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Synthesis of Meso-tetraarylporphyrins and *in Situ* Producing the Valuable Nanoparticles as a Byproduct: Potential Application in Solar Cells

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Meso-tetraarylporphyrins are synthesized from pyrrole and aryl aldehydes cleanly and efficiently using an equimolar amount of $Cr(HSO_4)_3$ in the presence of chloranil as the oxidant. Also, for the first time, meso-tetraphenylporphyrinogen is oxidized by $HAuCl_4$ to obtain meso-tetraphenylporphyrin and valuable gold nanoparticles as a byproduct, in good yield. Transmission electron microscopy (TEM) analysis indicated that spherical gold nanoparticles in the 25 diameter were obtained in the presence of meso-tetraphenylporphyrinogen at room temperature without using any capping agents. The Fourier transform infrared spectroscopy (FT-IR) supports the presence of tetraphenylporphyrin dye molecules on the surface of gold nanoparticles. These obtained gold nanoparticles could be used for various unknown and known applications, especially for designing efficient dye-sensitized solar cells, selective catalysts, and photodynamic therapy agents.

Keywords: Meso-tetraarylporphyrins, Gold nanoparticles, Transmission electron microscopy, Dye molecules

INTRODUCTION

Porphyrin-based biomolecules play an important role in the divergent fields of research, including catalysis, solar energy conversion, spectroscopy and the development of organic materials [1-4]. These compounds have also shown selective affinity to tumor cells [5,6] and applied for photodynamic cancer therapy [7-9] as a photosensitizer and even for antiviral treatment [10]. Advances in porphyrin model systems are closely tied to methods for preparing synthetic porphyrins. Over the past years, numerous advances in porphyrin synthetic methodology have been realized [11-13]. In most cases, a solution of aldehyde and pyrrole in a high boiling acid, such as propionic acid as a solvent, is heated at reflux in the air. This method gives low yields of sensitive porphyrins, reflecting rather vigorous conditions, and intractable purification problems arise for porphyrins and a high percentage of undesirable byproducts are also formed [14]. Recent methods in the synthesis of tetraarylporphyrins from tetramerization of mono pyrrole include the use of an oxidizing cosolvent [15], Lewis acids [16], and various clays as catalysts [17]. Some of these methods require costly purification procedures and/or high-thermal conditions so that the reaction fails with benzaldehydes with bearing substituents in ortho positions and sensitive functional groups such as carboxy groups. However, porphyrins are known to be obtained by treatment of the precursor 'porphyrinogen' [18] with oxidizing agents such as DDQ or chloranil [19,20]. Therefore, the preparation of the porphyrinogen intermediate is an important step in this synthesis. To synthesize meso-tetraarylporphyrins efficiently, it is necessary to select the specific conditions for the generation of the corresponding porphyrinogen, followed by appropriate oxidative workup [14].

On the other hand, the metal nanostructures have been of much interest during the past decades because of their different performances from their bulk counterparts and also

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their unique optical, magnetic, biological, and catalytic properties [17,21-26]. Regarding noble metal nanoparticles, gold nanoparticles (GNPs) have been a major field of study, because of their strong surface plasmon resonance, and potential applications in medical and industrial fields. Typically, gold nanoparticles are generally obtained by chemical reduction of tetrachloroauric acid using toxic reagents such as sodium borohydride [27]. It has been noted that the variation of particle growth medium plays a profound role in controlling the size and colloidal stability [28-30].

So, in this paper, we report a method for preparing porphyrins with bearing both electron-donating and withdrawing substituents in para, meta and ortho positions and sensitive functional groups such as carboxy groups under mild conditions. Pyrrole and benzaldehyde in the presence of $Cr(HSO_4)_3$ as an eco-friendly efficient catalyst and chloranil as an oxidant react to form tetraphenylporphyrin in 28-64% yields. Also, we have developed a facile route for the oxidation of meso-tetraphenylporphyrinogen to meso-tetraphenylporphyrin using $HAuCl_4$ as a new and effective oxidizing agent at room temperature. Under this reaction condition, spherical gold nanoparticles in the 25 diameter also were obtained in situ without using any capping agents. To the best of our knowledge, the use of $HAuCl_4$ as an oxidizing agent in the synthesis of meso-tetraphenylporphyrin and especially producing gold nanoparticles as valuable byproducts have not been reported in the literature. These obtained gold nanoparticles could be used for various unknown and known applications, especially for designing efficient dye-sensitized solar cells, selective catalysts, and photodynamic therapy agents.

EXPERIMENTAL

Materials and Physical Methods

Gold chloride trihydrate ($HAuCl_4.3H_2O$) was purchased from Aldrich and used without purification. Other chemical compounds used in this research were purchased from Merck. Pyrrole was distilled from calcium hydride, and stored samples were rejected when discoloration occurred. Melting points were recorded on an electrothermal type 9100 melting point apparatus. The ^1H NMR (100 MHz) spectra were recorded on a Bruker AC100 spectrometer. Elemental analysis was obtained on a Thermo Finnigan Flash EA microanalyzer. The FT-IR spectra were obtained on an Avatar 370 FT-IR Therma Nicolet spectrometer. UV-visible (UV-Vis) absorption spectroscopic measurements were recorded on a UV-Vis spectrometer, Shimadzu UV1700, using quartz cells of 1 cm path length. Transmission electron microscopic (TEM) images of the nanoparticles were taken with a LEO 912AB instrument operated at an accelerating voltage of 120 kV with a line resolution of 0.3 nm at room temperature. The samples for TEM measurements were prepared by placing a droplet of the colloidal solution onto a carbon-coated copper grid and allowing it to dry in the air naturally. Based on the TEM images, we determined the size distribution of the final product by counting at least 300 particles.

Preparation of $Cr(HSO_4)_3$

A 50 ml suction flask was equipped with a dropping funnel. The gas outlet was connected to a vacuum system through an alkaline solution trap. Chromium(III) chloride (10 mmol) was charged into the flask and concentrated sulfuric acid 98% (30 mmol) was added dropwise over a period of 30 min at room temperature. HCl gas was evolved immediately. After completion of the addition, the mixture was shaken for 30 min at 100 °C, while the residual HCl was eliminated by suction. Finally, $Cr(HSO_4)_3$ was obtained in 95% yield. The FT-IR spectrum of $Cr(HSO_4)_3$ shows absorption bands at 1610 (υS=O asymmetric stretching), 1225 (υS=O symmetric stretching), and 600-700 cm^{-1} corresponding to υ S-O. Moreover, a broadband from 2700-3400 cm^{-1} corresponds to acidic O-H stretching.

Synthesis of Substituted Meso-tetraarylporphyrins in the Presence of $Cr(HSO_4)_3$ and Chloranil

A standard reaction was performed in a three-neck, round-bottom flask fitted with a septum port, a reflux condenser, and a gas inlet port. The inlet port consisted of a glass disk immersed in the solution with nitrogen flow. The flask was charged with 100 ml of distilled CH_2Cl_2, benzaldehyde (0.1 ml, 1 mmol, 10^{-2} M), and pyrrole (0.07 ml, 1 mmol, 10^{-2} M). The resulting solution was magnetically stirred at room temperature. After stirring the solution for 10 min, an appropriate amount of $Cr(HSO_4)_3$

(0.3 g, 1 mmol) was added *via* syringe. The progress of the reaction was followed by TLC. After 2 h, the yield of porphyrinogen was maximum. Then, chloranil (0.18 g, 0.75 mmol) was added to the mixture and stirred at 40 °C for 1 h to oxidize the porphyrinogen to porphyrin. During this time, the mixture became dark purple, and porphyrinogen under oxidation was converted to porphyrin. The mixture was filtered to remove the catalyst, and the filtrate was then concentrated by rotary evaporation and chromatographed (silica gel; with CH_2Cl_2/petroleum ether 1:1) to give 1a in 64% yield.

5,10,15,20-Tetraphenylporphyrin (1a). Purple crystal [14]; m.p. > 300 °C; yield = 64%; λ_{max} (H_2O/DMSO): 417, 483, 517, 550, 591, 647 nm. δ_H (100 MHz, $CDCl_3$): 7.20-7.65 (m, 12H-arom.); 7.95-8.12 (m, $8H_o$); 8.58 (s, 8H, pyrrole-H). FT-IR (cm^{-1}; group): (3318, 3052, 3027, 1810, 1708, 1594, 1471, 1178, 964, 799, 701). Anal. Calcd. for $C_{44}H_{30}N_4$: C, 85.97; H, 4.92; N, 9.11. Found: C, 85.72; H, 5.02; N, 8.93.

5,10,15,20-Tetra(*p*-methylphenyl)porphyrin (2a). Purple crystal [14]; m.p. > 300 °C; yield = 58%; λ_{max} (H_2O/DMSO): 420, 485, 517, 550, 594, 651 nm. δ_H (100 MHz, $CDCl_3$): 2.10 (s, 12H, CH_3); 7.55 (d, $8H_m$); 8.12 (d, $8H_o$); 8.88 (s, 8H, pyrrole-H). Anal. Calcd. for $C_{48}H_{38}N_4$: C, 85.94; H, 5.71; N, 8.35. Found: C, 85.92; H, 5.38; N, 9.01.

5,10,15,20-Tetra(*p*-methoxyphenyl)porphyrin (3a). Purple crystal [14]; m.p. > 300 °C; yield = 63%; λ_{max} (H_2O/DMSO): 424, 488, 519, 556, 595, 653 nm. δ_H (400 MHz, $CDCl_3$): 4.19 (s, 12H, OCH_3); 7.55 (d, $8H_m$); 8.54 (d, $8H_o$); 8.50 (s, 8H, pyrrole-H). FT-IR (cm^{-1}; group): (3322, 2954, 2954, 2923, 2852, 1716, 1605, 1509, 1248, 804). Anal. Calcd. for $C_{48}H_{38}N_4O_4$: C, 78.45; H, 5.21; N, 7.62. Found: C, 78.40; H, 5.14; N, 7.65.

5,10,15,20-Tetra(*p*-chlorophenyl)porphyrin (4a). Purple crystal [14]; m.p. > 300 °C; yield = 53%; λ_{max} (H_2O/DMSO): 421, 485, 515, 549, 591, 649 nm. δ_H (100 MHz, $CDCl_3$): 7.75 (d, $8H_m$); 8.15 (d, $8H_o$); 8.84 (s, 8H, pyrrole-H). Anal. Calcd. for $C_{44}H_{26}Cl_4N_4$: C, 70.23; H, 3.48; N, 7.45. Found: C, 70.92; H, 3.44; N, 7.90.

5,10,15,20-Tetra(*p*-nitrophenyl)porphyrin (5a). Purple crystal [14]; m.p. > 300 °C; yield = 35%; λ_{max} (H_2O/DMSO): 421, 485, 515, 549, 590, 649 nm. δ_H (100 MHz, $CDCl_3$): 8.05 (d, $8H_m$); 8.40 (d, $8H_o$); 8.85 (s, 8H, pyrrole-H). Anal. Calcd. for $C_{44}H_{26}N_8O_8$: C, 66.50; H, 3.30; N, 14.10. Found: C, 66.37; H, 3.41; N, 14.01.

5,10,15,20-Tetra(*p*-carboxyphenyl)porphyrin (6a). Purple crystal [31]; m.p. > 300 °C; yield = 47%; λ_{max} (H_2O/DMSO): 430, 525, 560, 595, 650 nm. δ_H (100 MHz, DMSO): -2.95 (br. s, 2NH); 8.33 (m, 16H-arom.); 8.82 (s, 8H, pyrrole-H). FT-IR (cm^{-1}; group): (3072, 2631, 2521, 1697, 1604, 1405, 1271, 1103, 968, 796, 719). Anal. Calcd. for $C_{48}H_{30}N_4O_8$: C, 72.90; H, 3.82; N, 7.09. Found: C, 72.74; H, 3.71; N, 7.23.

5,10,15,20-Tetra(*p*-isopropylphenyl)porphyrin (7a). Purple crystal [14]; m.p. > 300 °C; yield = 59%; λ_{max} (H_2O/DMSO): 421, 489, 518, 550, 599, 652 nm. δ_H (100 MHz, $CDCl_3$): 1.65 (d, 24H, J = 4.4 Hz, CH_3); 3.25 (m, 4H, CH); 7.60 (d, $8H_m$); 8.15 (d, $8H_o$); 8.80 (s, 8 H, pyrrole-H). Anal. Calcd. for $C_{56}H_{54}N_4$: C, 85.89; H, 6.95; N, 7.15. Found: C, 85.83; H, 6.90; N, 7.16.

5,10,15,20-Tetra(m-methoxyphenyl)porphyrin (8a). Purple crystal [14]; m.p. > 300 °C; yield = 44%; λ_{max} (H_2O/DMSO): 418, 518, 551, 589, 650 nm. δ_H (400 MHz, $CDCl_3$): 4.18 (s, 12H, OCH_3); 7.54 (dd, J_1 = 5.0 Hz, J_2 = 2.8 Hz, 4Hp); 7.94 (t, J = 8.0 Hz, $4H_m$); 8.16-8.22 (m, $8H_o$); 8.65 (s, 8H, pyrrole-H). Anal. Calcd. for $C_{48}H_{38}N_4O_4$: C, 78.45; H, 5.21; N, 7.62. Found: C, 78.37; H, 5.14; N, 7.61.

5,10,15,20-Tetra(*m*-nitrophenyl)porphyrin (9a). Purple crystal [14]; m.p. > 300 °C; yield = 28%; λ_{max} (H_2O/DMSO): 418, 480, 515, 550, 591, 646 nm. δ_H (100 MHz, $CDCl_3$): 7.90-8.70 (m, 16H-arom.); 8.95 (s, 8H, pyrrole-H). FT-IR (cm^{-1}; group): (3358, 2917, 2848, 1690, 1569, 1345, 1110, 710). Anal. Calcd. for $C_{44}H_{26}N_8O_8$: C, 66.50; H, 3.30; N, 14.10. Found: C, 66.58; H, 3.27; N, 14.22.

5,10,15,20-Tetra(*o*-methoxyphenyl)porphyrin (10a). Purple crystal [32]; m.p. > 300 °C; yield = 40%; λ_{max} (H_2O/DMSO): 417, 512, 548, 589, 643 nm. δ_H (400 MHz, $CDCl_3$): 3.71-3.86 (m, 12H, OCH_3); 7.42-7.55 (several singlet, $8H_m$); 7.85-7.95 (m, $4H_p$); 8.25-8.40 (m, $4H_o$); 8.45 (s, 8H, pyrrole-H). Anal. Calcd. for $C_{48}H_{38}N_4O_4$: C, 78.45; H, 5.21; N, 7.62. Found: C, 78.30; H, 5.21; N, 7.69.

Synthesis of Meso-tetraphenylporphyrins in the Presence of $Cr(HSO_4)_3$ and $HAuCl_4$

According to the procedure discussed above, a standard

reaction was performed in a three-neck, round-bottom flask fitted with a septum port, a reflux condenser, and a gas inlet port. The inlet port consisted of a glass disk immersed in the solution with nitrogen flow. The flask was charged with 100 ml of distilled CH_2Cl_2, benzaldehyde (0.1 ml, 1 mmol, 10^{-2} M), and pyrrole (0.07 ml, 1 mmol, 10^{-2} M). The resulting solution was magnetically stirred at room temperature. After stirring the solution for 10 min, an appropriate amount of $Cr(HSO_4)_3$ (0.3 g, 1 mmol) was added via syringe. The progress of the reaction was followed by TLC. After 2 h, the yield of porphyrinogen was maximum. In this step, in order to remove the catalyst, filtration was done. Then, $HAuCl_4$ (0.4 g, 1 mmol) was added to obtain porphyrinogen solution and stirred at room temperature for 1 h to oxidize the porphyrinogen to porphyrin. During this time, the mixture became dark purple, and porphyrinogen under oxidation was converted to porphyrin. The dark purple mixture was centrifuged at 10,000 rpm. Then, the obtained solution was concentrated by rotary evaporation and chromatographed (silica gel; with CH_2Cl_2/petroleum ether 1:1) to give 1a in 68% yield. Also, the in situ prepared gold nanoparticles separated by precipitation under centrifuge were washed using three times with deionized water and twice with ethanol.

RESULTS AND DISCUSSION

Synthesis of Meso-tetraphenylporphyrin in the Presence of $Cr(HSO_4)_3$ and Chloranil

The synthesis of porphyrins has gained special attention in recent years because of their importance in bioorganic and bioinorganic chemistry and their applications in biomedical sciences [33]. Each research area requires porphyrins with different and specific structural features, bearing a variety of different substituents. The conversion of aldehydes and pyrroles to porphyrins is a multi-step process involving condensation (polymerization and cyclization) followed in time sequence by oxidation. The formation of porphyrin is known to depend on a variety of factors such as oxidant, catalyst, solvent, and reaction concentration. For this reason, the method has been widely employed over recent years. As mentioned, porphyrins are known to be easily obtained by treatment of the porphyrinogen intermediate with oxidizing agents such as chloranil. Therefore, to synthesize meso-tetraarylporphyrins efficiently, it is necessary to select the specific conditions for the generation of the corresponding porphyrinogen, followed by the appropriate oxidative workup.

Our efforts in this area have been largely directed toward the investigation of the best conditions for the synthesis of meso-tetraarylporphyrins. To obtain the best reaction conditions, the effects of different reaction parameters were investigated on the condensation of pyrrole and benzaldehyde as a model reaction. Initially, a systematic study was performed with various catalysts and solvents and it was found that $Cr(HSO_4)_3$ has an excellent activity for the condensation of pyrrole and benzaldehyde for the preparation of 1a (Table 1). In a typical trial reaction, 1 mmol of $Cr(HSO_4)_3$ was added to a solution of benzaldehyde (1 mmol) and pyrrole (1 mmol) in CH_2Cl_2 (10^{-2} M). After 2 h, 0.75 mmol of chloranil (40 °C, 1 h) was added to oxidize the porphyrinogen to porphyrin (Scheme 1). The general workup involves the concentration of the crude reaction mixture, followed by passing over a chromatography column. The porphyrin product obtained by this method is relatively pure.

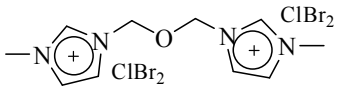
Reusability of the $Cr(HSO_4)_3$ catalyst was studied in the reaction of benzaldehyde and pyrrole. After completion of each run, the catalyst was simply recovered. As shown in Fig. 1, the catalyst could be reused without significant loss of catalytic activity up to at least 4 times.

The reactions were also carried out in CH_2Cl_2, $C_6H_5NO_2$, EtOH and H_2O. As shown in Table 1, CH_2Cl_2 is a suitable solvent for the $Cr(HSO_4)_3$ system. The results from Table 1 show the influence of the nature of the catalyst and solvent on porphyrin synthesis and clearly indicate that $Cr(HSO_4)_3$ in CH_2Cl_2 is the best condition for this condensation reaction.

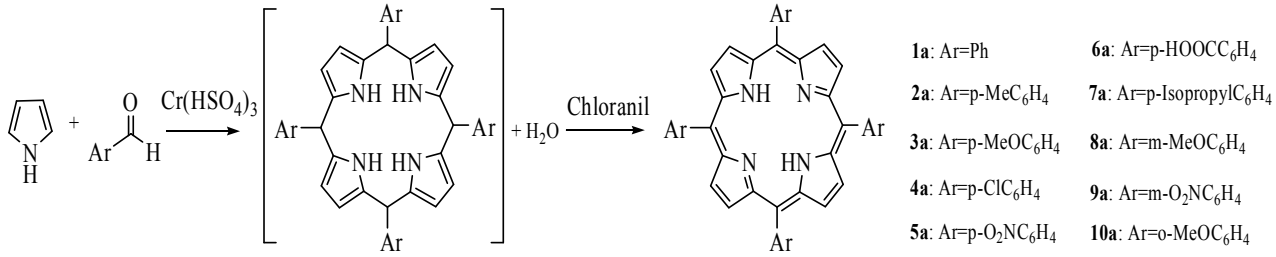
In an effort to evaluate the range of applicability of our method, we also examined some other benzaldehydes having a wide variety of *para*, *meta* and *ortho* substitutions, both electron-donating and withdrawing groups (Table 2).

This synthetic procedure can be used for the synthesis of a large number of tetraarylporphyrins, with pyrrole and aryl aldehydes. A comparison of the reaction of aldehydes with pyrrole in the presence of $Cr(HSO_4)_3$ indicates that under the influence of the heterogeneous acidic catalyst, substituted functionalities and their positions on a benzene ring

Table 1. Reaction of Pyrrole (1 mmol) and Benzaldehyde (1 mmol) in the Presence of Chloranil as Oxidant under Various Catalysts and Solvents[a]

Entry	Catalyst	Solvent	Yeild (%) of 1a
1	CF_3COOH	CH_2Cl_2	25%
2		CH_2Cl_2	Trace
3	$AlCl_3$	CH_2Cl_2	15%
4	$Fe(HSO_4)_3$	CH_2Cl_2	0%
5	$Cr(HSO_4)_3$	CH_2Cl_2	64%
6	$Cr(HSO_4)_3$[b]	CH_2Cl_2	10%
7	$Cr(HSO_4)_3$	$C_6H_5NO_2$	0%
8	$Cr(HSO_4)_3$	EtOH	Trace
9	$Cr(HSO_4)_3$	H_2O	0%

[a]The reactions were performed with 1 mmol of pyrrole and 1 mmol benzaldehyde in solvent (100 ml) in the presence of 1 mmol catalyst and 0.75 mmol chloranil as the oxidant. [b]0.1 mmol catalyst was used.



Scheme 1. Preparation of different meso-tetraarylporphyrins in the presence of $Cr(HSO_4)_3$ and chloranil

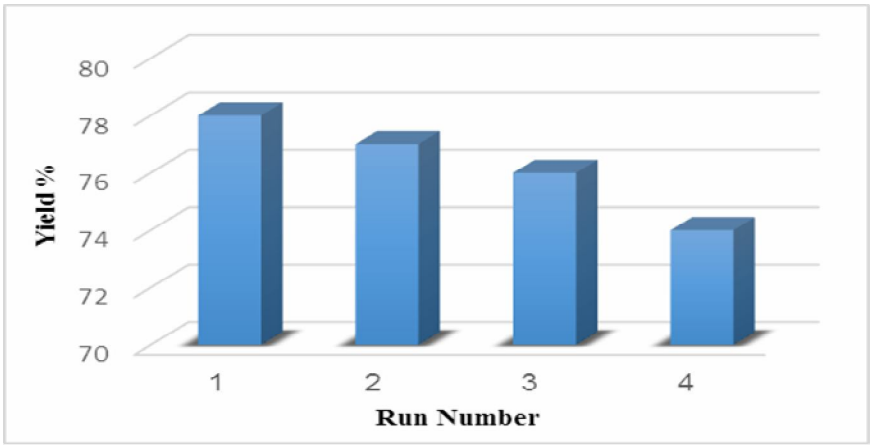


Fig. 1. Reusability of the $Cr(HSO_4)_3$ catalyst in the synthesis of tetraphenylporphyrin.

Table 2. Synthesis of Meso-tetraarylporphyrins from Pyrrole (1 mmol) and Aryl Aldehydes (1 mmol) in the Presence of $Cr(HSO_4)_3$ and Chloranil

Entry	Ar	Product	Reaction time (h)	Yield (%)
1	Ph	1a	3	64
2	*p*-MeC_6H_4	2a	3	58
3	*p*-$MeOC_6H_4$	3a	3	63
4	*p*-ClC_6H_4	4a	3	53
5	*p*-$O_2NC_6H_4$	5a	3	35
6	*p*-$HOOCC_6H_4$	6a	3	47
7	*p*-IsopropylC_6H_4	7a	3	59
8	*m*-$MeOC_6H_4$	8a	3	44
9	*m*-$O_2NC_6H_4$	9a	3	28
10	*o*-$MeOC_6H_4$	10a	3	40

All reactions were run under standard conditions: 10^{-2} M aldehyde and 10^{-2} M pyrrole with an equimolar amount of $Cr(HSO_4)_3$ in CH_2Cl_2 in the presence of chloranil at 39 °C.

sensitively affected the yields of meso-tetraarylporphyrins. The advantage of this method is that it allows the formation of porphyrins from sensitive aldehydes such as *p*-carboxybenzaldehyde. In most previous methods, the synthesis of porphyrins bearing carboxy groups often requires the acid groups to be masked as esters. This consequently involves an extra step of group deprotection after the formation of porphyrin [34]. However, carboxy substituted porphyrins are attractive synthetic targets. These substituents are present in natural porphyrins such as protoporphyrin IX. The carboxy group confers an amphyphilic character to the porphyrins, and this is very important to improve the selectivity in tumor localization in PDT [35]. Also, carboxy groups can act as linkers to attach porphyrins to other materials, for example, they can be anchored to solid supports by amidation [36]. Therefore, the advantages of our method are the preparation of a large variety of porphyrins in high yields from the corresponding aldehydes, ease of isolation and purification of the porphyrins obtained, and the formation of porphyrins from sensitive aldehydes.

Synthesis of Meso-tetraphenylporphyrin in the Presence of $Cr(HSO_4)_3$ and $HAuCl_4$

In another study, we investigated the synthesis of tetraphenylporphyrin in the presence of $Cr(HSO_4)_3$ and $HAuCl_4$. As mentioned above, we investigated the performance of $Cr(HSO_4)_3$ as an efficient heterogeneous acidic catalyst for the synthesis of tetraarylporphyrinogen as an intermediate. This intermediate can be oxidized to tetraarylporphyrin by oxidizing agents such as DDQ or chloranil. Under these reaction conditions, tetraarylporphyrins were formed. In this paper, for the first time, we show that $AuCl_4^-$ ions can oxidize tetraphenylporphyrinogen to produce tetraphenylporphyrin and these Au ions themselves are reduced to form gold atoms *in situ*.

However, as it is obvious, interest in research on nanoparticles is mainly due to their potential applications over a wide range of aspects starting from photonics to biology and catalysis [17,21-26]. The gold nanoparticles are the most employed metallic nanoparticles in the fields of nanomedicine and nanobiotechnology. Therefore, the preparation and synthesis of gold nanoparticles with suitable particle size, stability and shape are very important to obtain nanoparticles with high activity and efficiency. On the other hand, porphyrin conjugated gold nanoparticles are valuable products that are very important in nanomedicine, such as photodynamic therapy and nanotechnology such as solar cells. For the preparation of porphyrin conjugated gold nanoparticles, usually, chemical toxic reducing agents such as sodium borohydride is used for the synthesis of gold nanoparticles. So, it makes some problems in its applications. In this research, $HAuCl_4$ acts as an oxidant for porphyrinogen to produce porphyrin and simultaneously prepare *in situ* valuable porphyrin conjugated gold nanoparticles without any additional reducing toxic reagent. So, the main advantage of using $HAuCl_4$ as an oxidant is synthesizing gold nanoparticles coating with porphyrins that are useful in nanomedicine and nanotechnology.

So, for this purpose, we examined the condensation of pyrrole and benzaldehyde as a model reaction in the presence of $HAuCl_4$ as an oxidizing reagent. In a typical reaction, 1 mmol of $Cr(HSO_4)_3$ was added to a solution of benzaldehyde (1 mmol) and pyrrole (1 mmol) in CH_2Cl_2 (10^{-2} M). After 2 h, when the yield of porphyrinogen was maximum, we removed $Cr(HSO_4)_3$ catalyst by filtration. Then, 1 mmol $HAuCl_4$ was added to oxidize the porphyrinogen to porphyrin at room temperature. Finally, the dark purple mixture was centrifuged. The obtained solution was concentrated by rotary evaporation and chromatographed to obtain pure meso-tetraphenylporphyrin. Also, the in situ prepared gold nanoparticles separated by precipitation under centrifuge were washed several times using different solvents.

The porphyrin product (1a) obtained by this method (in 68% yield) is relatively pure and was characterized by IR, UV-Vis and ^{1}H NMR. So, we have demonstrated for the first time, a simple method for the simultaneously synthesis of tetraphenylporphyrin and gold nanoparticles using $Cr(HSO_4)_3$ and $HAuCl_4$ as an oxidizing agent. In the other words, the use of tetraphenylporphyrinogen as an organic reducing reagent in the synthesis of gold nanoparticles under mild conditions has not been reported in the literature. High yield of porphyrin, simplicity of operation, easy workup and especially producing valuable byproducts are some advantages of this method.

For the characterization of the gold nanoparticles

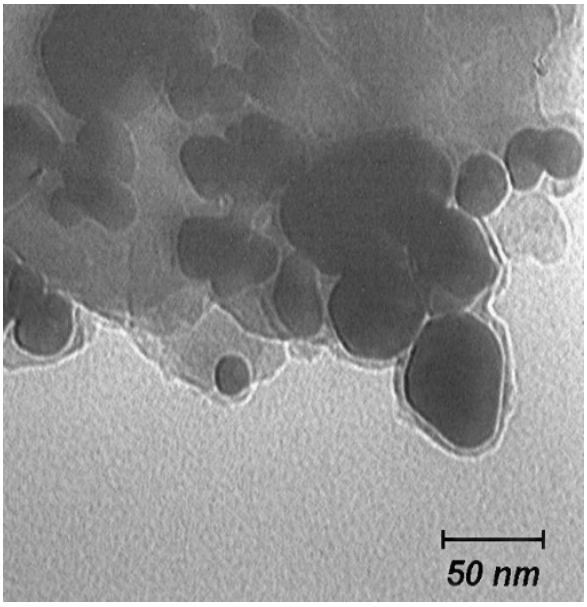


Fig. 2. Typical TEM image of individual gold nanoparticles in water medium. The scale bar is 50 nm.

prepared *in situ* by this method, the TEM image of these particles was taken (Fig. 2). The micrograph clearly indicates the formation of nanoparticles with 25 nm diameter. As it is indicated in this image, the porphyrin compound is obtained from the oxidation of porphyrinogen acting as a capping agent. Therefore, the particles do not get self-assembled.

On the basis of the recent study of Garabagiu *et al*., it was revealed that a strong and large absorption band is obtained between gold nanoparticles and porphyrin [37]. In this work, they investigated the coupling between gold nanoparticles and porphyrins *via* nitrogen atoms in the porphyrinic structure.

Therefore, to clearly learn the structures of meso-tetraphenylporphyrin dye on the particle surface, the FT-IR spectra of the 25 nm sample were determined and compared with free meso-tetraphenylporphyrin (Fig. 3). The bands seen at 3052 cm^{-1} and 3023 cm^{-1} were assigned to the C-H stretching vibration of aromatic groups. The presence of one weak peak in the FT-IR spectra of gold nanoparticles at 3319 cm^{-1} and a medium peak at 1693 cm^{-1} correspond to the N-H and C=N stretching vibration of pyrrolic rings, respectively. So, this FTIR spectrum supports the presence of meso-tetraphenylporphyrin on the surface of gold nanoparticles. Also, because the N-H stretching vibration band of pyrrolic rings of meso-tetraphenylporphyrin present on the surface of gold nanoparticles is weaker compared to its free meso-tetraphenylporphyrin, it might be confirmed the linking of gold nanoparticles to nitrogen atoms of the meso-tetraphenylporphyrin structure and might play an important role in the stabilization of the formed nanoparticles. Thus, these new dye nanomaterials will be helpful in the design of dye-sensitized solar cells, selective catalysts and photodynamic therapy agents.

The proposed mechanism for the porphyrin synthesis in the presence of $Cr(HSO_4)_3$ and $HAuCl_4$ is shown in Scheme 2. $HAuCl_4$ might be expected to oxidize meso-tetraarylporphrinogen by electron transfer yielding the corresponding meso-tetraarylporphyrin. The prepared gold nanoparticles were stable in the porphyrinic shield for several months.

CONCLUSIONS

In this paper, we demonstrated two efficient routes to synthesize meso-tetraarylporphyrins from pyrrole and aryl aldehydes with bearing various substituents and sensitive functional groups by using $Cr(HSO_4)_3$ catalyst in the

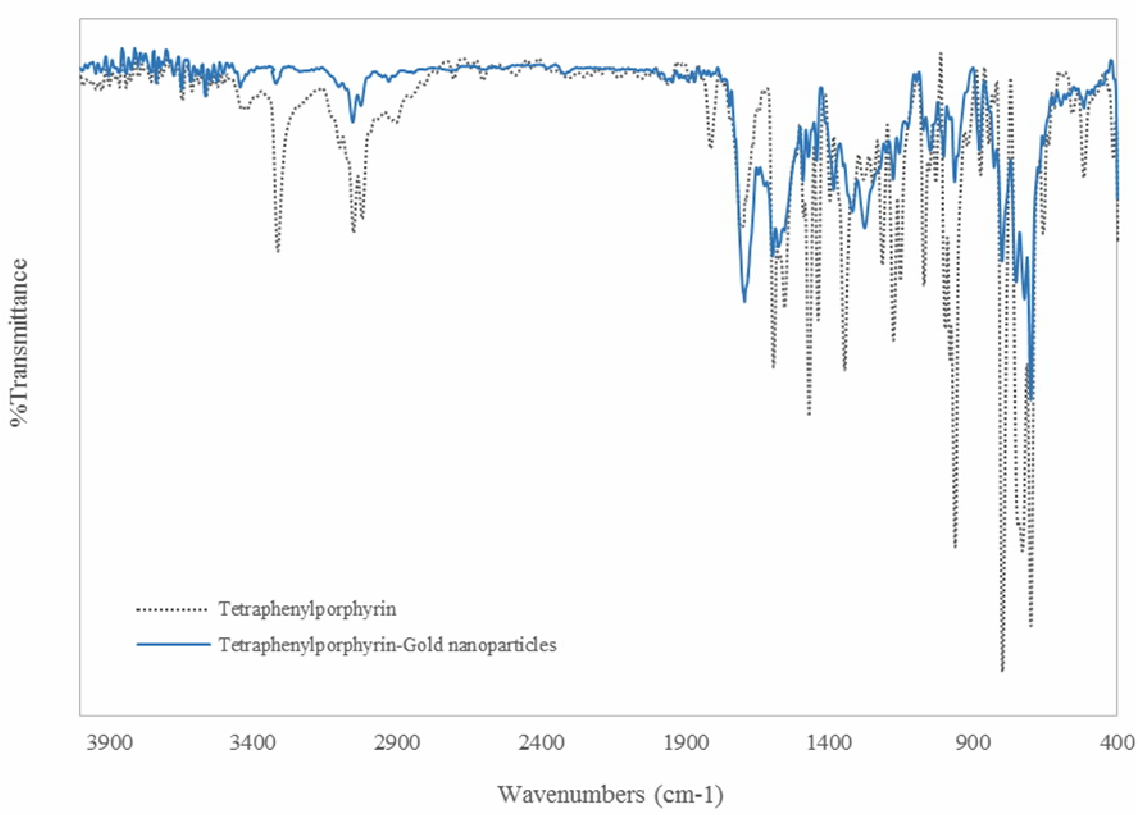
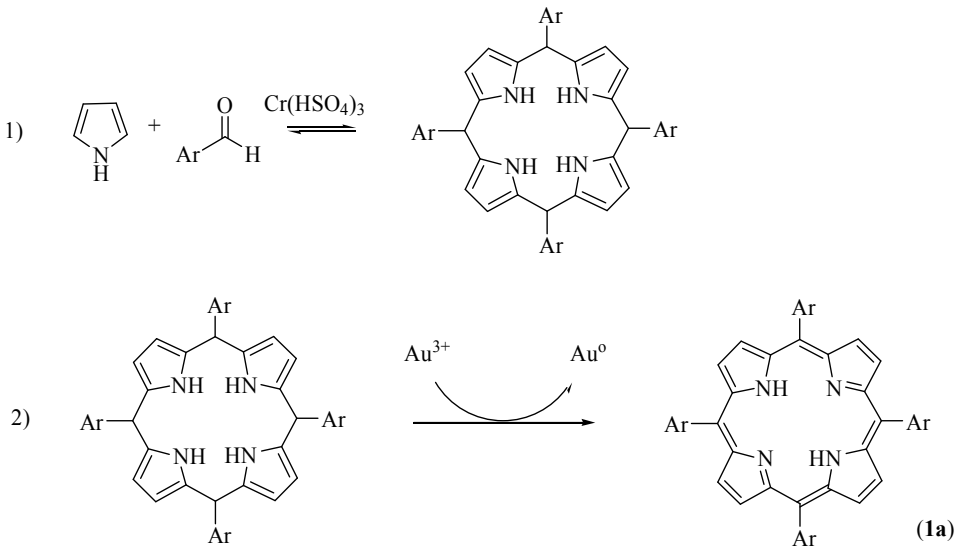


Fig. 3. The FT-IR spectra of gold nanoparticles (blue line) and free meso-tetraphenylporphyrin (dash line).



Scheme 2. The proposed mechanism for the synthesis of meso-tetrarylporphyrin in the presence of $Cr(HSO_4)_3$ and $HAuCl_4$.

presence of chloranil and $HAuCl_4$ as oxidants. Short reaction time, high yield, simplicity of operation and easy workup are some advantages of these methods. In addition, for the first time, gold nanoparticles were formed in the presence of meso-tetraphenylporphyrinogen as the reducing agent at room temperature without the presence of any stabilizing or capping agents. To the best of our knowledge, the use of $HAuCl_4$ as an oxidizing agent in the synthesis of meso-tetraphenylporphyrin and especially in situ producing gold nanoparticles as valuable byproducts has not been reported in the literature. These obtained gold nanoparticles were stable in the porphyrinic shield for about three months. These nanoparticles may find potential applications in designing efficient dye-sensitized solar cells, selective catalysts and photodynamic therapy agents.

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