

1 Surface Coating by Gold Nanoparticles on Functional Polymers: On- 2 Demand Portable Catalysts for Suzuki Reactions

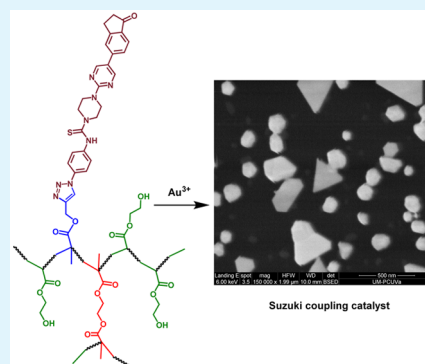
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7 **S** Supporting Information

8 **ABSTRACT:** We have developed new functionalized polymers capable of being
9 easily coated by gold nanoparticles, uniformly distributed on the surface of the
10 polymers, by simply adding a gold(III) solution in water to the polymers. The
11 polymer-supported gold nanoparticle material was used as an efficient portable and
12 reusable catalyst for Suzuki reactions in mixed organic–aqueous solvents.



13 **KEYWORDS:** functionalized polymers, gold nanoparticles, surface coating, Suzuki reaction, reusable catalyst

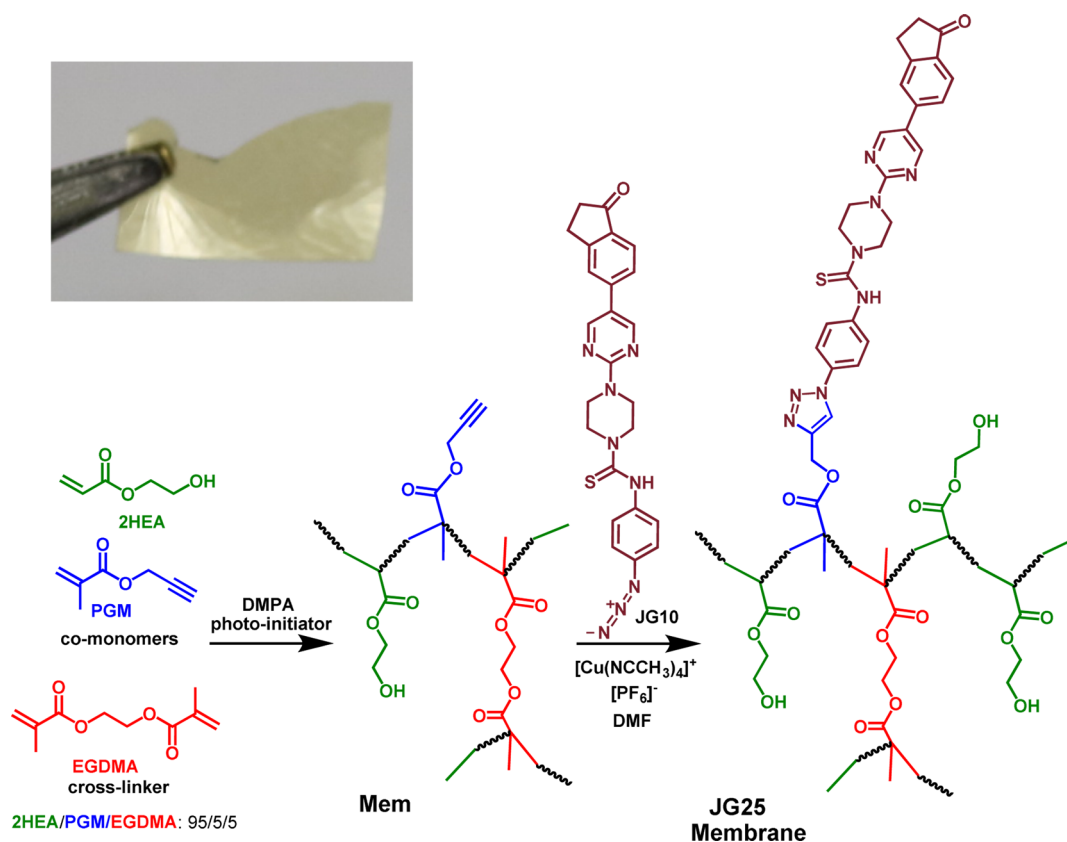
14 **G**old nanoparticles exhibit a range of physical and chemical
15 properties that are promising for potential applications in
16 a new generation of optical, electronic, and chemical devices.¹
17 Many of these devices will require immobilization of gold
18 nanoparticles in a single layer or in multilayers on conducting
19 or dielectric surfaces.² The immobilization is often accom-
20 plished through the surface modification with functional groups
21 that provide attractive interaction to gold nanoparticles.^{3,4} The
22 search for the optimal routes of the formation of monolayer
23 ensembles of gold nanoparticles on various substrates is much
24 required. Such nanostructured systems possess unique optical
25 and electronic properties, which depend on the particle size and
26 shape, as well as on the interparticle distance.⁵ These systems
27 are quite promising for the application in microelectronics,
28 solid state chemical or biological sensors, and catalysis.^{6–9} The
29 formation of continuous films of metal nanoparticles on a
30 polymer substrate is not a simple task, because the size of metal
31 clusters and their concentration on the polymer surface are
32 rather difficult to control. The adsorption of metal nano-
33 particles from their colloidal solutions has been employed,¹⁰
34 but highly dispersed gold nanoparticles are difficult to obtain in
35 a solution phase without using organic stabilizer and the
36 presence of reductive agents such as citric acid, alkylamine,
37 alkylthiol, and cationic surfactants, complicating the adsorption
38 step. Therefore, the approaches with prebound reductants on a
39 certain support are quite desirable. For some time we have been
40 working in the detection of Hg²⁺, which is a known thiophilic
41 cation. A productive way to develop chemical probes for the
42 detection of Hg²⁺ is the complexation of Hg²⁺ by colorimetric

or fluorogenic reagents having sulfur atoms. We have prepared 43
sulfur containing chromogenic probes¹¹ and new fluorogenic 44
probes for fluorogenic detection and speciation of Hg²⁺ and 45
MeHg⁺ in aqueous–organic mixtures.¹² Now, with the purpose 46
of preparing solid supported chemical probes, we have bonded 47
a fluorogenic probe to a polymeric hydrophilic matrix to 48
develop a new fluorescent polymer useful for the preparation of 49
chemical sensors for thiophilic cations. During the preliminary 50
experiments of sensitivity of the functional membrane and 51
cation solutions we noticed that the polymer became purple in 52
contact with HAuCl₄ solutions in water. The intensity of the 53
color depended on the concentration, volume of added solution 54
and time of contact, therefore we studied in depth the behavior 55
of all membranes and the gold(III) solution. In this paper, we 56
report our findings in the surface coating by gold nanoparticles 57
on functional polymers and their applications to the catalysis of 58
Suzuki reactions. The film-shaped functional membrane 59
(Mem) was prepared by the photochemically initiated radical 60
polymerization¹³ of the hydrophilic monomer 2HEA and 61
PGM. EGDMA was used as cross-linking agent (Scheme 1). 62 st
The comonomer molar ratio 2HEA/PGM/EGDMA was 63
95/5/5, respectively. 2,2-Dimethoxy-2-phenylacetophenone 64
(DMPA, 1.5 wt %) was employed as a photochemical initiator. 65
The photoinitiated bulk polymerization was performed in a 100 66
μm thick silanized glass hermetic mold upon irradiation with a 67

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Scheme 1. Synthesis of the Fluorogenic Polymer JG25; Inset: Picture of the Polymer under White Light



68 UV mercury lamp (250w, Philips HPL-N, emission band in the
 69 UV region at 304, 314, 335, and 366 nm, with maximum
 70 emission at 366 nm), at 20 °C, for 4 h. The water-swelling
 71 percentage (WSP) of the membrane was 60% and the DMF
 72 swelling 300%. Then *N*-(4-azidophenyl)-4-(5-(1-oxo-indan-5-
 73 yl)pyrimidin-2-yl)piperazin-1-carbothioamide¹² (JG10, 0.17
 74 mmol) in DMF was stirred under nitrogen in an orbital shaker
 75 with 0.40 g of the polymer membrane Mem and 3 mg (5%
 76 mol) of $\text{Cu}(\text{NCCH}_3)_4^+[\text{PF}_6]^-$ as catalyst for 72 h. After that,
 77 the reaction was finished and the functionalized polymer JG25
 78 had a light orange-yellow color. The polymer was washed with
 79 water and left to dry (Scheme 1). The characterization of the
 80 membrane was carried out by SEM analysis, with gold and
 81 carbon recap. The atomic proportion was taken by X-ray
 82 analysis on different areas of the polymer. The proportion
 83 between oxygen or carbon and sulfur atoms was very similar to
 84 the theoretical results associated with a 100% stoichiometric
 85 reaction. The appearance of IR signals at 1514 and 1598 cm^{-1} ,
 86 that were not present on the IR spectrum of Mem, were the
 87 associated with the presence of the fluorogenic probe, their
 88 intensity was low according to the low percentage (5%) of the
 89 probe in the polymer JG25. Then we submitted fragments of
 90 JG25 to HAuCl_4 solutions in water until the polymer became
 91 purple. By systematically changing conditions of Au^{3+}
 92 concentration, volume of the added solution and time of
 93 contact of the polymer with the Au^{3+} solution, we got different
 94 degrees of intensity of the purple color and therefore different
 95 patterns of covering of the polymer with gold nanoparticles. In
 96 a representative experiment, 100 μL Au^{3+} (5×10^{-3} M HAuCl_4
 97 in water) were added to a 1×1 cm square piece of JG25 and
 98 the set was left standing for 24 h, becoming dark purple.
 99 Scanning electron microscopy (SEM) showed the surface of the

polymer uniformly coated by gold nanoparticles, in addition of 100
 some flat gold nanoplates and short gold nanorods (Figure 1). 101 f
 The covering area of the gold nanoparticles was around 27%. A 102
 more detailed view of the gold nanoparticles was obtained by 103
 transmission electron microscopy (TEM) of related types of 104
 nanoparticles obtained in solution. By lowering the concen- 105
 tration of Au^{3+} and decreasing the time in which the gold(III) 106
 solution remained in contact with the polymer, the coating of 107
 the surface was still homogeneous but the overall size of the 108
 gold nanoparticles was much smaller and regular. In that case, 109
 the UV-vis spectrum showed a maximum of absorbance at 540 110
 nm (Figure 1). 111

We then tested the film-shaped functional membrane (Mem) 112
 in similar conditions to verify if the presence of the fluorogenic 113
 dye was required for the generation of the gold nanoparticles 114
 on the surface of the polymer in contact to a gold(III) solution. 115
 In this case, we also got uniformly coated surfaces of the 116
 polymer by gold nanoparticles of regular size (Figure 2a, b). In 117
 a representative experiment, 100 μL Au^{3+} (HAuCl_4 5×10^{-3} M 118
 in water) were added to a 1 cm square of Mem and then it was 119
 left standing for 25 min, becoming dark purple (Figure 2c). In 120
 this case, only smaller nanoparticles are obtained with very few 121
 nanoplates but the distribution of the size was more disperse 122
 than in previous case (Figure 2d). The gold nanoparticles were 123
 well distributed and covered a relative area of around 23%. By 124
 cryofracture and SEM imaging of the transversal section of one 125
 of the samples of polymer coated by gold nanoparticles, we 126
 verified that the gold nanoparticles were located only on the 127
 surface of the polymer, with very few and very small 128
 nanoparticles inside the bulk of the polymer (Figure 2g, h). 129

By adding the gold solution in one side of the polymer and 130
 leaving it to extend to the rest of the polymer, long nanorods 131

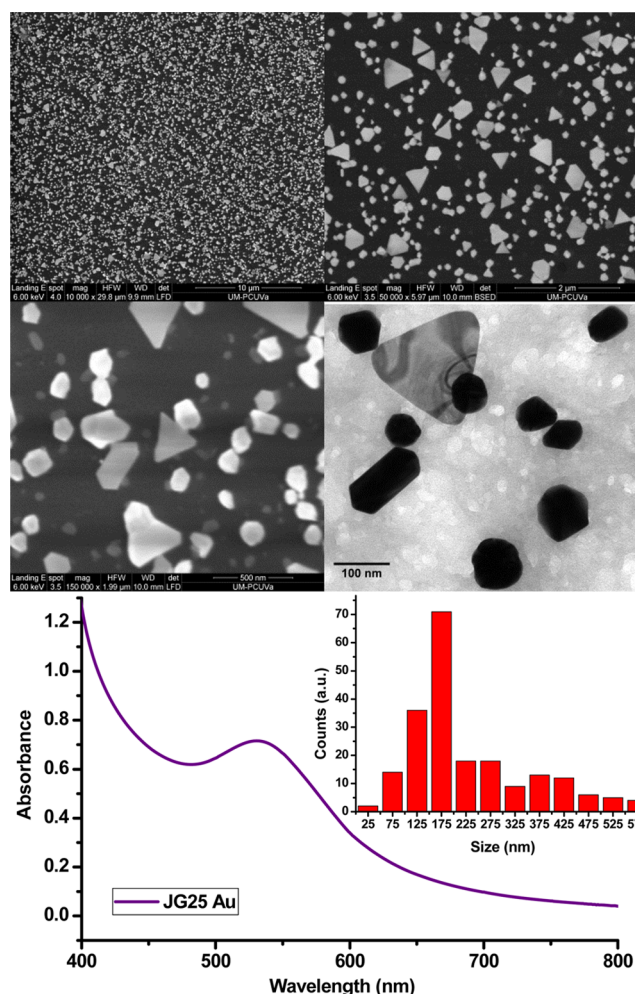


Figure 1. Top: SEM images of the homogeneous coating of the polymer JG25 by gold nanoparticles ($100 \mu\text{L Au}^{3+}$, $5 \times 10^{-3} \text{ M HAuCl}_4$ in water), (upper left) scale bar $10 \mu\text{m}$, (upper right) scale bar $2 \mu\text{m}$, (lower left) scale bar $500 \mu\text{m}$; (lower right) TEM image of related gold nanoparticles obtained in solution, scale bar 100 nm . Bottom: UV-vis spectrum of a sample of polymer covered with gold nanoparticles. Inset: Distribution of the particle size.

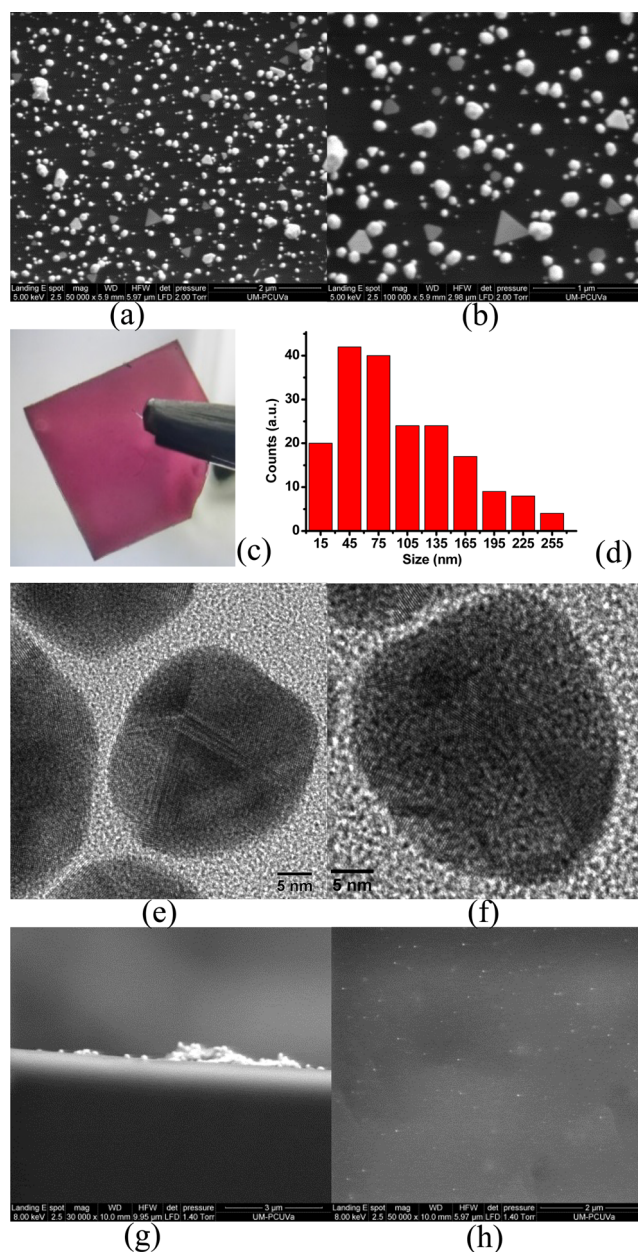


Figure 2. SEM images of the polymer membrane surface homogeneously coated by gold nanoparticles ($100 \mu\text{L Au}^{3+}$, $5 \times 10^{-3} \text{ M HAuCl}_4$ in water), (a) scale bar $2 \mu\text{m}$, (b) scale bar $1 \mu\text{m}$. (c) Image showing the color of the polymer by transmitted light. (d) Distribution of the particle size. (e, f) TEM images of related gold nanoparticles obtained in solution, scale bar 5 nm . (g) SEM images of the polymer membrane surface and section on which gold nanoparticles are grown, scale bar $3 \mu\text{m}$. (h) SEM image of the cryofracture section of the polymer Mem with very few small gold nanoparticles, scale bar $2 \mu\text{m}$.

132 up to $1.5 \mu\text{m}$ were obtained with very few flat gold nanoplates,
 133 triangles and hexagons,^{14–16} albeit the gold nanorods lengths
 134 ranged from 100 nm to $1.5 \mu\text{m}$. In this case, the experiment was
 135 performed by adding $40 \mu\text{L Au}^{3+}$ (HAuCl_4 $5 \times 10^{-3} \text{ M}$ in
 136 water) to a $1 \times 1 \text{ cm}$ square piece of Mem and then left
 137 standing for 24 h, becoming dark purple (Figure 3).

138 By changing water for dimethylformamide (DMF) as solvent,
 139 a homogeneous coating of the polymer by gold nanoparticles
 140 was also obtained. In this case, a representative experiment
 141 consisted on addition of $100 \mu\text{L Au}^{3+}$ (HAuCl_4 $5 \times 10^{-3} \text{ M}$ in
 142 DMF) to a $1 \times 1 \text{ cm}$ square piece of Mem and then left
 143 standing for 24 h, becoming purple (Figure 4a, b). In this case,
 144 the polymer appeared blue translucent with purple reflection
 145 (Figure 4a–c). The gold nanoparticles formed in DMF covered
 146 a very small relative area of approximately 3%. As in previous
 147 cases, the size of the gold nanoparticles depended on the time
 148 of contact between the polymer and the gold solution, giving
 149 larger nanoparticle sizes at longer times (Figure 4f).

150 By cryofracture and SEM imaging of the transversal section
 151 of one of the samples of polymer coated by gold nanoparticles
 152 in DMF, we verified that the gold nanoparticles were in this

case evenly distributed also inside the bulk of the polymer 153
 (Figure 4gm h), albeit they were much smaller ($50\text{--}90 \text{ nm}$ 154
 average) than the nanoparticles on the surface ($200\text{--}250 \text{ nm}$). 155
 The presence of small gold nanoparticles inside the polymer 156
 could explain the optical characteristics found for polymer 157
 membranes on which gold nanoparticles are grown by using 158
 DMF (Figure 4c–e). 159

We also checked whether a simple 2HEA polymer, a polymer 160
 with the same characteristics but without the 5% of propargyl 161

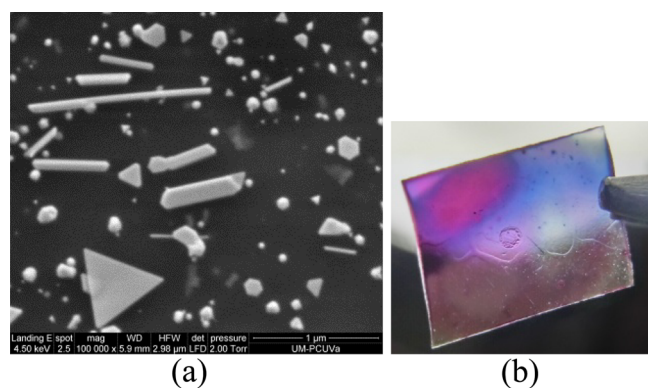


Figure 3. (a) SEM image of the polymer membrane surface coated by gold nanorods, nanoplates, and nanoparticles ($40 \mu\text{L Au}^{3+}$, $\text{HAuCl}_4 5 \times 10^{-3} \text{ M}$ in water), scale bar $1 \mu\text{m}$. (b) Image showing the color of the polymer by transmitted and reflected light.

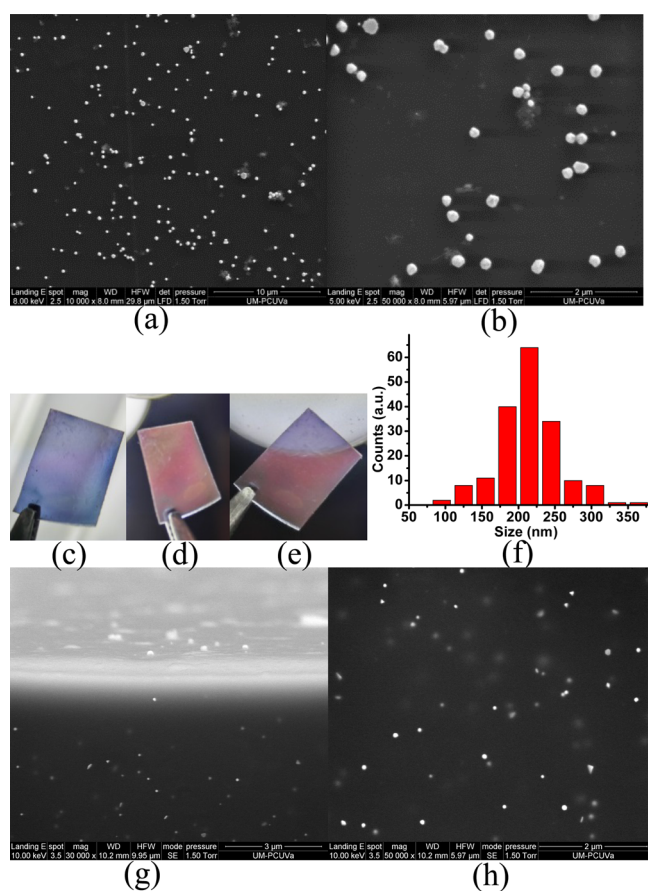
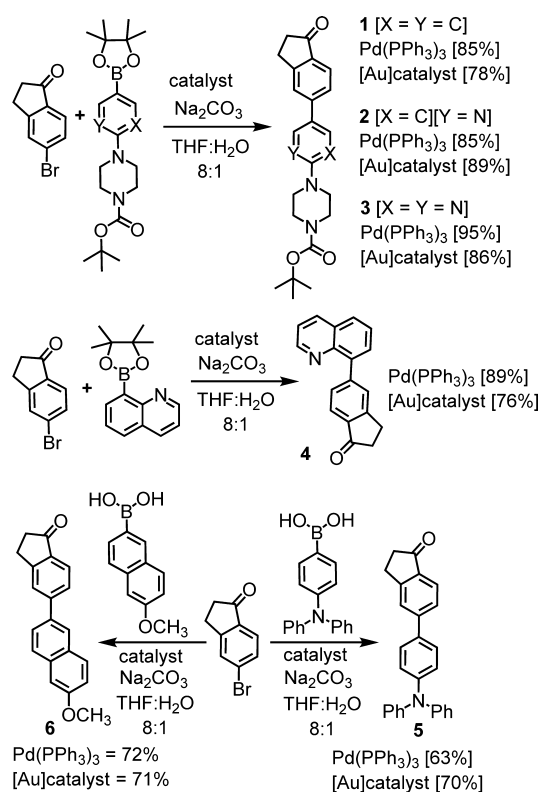


Figure 4. SEM images of the polymer membrane surface on which gold nanoparticles are grown by using DMF ($100 \mu\text{L Au}^{3+}$, $\text{HAuCl}_4 5 \times 10^{-3} \text{ M}$ in DMF), (a) scale bar $10 \mu\text{m}$, (b) scale bar $2 \mu\text{m}$. Images showing the color of the polymer by means of (c) transmitted light, (d) reflected light, (e) transmitted and reflected light. (f) Distribution of the particle size. (g) SEM image of the surface and the cryofracture section of the polymer Mem by gold nanoparticles, scale bar $3 \mu\text{m}$. (h) SEM image of the cryofracture section of the polymer Mem with gold nanoparticles in the bulk of the polymer, scale bar $2 \mu\text{m}$.

Scheme 2. Representative Experiments of Suzuki Reactions by Using the Polymer-Supported Gold Nanoparticle Material As Catalyst



for the formation of gold nanoparticles. The different nucleation due to the presence of different functional groups on the polymer surface was responsible for the shape of the gold nanoparticles, as has been recently stated for the anisotropic growth of gold nanoprims in plasmon-driven synthesis.¹⁷

Once the coating of the surface of the polymer by gold nanoparticles was sufficiently studied, we looked for practical applications of the material. Between many reactions catalyzed by solid-supported gold nanoparticles,^{18,19} poly(2-aminothiophenol)-supported gold nanoparticles have shown excellent catalytic activity for Suzuki-Miyaura cross-coupling reactions.²⁰ In our case, the polymer-supported gold nanoparticles material was found to be useful as a solid reusable catalyst in Suzuki reactions intended to prepare useful starting materials for the synthesis of chemical sensors.^{12,21,22} The conditions to perform these reactions were very similar to the classical reactions performed with $\text{Pd}(\text{PPh}_3)_3$ as the catalyst. In a representative experiment, a 25 mL round-bottom flask was filled with 30 mg (0.14 mmol) of 5-bromoindan-1-one, 1 equiv. of the boronic ester or acid, 75 mg (0.7 mmol) of Na_2CO_3 , and a $0.3 \times 0.3 \text{ cm}$ polymer piece coated with gold nanoparticles obtained from previous synthesis. After that, a solvent mixture composed of 4 mL of THF and 0.5 mL of water was added. The mixture was refluxed for 20 h, extracted by partition in DCM:water and purified by column chromatography. The corresponding spectral and physical characterization of every obtained product was checked in each case to be identical to previously reported compounds. Yields were compared to the reported yields for every compound, 1–3,¹² 4,²¹ 5,²² and 6.^{22,23} The polymer could be recovered from the solution and reused again in 196

162 metacrylate, could deposit gold nanoparticles, but there was no
163 response to the presence of a water solution $5 \times 10^{-4} \text{ M}$
164 HAuCl_4 for 2 days. Therefore, the presence of bonded JG10 or
165 the triple bonds on the surface of the polymers were necessary

197 another synthetic process (see the Supporting Information,
198 pages S-17 to S-19). In all cases, the gold-catalyzed process was
199 comparable to the previously reported procedure with respect
200 of reaction yields with the advantage of the easy recovery of the
201 catalyst (Scheme 2).

202 The simplicity of the preparation of the catalyst, with no
203 need of additional ligands for protection,²⁴ makes the system
204 competitive to gold nanoparticles suspended in solution,²⁵
205 supported on paper,^{26,27} or to other solid-supported gold
206 nanoparticles catalysts^{28,29} for Suzuki reactions. Therefore, the
207 polymer-supported gold nanoparticles material can be consid-
208 ered as a useful material for green catalysis in the synthesis of
209 fine chemicals by heterogeneous catalysis on the way to a more
210 sustainable chemistry.³⁰

211 In conclusion, we have developed a new functional polymer
212 capable to be easily coated by gold nanoparticles, uniformly
213 distributed on the surface of the polymers, by simply adding a
214 gold(III) solution in water to the polymers. The polymer-
215 supported gold nanoparticles material was used as an efficient
216 portable and reusable catalyst for Suzuki reactions in mixed
217 organic–aqueous solvents.

218 ■ ASSOCIATED CONTENT

219 ● Supporting Information

220 The Supporting Information is available free of charge on the
221 ACS Publications website at DOI: 10.1021/acsami.6b07746.

222 Figures S1–S12 and accompanying text, experimental
223 details for all materials; Figures S13–S16, character-
224 ization data for the functional polymers; Figures S17–
225 S26 and the accompanying text, deposition and use of
226 gold nanoparticles on the surface of the synthetic
227 polymers; and Figures S27–S30 and the accompanying
228 text, additional experiments about the synthesis of a
229 2HEA polymer and the preparation of gold nanoparticles
230 in solution (PDF)

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235 Notes

236 The authors declare no competing financial interest.

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