AuNPs amount and reaction time (Figure **6**).

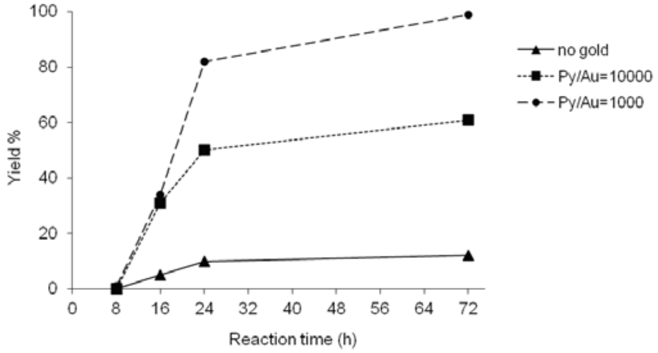

Figure 6: Polypyrrole yield vs reaction time using molecular oxygen as the oxidant.

Once the reaction was finished, the catalyst was not recovered from the polymeric matrix either because the amount of AuNPs employed was too low to justify the cost of the catalyst recovery or the presence of gold in the organic matrix might slightly contribute to the conductivity of the material.

The presence of AuNPs in the polymeric matrix was actually detected by X-ray powder diffraction spectroscopy (XRPD, data not reported) and the results showed that during the polymerization reaction agglomeration phenomena occurred, causing a growth of the mean diameter from 3.6 to 42 nm.

The TEM microscopy (Transmission Electron Microscopy) did not allow to identify metallic nanoparticles in the final polymer, likely owing to the small amount of AuNPs below the sensitivity of the instrument, but emphasized the influence of the type of oxidant on the PPY morphology: from rod-like to square-like.

Concerning the conductivity measurements, the low gold nanoparticles concentration in the polymer did not seem to enhance the performances. The conductivity values ranged from $2.74 \cdot 10^{-4}$ to $4.09 \cdot 10^{-3}$ S/cm.

Polyaniline Synthesis

Until 2008, for the PANI/Au composites preparation $HAuCl_4$ played the role of oxidant. During the reaction $HAuCl_4$ was reduced to Au nanoparticles, leading to a final Au-decorated polymer [18, 19, 34-36]. After the discovery of AuNPs catalytic activity in the pyrrole oxidative polymerization, [27] we decided to extend our investigation to the aniline oxidative polymerization reaction [28].

Unlike polypyrrole, the high redox potential of the couple aniline/emeraldine emichloridrate (ca. 1.46 V)[37] does not allow to carry out the polymerization reaction using molecular oxygen or air as the oxidants. On the contrary, thanks to its higher redox potential (E°= 1.78 V), hydrogen peroxide would be effective in aniline polymerization. However, the reaction resulted to be too low and for this reason it was carried out in the presence of proper catalysts [22-24, 37-41].

We demonstrated that the addition of a colloidal dispersion of AuNPs (mean diameter of 3.6 nm) to an aniline hydrochloric solution in the presence of hydrogen peroxide as the oxidant had only a modest catalytic effect (4-5% yield), while in the absence of AuNPs H_2O_2 alone was not able to perform the reaction (Table **1**) [28].

Table 1: Oxidative Polymerization of Aniline with Different Amounts of H_2O_2

Entry	Aniline/Au (molar ratio)	H_2O_2 : Aniline (molar ratio)	Yield %
1	0	1	0
2	1000	1	4.8
3	1000	2	4.8
4	1000	4	4.0

Acting on aniline/Au molar ratio and maintaining the reaction conditions reported in Table **1,** yield increased up to the asymptotic value of 27%, reached at An/Au = 250 molar ratio (Figure **7**).

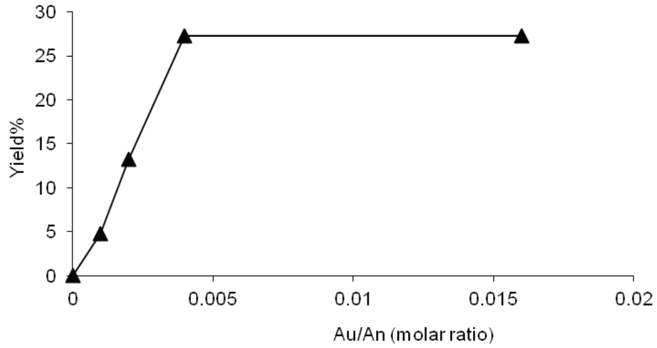

Figure 7: AuNPs catalytic effect on aniline polymerization using H_2O_2 as the oxidant.

Such a limitation can be attributed to the short life-time of unsupported gold nanoparticles, easily under-going agglomeration, as confirmed by XRPD analyses (data not reported).

In order to overcome this limit, AuNPs were supported on two kinds of supporting materials (carbon X40S and titania P25) and the results are summarized in Figure **8.**

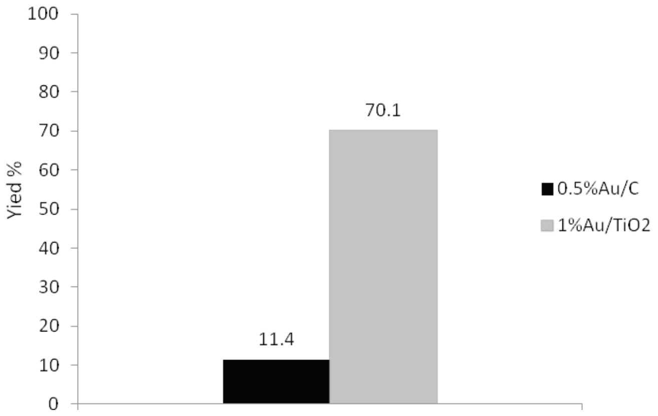

Figure 8: Comparison between 0.5%Au/C and 1%Au/TiO_2 catalysts during aniline polymerization (Aniline/Au = 1000 molar ratio, room temperature, H_2O_2/An= 1, molar ratio).

Even though carbon-supported AuNPs resulted to be more stable than the corresponding colloids, the achievements in terms of yield were still poor (11.4%). On the contrary, when TiO_2 was used as the support, the catalytic activity of AuNPs surprisingly grew, thus producing polyaniline in 70.1% yield.

The superior performance of titania with respect to carbon was already evident during the blank tests: whereas unloaded titania led to a dark color of the reaction mixture, sign of an incipient aniline polymerization, unloaded carbon resulted to be completely inert.

This suggests that the extraordinary activity of Au/TiO_2 catalyst is due to a synergistic effect between gold and support.

Metal Copper and Copper Salts Catalysts for the Synthesis of Polyaniline

The first work on copper-catalyzed aniline polymerization is dated 1994 [24]. In this paper Toshima *et al.* reported the use of copper salts (Cu^{2+}) as catalysts for the aerobic polymerization of aniline. However, polyaniline was obtained in insulating form (*emeraldine base*) with a modest yield (50%). These investigations were continued by Bicak and Karagoz [42].

Afterwards, Dias *et al.* elaborated new sophisticated copper complexes for the preparation of polyaniline starting from aniline and aniline dimer, *N*-(4-aminophenyl)aniline, using H_2O_2 as the oxidant and water/acetonitrile mixture as the solvent [22, 23].

For the materials prepared by aniline dimer, the authors reported 50% yield in the presence of pyrazolylcopper (II) complex and no solid material in the absence of organometallic complex, justifying this result with a catalytic effect of the copper species.

Recently, we have revisited the oxidative polymerization of *N*-(4-aminophenyl) aniline in eco-friendly conditions, using molecular oxygen or hydrogen peroxide as the oxidants in aqueous solution and in the presence of metal copper and copper salts as the catalysts [28].

First of all it is important to highlight the advantages but also the disadvantages related to the use of *N*-(4-aminophenyl) aniline rather than aniline monomer. If on the one hand aniline dimer is more than four times expensive than the corresponding monomer, on the other hand its oxidative polymerization reaction is easier, it does not need strong stoichiometric oxidants and does not lead to toxic co-products formation, such as benzidine. Until now all these drawbacks have limited the PANI preparation in large scale [43, 44].

We observed that stirring an aqueous solution of aniline dimer (AD) and hydrochloric acid (AD/HCl = 1, molar ratio) under oxygen (P = 3 bar) for three days, a green insoluble material with 13% yield, identified as emeraldine salt, was obtained. To test the catalytic activity of metallic copper and copper salts (Cu^{2+} and Cu^{1+}), the reaction was repeated in the presence of copper species (AD/Cu = 20, molar ratio) under the same conditions. The results are reported in Figure **9.**

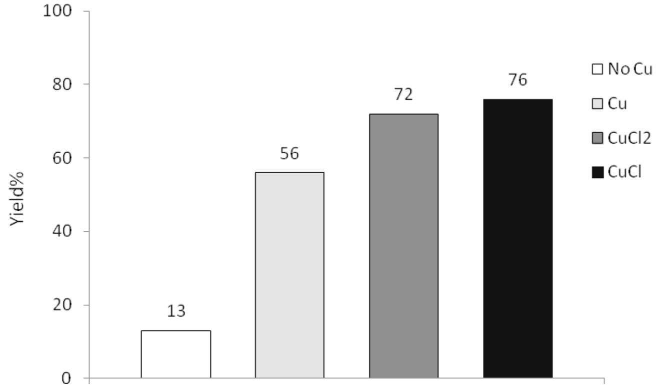

Figure 9: Polyaniline synthesis using metallic copper (Cu), $CuCl_2$ and CuCl as the catalysts (AD/Cu = 20, molar ratio), molecular oxygen as the oxidant (P = 3 bar), water as the solvent, room temperature for three days.

All the copper species exhibited a strong catalytic effect on AD polymerization, with yields ranging from 56% (metallic Cu) to 72% ($CuCl_2$) as well as 76% (CuCl).

The effect of the temperature on the reactions is reported in Figure **10.**

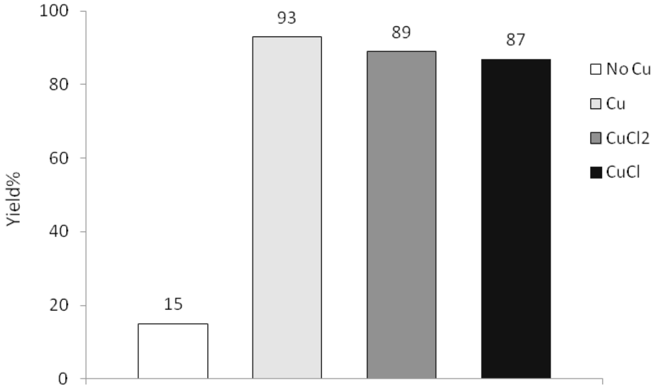

Figure 10: Polyaniline synthesis using metallic copper (Cu), $CuCl_2$ and CuCl as the catalysts (AD/Cu = 20, molar ratio), molecular oxygen as the oxidant (P = 3 bar), water as the solvent, at T = 80°C for

The best result (93% PANI yield) was obtained operating at T = 80°C in the presence of Cu (0) as the catalyst.

However, to reproduce the reaction conditions used by Dias *et al.* [23] but replacing their sophisticated copper scorpionate catalyst with metallic copper (our most active catalyst) at T = 80°C a mixture acetonitrile: water = 1: 1 v/v was used. Surprisingly, yield dropped from 93% to 77%, thus revealing an inhibiting effect of acetonitrile during AD polymerization.

Hydrogen peroxide was also tested as an alternative to molecular oxygen. In this case the AD polymerization reaction was investigated at room temperature for 1 day in the presence and in the absence of acetonitrile. The results are summarized Figure **11.**

Despite the inhibiting effect of acetonitrile, all the copper species employed in the AD polymerization reaction showed an important catalytic effect which enabled to produce a high quality conducting polyaniline, as confirmed by the conductivity measurements ($2 \cdot 10^{-2}$ S/cm).

As reported by Toshima and Genies, [24, 45] the couple Cu(I)-Cu(II) can act as an electron transfer from an organic radical species to molecular oxygen or hydrogen peroxide.

Concerning metallic copper, it must be underlined that a preliminary fast dissolution process is necessary.

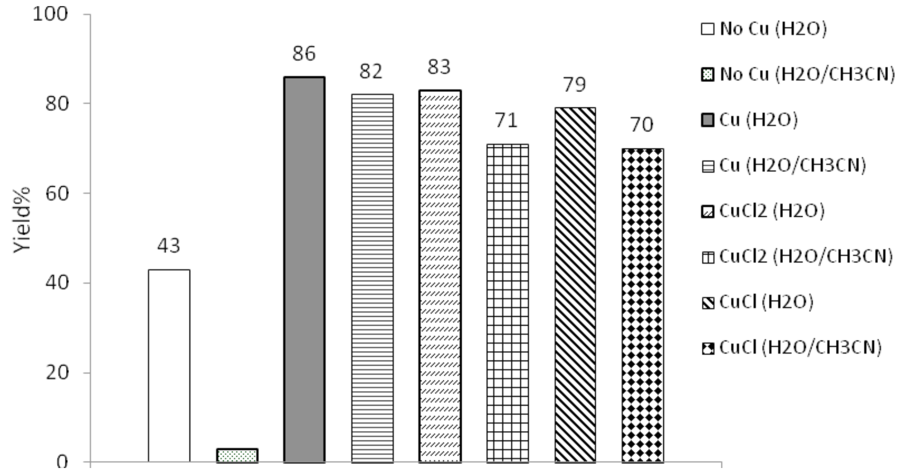

Figure 11: Polyaniline synthesis using metallic copper (Cu), $CuCl_2$ and CuCl as the catalysts (AD/Cu = 20, molar ratio), H_2O_2 as the oxidant (H_2O_2/AD= 1.5, molar ratio), at room temperature for 1 day in H_2O and H_2O/CH_3CN as the solvents.

Fe_3O_4 Nanoparticles Catalysts for the Synthesis of Polyaniline

Among the catalysts employed in the aniline oxidative polymerization by hydrogen peroxide, Fe-based species are probably the most investigated [40, 46-59].

Among them Fe_3O_4 nanoparticles are particularly interesting for their outstanding magnetic properties.

The possibility to combine the electroconductivity of PANI with the magnetic behaviour of nanosized magnetite opens the way to innovative materials characterized by new properties, useful for many applications, such as colour imaging, magnetic recording media, soft magnetic materials and ferrofluids.

Starting from the pioneering investigations of Yang *et al*. [60] and motivated by our will to produce COPs by innovative environmentally friendly approaches, we recently reported a new one-pot method to produce electrical and magnetic PANI/Fe_3O_4 nanocomposites [30].

Fe_3O_4 NPs were synthesized as powder and ferrofluid (dispersion in toluene) with a mean diameter of 11 nm. In the presence of both molecular oxygen and hydrogen peroxide as the oxidizing agents the two types of magnetic NPs showed similar catalytic activity, as reported in Tables **2** and **3**.

As confirmed by absorption atomic spectroscopic analyses and XRPD investigations, at the end of the reaction all the inorganic nanoparticles were transferred in the final composites and their mean diameter remained unchanged, thereby demonstrating that the catalytic activity of Fe_3O_4 NPs is not due to dissolution phenomena.

Table 2: Catalytic Oxidative Polymerization of *N*-(4-Aminophenyl) Aniline (AD) in the Absence and in the Presence of Fe_3O_4, Using O_2 (3 bar) as Oxidant. Reaction Time = 3 Days

AD/Fe_3O_4 (Molar Ratio)	Ferrofluid NPs	Powder NPs
	Yield %	Yield %
no Fe_3O_4	0	0
681	2	9
343	7	10
228	10	14
137	15	25
50	46	48
20	55	57
10	60	62
5	69	68

Even though the two types of Fe_3O_4 NPs, powder and ferrofluid, exhibited similar catalytic activity in the *N*-4(aminophenyl)aniline oxidative polymerization, they differently affected the morphology of the final composites. More in detail, the ferrofluid-type magnetic NPs produced PANI/Fe_3O_4 nanocomposites with a preferential morphology of nanorods with a broad diameter distribution (30–110 nm). On the contrary, the powder-type Fe_3O_4 NPs led to materials with a more irregular structure.

In order to explain this different behaviour and inspired by the literature [61-66] a mechanism of nanorods formation was proposed, consisting in an interfacial polymerization.

Table 3: Catalytic Oxidative Polymerization of *N*-(4-Aminophenyl) Aniline (AD) in the Absence and in the Presence of Fe3O4, Using H2O2 as Oxidant (H2O2/AD= 3 Molar Ratio). Reaction Time = 24 h

AD/Fe_3O_4 (Molar Ratio)	Ferrofluid NPs	Powder NPs
	Yield %	Yield %
no Fe_3O_4	40	40
3000	39	40
1000	42	41
681	61	55
342	60	54
50	67	62
20	88	87
10	85	83
5	87	91

It was observed that the *inter*-particle interactions play a key role in the magnetic properties of PANI/Fe_3O_4 nanocomposites. The products exhibited a superparamagnetic behaviour at room temperature, whereas at low temperature they were in a blocked state, characterized by remanence and coercivity. Such a transition occurred between 100 and 200 K depending on the magnetite content. Moreover, their conductivity was similar to the traditional emeraldine salt one.

CONCLUSIONS

We have presented innovative sustainable ways for the preparation of conductive polyaniline and polypyrrole, using H_2O_2 or molecular oxygen as the oxidizing agents in the presence of different types of catalysts: gold nanoparticles, metallic copper, copper salts and Fe_3O_4 nanoparticels.

These catalytic approaches are a promising sign of a viable eco-friendly route towards these conductive polymers, essential feature that cannot be disregarded both for fulfilling the environmental restrictions and innovative applications.

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