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Graphical Abstract

Cauliflower-like porous magnetic MOFs embedded with noble metallic nanoparticles

possesses superior catalytic performance and can be easily recycled.
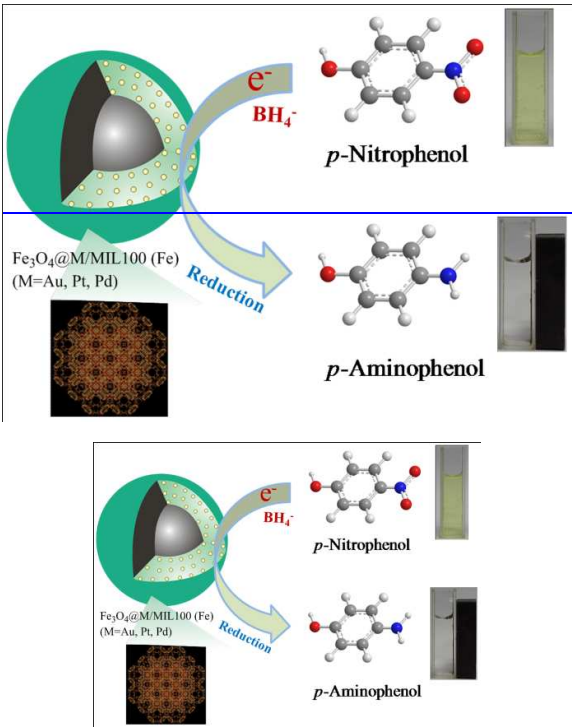
1 **Metallic nanoparticles immobilized in magnetic metal-organic**

2 **frameworks: preparation and application as highly active,**

3 **magnetically isolable and reusable catalysts**

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15

16 **Abstract**

17   Separation and recycling of catalysts after catalytic reactions are critically

18 required to reduce the cost of catalysts as well as to avoid the generation of waste in

19 industrial applications. In this paper, ultrafine noble metallic nanoparticles are

20 incorporated into cauliflower-like porous magnetic metal-organic frameworks

21 (MOFs). With the restriction effects of the pore/surface structure in the MOFs,

22 "surfactant-free" metallic nanoparticles are successfully obtained on a 2-3 nm scale.

23 In addition, both the thickness of MOFs shell and the content of noble metallic NPs

24 are tunable on the MOFs coating. Moreover, the microspheres exhibit excellent

25 performance for the catalytic reduction of p-nitrophenol with a turnover frequency of

26 3094 h^{-1}. The uniform cavities in the MOFs shell provide docking sites for

27 p-nitrophenol and act as confinement nanoreactors, which greatly improve the

28 catalytic performance. Most importantly, the magnetically responsive microspheres

29 can be easily recovered by a magnetic field and show excellent reusability. The

30 as-prepared catalyst also shows good activity for the reduction of other nitrobenzenes.

31 Consequently, this work provides a highly active, magnetically isolable, and

32 recyclable catalyst, which can be used for various catalytic industry processes. The

33 fundamental model can be further employed in a variety of biomedical fields

34 including drug delivery and biological molecules separation.

35

36

1. Introduction

38   Noble metallic nanoparticles (NPs) have attracted growing attention owing to

39 their unique physical, chemical, and biological properties and great potential in

40 various fields. [1-7] They are expected to be the suitable candidates for design of highly

41 active and selective catalysts. However, nanoparticles tend to aggregate to form larger

42 particles due to their large surface area, leading to the decrease of their initial

43 activities during the catalytic cycles [8-9]. Therefore, many attempts have been made to

44 immobilize noble metallic NPs on solid supports [9-11]. Among the wide range of

45 supports, magnetic nanomaterials exhibit distinct advantages. Magnetic supports not

46 only enable the catalysts to have magnetic separation property, but also facilitate them

47 to be recycled. Recent examples demonstrate the successful synthesis of metallic NPs

48 on the surface of magnetic substrates. [12-13] However, it is fairly difficult to obtain the

49 metallic NPs on the sub-10 nm scale, especially in the absence of a

50 stabilizer/surfactant [14]. Consequently, the development of producing monodispersed

51 noble metallic NPs on solid supports within several nanometers is highly desirable.

52   MOFs are crystalline materials composed of metal ions or metal clusters that are

53 connected by organic linkers. They have crystalline structures, large internal surface

54 areas, uniform but tuneable cavities and tailorable chemistry. These distinct

55 characteristics make them very promising for a variety of applications, including gas

56 storage [15-16], chemical separation [17], catalysis [18-19], sensing [20] and drug delivery [21]. In

57 the context of catalysis, the uses of MOFs as heterogeneous catalysts have recently

58 received tremendous attention. The nodes of most MOFs are reasonably good Lewis

59 acid sites, and terminal ligands can present Lewis basic sites. These acid and basic

60 sites may well function as organic reactions catalysts [22-23]. Recently, by serving as

61 unique host matrices, the potential applications of MOFs can be extended further by

62 encapsulating noble metallic (e.g., Pd, Au, Ru, and Pt) or bimetallic alloy NPs within

63 the frameworks [24]. MOFs limit the growth of NPs in the confined cavities to produce

64 monodispersed metallic or bimetallic NPs [25-28]. Taking into account the novelty of

65 MOFs and the recent interest in exploiting their properties as solid catalysts, there is

66 no doubt that the field of catalysis by embedded NPs in MOFs will continue to attract

67 much interest in the recent years. However, many unresolved problems still remain a

68 great challenge. The synthetic procedures require hydrogen and plasma reduction

69 procedure at high temperature, leading to a high cost and energy wastage. Besides,

70 efficient separation and recycling of MOFs catalysts after catalytic reactions is

71 specifically required. Therefore, it is still a challenge to fabricate the type of

72 multifunctional MOFs materials with a hierarchical structure, which can be applied in

73 heterogeneous catalysis as well as efficient separation of biological molecules.

74   Herein, we report a facile and efficient method for the fabrication of

75 magnetically recyclable nanocatalyst with noble metallic NPs encapsulated into

76 magnetite MOFs. The cauliflower-like microspheres consist of a magnetite core and an

4

77 ordered shell of MIL-100(Fe) crystals *via* a layer-by-layer assembly process.

78 Encapsulating the noble metallic NPs within the frameworks was carried out through

79 a simple deposition-reduction method. The whole process is shown in Scheme 1.

80 Compared with other methods of magnetic-Au heterogeneous catalyst formation, no

81 additional toxic reagent is needed. At the same time, both the thickness of MOFs shell

82 and the content of noble metallic NPs are tuneable on the MOFs coating. The

83 synergistic effect between the ultrafine noble metallic NPs (2-3 nm) and MOF shell

84 significantly improved the catalytic performance for the reduction of nitrobenzenes.

85 Moreover, due to the high saturation magnetization and super-paramagnetic property,

86 the as-synthesized nanocatalyst shows high efficiency in magnetic separation and

87 recovery. Thus a magnetically controllable on-off reaction was achieved in the

88 catalytic reduction process. Long-life and high reusability of the as-prepared

89 Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres are demonstrated without

90 visible decrease in the catalytic performance after several running cycles. These

91 facilitate the practical applications of the catalyst in catalysis.

92

93 **2. Experimental section**

94 *2.1 Materials*

95   All chemicals were from commercial and used without further purification:

96 mercaptoacetic acid (MAA, Tianjin Chemical Reagent Factory), ferric chloride

97   hexahydrate (FeCl$_3$·6H$_2$O, Sinopharm Chemical Reagent Co., Ltd., analytical grade),

98   1,3,5-benzenetricarboxylic acid (H$_3$btc, J&K Scientific Ltd., 98%), sodium

99   borohydride (NaBH$_4$, Sinopharm Chemical Reagent Co., Ltd., 96%), hydrogen

100   tetrachloroaurate (III) tetrahydrate (HAuCl$_4$·4H$_2$O, Shenyang research institute of

101   nonferrous metals, analytical grade), hydrogen hexachloroplatinate hexahydrate

102   (H$_2$PtCl$_6$·6H$_2$O, Shenyang keda reagent factory, analytical grade), palladium chloride

103   (PdCl$_2$, Shenyang keda reagent factory, analytical grade), *o*-nitrophenol,

104   *m*-nitrophenol, *p*-nitrophenol, 2,4-dinitrophenol, *o*-nitroaniline, *m*-nitroaniline,

105   *p*-nitroaniline, 4-Methyl-2-nitroaniline, 4-Methyl-3-nitroaniline and

106   *p*-Nitrophenylhydrazine (Tianjin Chemical Reagent Factory, analytical grade). A

107   stock solution of tetrachloropalladinic acid (H$_2$PdCl$_4$) was prepared by dissolving 520

108   mg of PdCl$_2$ into 20 mL of 10% v/v HCl ethanol solution with sonication at room

109   temperature until complete dissolution.

110   *2.2 Preparation of magnetic Fe$_3$O$_4$ microspheres*

111   The magnetic particles were prepared *via* a solvothermal method [29]. Briefly, 2.70

112   g of FeCl$_3$·6H$_2$O and 7.20 g of sodium acetate were dissolved in 100 mL of ethylene

113   glycol under vigorous stirring. The resultant homogeneous yellow solution was

114   transferred to a Teflon-lined stainless-steel autoclave, sealed and heat at 200 °C for 8

115   h. Then the autoclave was cooled to room temperature. The obtained black magnetite

116   particles were washed with ethanol for 6 times, and dried in vacuum at 60 °C for 12 h.

117   *2.3 Preparation of MAA-functionalized Fe_3O_4 microspheres*

118   100 mg Fe_3O_4 was dispersed in 20 mL of 0.29 mM MAA ethanol solution and

119   stirred for 24 h. The solid products were collected using an external magnetic field

120   and rinsed with ultrapure water and ethanol for three times, then re-dispersed in

121   ethanol for further use.

122   *2.4 Preparation of core-shell magnetic Fe_3O_4@MIL-100 (Fe) microspheres*

123   Fe_3O_4@MIL-100 (Fe) core-shell magnetic microspheres were synthesized

124   according to a previous report of Qiu [30]. Typically, the as-prepared

125   MAA-functionalized Fe_3O_4 microspheres were dispersed into the ethanol solution of

126    $FeCl_3$ (for 15 min) and H_3btc (for 30 min) separately at 70 °C for a given repeated

127   cycles. Between each step the microspheres were separated with a magnet, and

128   washed with ethanol. Finally the samples were washed with ethanol for three times

129   and dried overnight at 150 °C under vacuum.

130   *2.5 Synthesis of magnetic Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres*

131   Prior to metal loading, the as-synthesized Fe_3O_4@MIL-100 (Fe) microspheres

132   described above were activated by heating at 150 °C for 10 h under dynamic vacuum.

133   Supported noble metallic NPs were prepared *via* a simple deposition-reduction

134   method. Typically, 20 mg of Fe_3O_4@MIL-100 (Fe) powder was dispersed in 2 mL of

135   ethanol and the mixture was sonicated until homogeneous. After stirring for 30 min,

136   ethanol solution of the precursor ($HAuCl_4·4H_2O$, $H_2PtCl_6·6H_2O$ and H_2PdCl_4, 10.00

137   μmol) was added dropwise with constant vigorous stirring. The resulting solution was

138   continuously stirred for 5 h. Then 500 μL ethanol was added into the slurry followed

139   by adding NaBH$_4$ (100 mM) ethanol solution under vigorous stirring for the complete

140   reduction of the anionic metal species (700 μL for Fe$_3$O$_4$@Au/MIL-100 (Fe), 325 μL

141   for Fe$_3$O$_4$@Pt/MIL-100 (Fe) and 93 μL for Fe$_3$O$_4$@Pd/MIL-100 (Fe)). After 30 min

142   stirring, the resulting Fe$_3$O$_4$@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres were

143   recovered by a magnet, rinsed with ethanol to remove Cl$^-$, and dried under vacuum at

144   25 °C for 12 h.

145   *2.6 Catalytic reduction of aqueous solution of p-nitrophenol*

146   Liquid-phase reduction of *p*-nitrophenol to *p*-aminophenol by NaBH$_4$ was used

147   to characterize the catalytic activity of the Fe$_3$O$_4$@M/MIL-100 (Fe) (M=Au, Pt, Pd)

148   microspheres. It is a well-known model reaction and has been extensively used to

149   evaluate the catalytic rate of functional composite nanomaterials [31-32]. Typically, 2.75

150   mL ultrapure water and an aqueous solution (200 μL) of freshly prepared NaBH$_4$ (100

151   mM, 20 μmol) were added to a solution (25 μL) of *p*-nitrophenol (10 mM, 0.25 μmol),

152   respectively. Subsequently, 25 μL of aqueous dispersion of the 5.09 wt%

153   Fe$_3$O$_4$@Au/MIL-100 (Fe) (1.0 mg/mL, 6.46 nmol, Au/*p*-nitrophenol=2.58 mol%),

154   4.29 wt% Fe$_3$O$_4$@Pt/MIL-100 (Fe) (1.0 mg/mL, 5.50 nmol, Pt/*p*-nitrophenol=3.65

155   mol%) or 3.88 wt% Fe$_3$O$_4$@Pd/MIL-100 (Fe) (1.0 mg/mL, 9.11 nmol,

156   Pd/*p*-nitrophenol=2.58 mol%) catalyst was added to start the reaction. After addition

157　of the as-synthesized microspheres, the bright yellow solution gradually faded as the

158　reaction proceeded which could be observed by naked eye. The kinetic study of the

159　reaction was performed by measuring the change in the absorbance at 400 nm with

160　time. The absorbance spectra of the solution were measured with a UV-Vis

161　spectrometer in the range 250-550 nm.

162　　　The recyclability of the as-prepared catalyst was investigated in the reaction of

163　*p*-nitrophenol reduction. The reduction reaction was amplified twenty times than in

164　previous investigations to facilitate separation and minimize handling errors. After

165　each run, the solid catalyst was recovered using a magnet (complete separation within

166　30 s), washed with water and ethanol (twice each), dried under vacuum, and reused in

167　the next cycle. The catalytic reduction of other nitrobenzenes was conducted under

168　the same condition of *p*-nitrophenol. The conversions were determined by the gas

169　chromatography/mass spectroscopy (GC/MS) analysis of the residual nitrobenzene in

170　the mixture after reaction.

171　*2.7 Characterization*

172　　　The powder X-ray diffraction (XRD) patterns of the samples were collected on a

173　D/MAX-2000 diffractometer (Rigaku, Japan) using Cu Ka radiation (wavelength λ=

174　1.514178 Å) in the 2θ range 0-80 º. FT-IR spectra were recorded on a Nicolet Nexus

175　670 fourier transform infrared spectrometer (FT-IR, America) using KBr pellets.

176　Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449C

177   thermal analyzer from room temperature to 800 ºC at a ramp rate of 10 ºC/min in a

178   flowing 100 mL/min air atmosphere. The morphologies and sizes of the as-prepared

179   samples were characterized by a Hitachi-600 transmission electron micro-scope

180   (TEM, Hitachi, Japan) equipped with an energy dispersive X-ray analyzer (EDX) and

181   a JSM-6701F field emission scanning electron microscope (FE-SEM) at an

182   accelerating voltage of 15 kV, respectively. Elemental analyses for C/H were

183   performed on a Perkin-Elmer 2400 Series II analyzer and the species of Fe, Au, Pt

184   and Pd were analyzed by inductively coupled plasma atomic emission spectrometry

185   (ICP-AES) (Thermo Jarrel Ash, Franklin, MA, USA). X-ray photoelectron spectra

186   (XPS) were acquired with a PHI 5702 spectrometer equipped with an Al Kα exciting

187   source. A 2 kV Ar+ sputter beam was used for depth profiling of Fe_3O_4@M/MIL-100

188   (Fe) (M=Au, Pt, Pd) samples after the initial data were collected. Nitrogen

189   adsorption-desorption isotherms were obtained at -196 ºC on a Quantachrome

190   AS1Win analyzer. The magnetic behavior was investigated using a vibrating sample

191   magnetometer (VSM, Lake Shore 7304, Lake Shore, USA) with an applied field

192   between -15 kOe and 15 kOe at room temperature. The UV-Vis spectra were recorded

193   on a UV-Vis spectrometer (TU-1901, Beijing, China).

194   **3. Results and discussion**

195   *3.1 Structural and Morphological Characterization*

196   The magnetite particles were prepared *via* a robust solvothermal method as

197   described above. The TEM image shows that the obtained magnetite particles are

198   uniform with a mean diameter of ~250 nm (Figure 1A). SEM image of the magnetite

199   particles further confirms the uniform size of ~250 nm and nearly spherical shape

200   with rough surface (Figure S1A). The surface roughness is attributed to the fact that

201   the particles are formed by packing many tiny nanocrystals. After 20 assembly cycles

202   coating with MIL-100 (Fe), core-shell Fe_3O_4@MIL-100 (Fe) microspheres with a

203   MOF layer of about 35 nm in thickness were obtained (Figure 1B). The microspheres

204   display uniform three-dimensional architecture with cauliflower-like morphology

205   (Figure 1I). Moreover, with increasing number of assembly cycles, the size of the

206   whole NPs increases (Figure S1 and Figure 2A-F). In fact, the size of

207   Fe_3O_4@MIL-100 (Fe) microspheres and the thickness of shell shows linear

208   dependence on the number of assembly cycles (Figure 2G). This suggests that the

209   thickness of the MOF shell can be rationally controlled by varying the number of

210   growth cycles using the step-by-step assembly strategy. The subsequent *in situ* growth

211   process results in a uniform loading of noble metallic NPs (Figure 1C-E). The average

212   sizes of noble metallic NPs (Figure S2) are about 2.0±0.2 nm (Au NPs), 1.9±0.2 nm

213   (Pt NPs) and 2.2±0.2 nm (Pd NPs), respectively, which are small enough to be

214   accommodated in the mesoporous cavities of MIL-100(Fe). However, metallic

215   particles with bigger sizes were tend to be located on framework surface, as in the

216   case of metallic NPs loaded into ZIF-8 (diameter of pore window, 11.6 Å), MOF-5

217   (diameter of pore window, 25.7 Å), and other porous materials [28, 33-35]. In addition, the

218   morphology of the magnetic MOFs microspheres remains unchanged after noble

219   metallic NPs loading (Figure 1J-L). The high-resolution transmission electron

220   microscopy (HRTEM) images show lattice fringes corresponding to an interfringe

221   distance of 0.24 nm (for Au NPs) and 0.23 nm (for Pt and Pd NPs), which can be

222   attributed to the (111) plane of Au [36], Pt [37] and Pd NPs [38], respectively (Figure 1F-H).

223   The EDX spectra of the microspheres (Figure S3) also show the presence of Fe and

224   Au/Pt/Pd. In addition, the C, H, Fe and M ratios of the Fe_3O_4@M/MIL-100 (Fe)

225   (M=Au, Pt, Pd) microspheres were obtained by elemental analysis and ICP-AES, and

226   the values were listed in Table 1.

227   To further verify the formation of the Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd)

228   microspheres, the XRD patterns of Fe_3O_4, Fe_3O_4@MIL-100 (Fe) and

229   Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) samples were carried out, as shown in

230   Figure 3. The diffraction peaks in curve a can be indexed to the face-centred cubic

231   lattice of Fe_3O_4 nanospheres according to JCPDS 75-1609 [39]. After coating with the

232   MOF layer, the diffraction pattern of the resulting material (curve b) shows some new

233   diffraction peaks (labeled with the symbol ⋆) in addition to the Fe_3O_4 reflections,

234   demonstrating the formation of the crystal MIL-100 (Fe) [30]. The sharp and strong

235   peaks at 2-4° reveal the presence of both micropores and mesopores [40]. After the *in*

236   *situ* growth process, there is no loss of crystallinity in the XRD patterns for the

237   resultant Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres (curves c, d and e).

238   Compared with the simulated pattern of MIL-100 (Fe) (curve f), we conclude that the

239   integrity of the MIL-100 (Fe) framework is maintained. The weak diffraction

240   reflections of typical cubic Au NPs [36] (curves c), face-centred Pt NPs [41] (curve d) and

241   Pd NPs [38] (curve e) are also detected, indicating the formation of very small M NPs

242   (M=Au, Pt, Pd), which matches well with the TEM observations. No diffraction peaks

243   from any other impurities are detected. The XRD results indicate that the metal

244   precursors are successfully reduced to metallic NPs.

245   Figure 4A shows the FT-IR spectrum of Fe_3O_4, Fe_3O_4@MIL-100 (Fe), and

246   Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) nanocomposites. The band at 590 and 636

247   cm^{-1} are assigned to Fe-O and C-S stretching vibrations of MAA-functionalized Fe_3O_4,

248   respectively. The peaks at 1435 and 1575 cm^{-1} are owing to the stretching vibrations

249   of C=C in benzene ring, while the peaks at 1376 and 1618 cm^{-1} are attributed to C=O

250   stretching vibrations of carboxylic acid, suggesting that MIL-100 (Fe) shell has been

251   successfully coated on the surface of Fe_3O_4. In addition, FT-IR and TGA analyses

252   (Figure 4B) show that the as-synthesized microspheres have similar peaks or curves to

253   Fe_3O_4@MIL-100 (Fe), indicating the retention of the MIL-100 (Fe) framework and

254   the absence of new bond/structure. The results are in good agreement with that

255   obtained from XRD pattern.

256   The BET surface area measurements were performed with N_2

257   adsorption/desorption isotherms at -196 ºC. Before measurements, all the samples

258   were evacuated at 150 °C for 12 h. The pore volume was calculated by a single point

259   method at P/P_0=0.992. As determined by N_2 sorption isotherms (Figure 5), the BET

260   surface areas of Fe_3O_4@MIL-100 (Fe), Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd)

261   microspheres are 319, 211, 173 and 186 m^2/g, respectively. And their pore volumes

262   are 0.45, 0.41, 0.39 and 0.40 cm^3/g, respectively. Furthermore, estimation of the pore

263   size distribution by the density functional theory (DFT) shows two maxima at 1.5 and

264   2.2 nm for Fe_3O_4@MIL-100 (Fe), which is consistent with the previously reported

265   data [42]. The pore sizes are big enough for the metallic precursors to diffuse into the

266   pores (the diameters of the metallic precursors ($AuCl_4^-$, $PtCl_6^{2-}$, and $PdCl_4^{2-}$) were

267   calculated by Chemdraw to be 3.8 Å, 4.6 Å, and 4.2 Å, respectively). The nucleation

268   can take place within it to form the noble metallic NPs. As compared with

269   Fe_3O_4@MIL-100 (Fe), the surface areas and the pore volumes of Fe_3O_4@M/MIL-100

270   (Fe) (M=Au, Pt, Pd) are appreciably decreased. The results indicate that the pores of

271   the host frameworks are occupied by dispersed M NPs (M=Au, Pt, Pd) and/or blocked

272   by the M NPs located on framework surface, as in the case of M NPs loaded into

273   ZIF-8, MOF-5, and other porous materials [28, 33-35].

274   The magnetic properties of the resultant multifunctional microspheres were

275   investigated at room temperature by VSM in the field range from -20 to +20 kOe, as

276 shown in Figure 6. They exhibit super-paramagnetic behaviour, little hysteresis,

277 remanence and coercivity due to the fact that the particles are composed of ultrafine

278 magnetite nanocrystals. A reduction of magnetization saturation (Ms) value is

279 observed for Fe_3O_4@MIL-100 (Fe) microspheres after growing assembly cycles

280 (Figure S4). This could be attributed to the decrease in the density of Fe_3O_4, which is

281 corresponding to the increase of outer-layer thickness as shown in SEM (Figure S1)

282 and TEM (Figure 2). After loading with Au, Pt and Pd NPs, the Ms values of

283 Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) are slightly decreased to 44.47, 43.90 and

284 45.07 emu/g, respectively (Figure 6A). It should be noted that the microspheres can

285 be dispersed in water by sonication or vigorous shaking, resulting in a

286 brown-coloured suspension. One can observe fast aggregation of the microspheres

287 from their homogeneous dispersion in the presence of an external magnetic field, and

288 quick redispersion with a slight shaking once the magnetic field is removed (Figure

289 6B). These results directly demonstrate the excellent magnetic responsivity and

290 redispersibility, which is important in terms of their practical manipulation.

291   In order to further demonstrate the composition details of the resulting hybrid

292 magnetic microspheres, XPS was performed. The sensitivity of XPS in chemical

293 analysis stems mostly from its ability to resolve the chemical identity of the atoms

294 from the measured binding energies. Figure 7A exhibits the overall surveys of the

295 as-synthesized Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres, which clearly

296 shows the signals of C, O and Fe elements. Well-defined peaks corresponding to

297 metallic Au, Pt and Pd species can also be detected (Figure 7B-D). The position of the

298 Au 4f, Pt 4f and Pd 3d peaks are corresponding to Au^0, Pt^0 and Pd^0, respectively,

299 which are in good agreement with the previous literature [43-44]. From these spectra, it

300 can be observed that all the metal ions (Au^{3+}, Pt^{4+} and Pd^{2+}) impregnated in

301 Fe_3O_4@MIL-100 (Fe) are reduced to noble metallic NPs after the *in situ* growth

302 process by $NaBH_4$ reduction.

3.2 Application in catalytic reduction of p-nitrophenol

304   In this investigation, the catalytic performance of Fe_3O_4@M/MIL-100 (Fe)

305 (M=Au, Pt, Pd) microspheres for efficient reduction of *p*-nitrophenol to

306 *p*-aminophenol has been intensively investigated [32, 45]. *P*-nitrophenol aqueous solution

307 exhibits a distinct spectral profile with an absorption maximum at 317 nm. After the

308 addition of $NaBH_4$, a red-shift of the absorption peak to 400 nm is observed (Figure

309 8A). A colour change from light yellow to bright yellow indicates the formation of

310 *p*-nitorphenolate [46]. Moreover, there is little change for the maximum absorption at

311 400 nm over time even after adding excess $NaBH_4$ solution, confirming that the

312 reduction couldn't proceed without catalyst. As a comparison, the catalytic ability of

313 an equal amount of Fe_3O_4 and Fe_3O_4@MIL-100 (Fe) is also studied. As shown in

314 Figure 8B, there is little change in absorbance at 400 nm within 30 min over Fe_3O_4

315 and Fe_3O_4@MIL-100 (Fe), while complete reduction of *p*-nitrophenol is achieved

316 within a short time over the as-synthesized catalysts. Superior catalytic performance

317 of the Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) catalysts confirm that the applied

318 magnetic MOFs can serve as an excellent support for noble metallic NPs.

319   Figure 9A-C unambiguously exhibit the time-dependent UV-Vis absorption

320 spectra for a typical reduction process using Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd)

321 microspheres as catalysts. After addition of the catalyst, the absorption intensity at

322 400 nm significantly decreases and the characteristic absorption of *p*-aminophenol

323 appears at 300 nm. The appearance of this new peak was verified by superimposing

324 the UV-Vis spectrum of pure *p*-aminophenol under identical conditions (Figure 8A, d).

325 The   formation   of   *p*-aminophenol   was   further   confirmed   from   gas

326 chromatography-mass (GC-MS) analytic technique (Figure S5). As can be seen from

327 Figure S5, after the reduction reaction, the characteristic peak of *p*-nitrophenol

328 (Figure S5A, M-1: 138.06) disappeared, accompanied by the appearance of

329 characteristic peak of *p*-aminophenol (Figure S5B, M+1: 110.06). The data provide a

330 supportive evidence for the efficient reduction of *p*-nitrophenol to *p*-aminophenol.

331 The UV-Vis spectra show an isosbestic point at 313 nm (Figure 8A), illustrating that

332 the catalytic reduction of *p*-nitrophenol yields *p*-aminophenol only, without

333 by-product [32]. Considering that the concentration of $NaBH_4$ is much higher than that

334 of *p*-nitrophenol ($C_{NaBH4}/C_{p\text{-nitrophenol}}$=80) in the reaction system, a pseudo first-order

335 kinetic equation with regard to *p*-nitrophenol only can be applied to evaluate the

336   catalytic rate [47]. The kinetic equation for the reduction reaction of *p*-nitrophenol can

337   be expressed as ln $(C_t/C_0) = -K_{app}t$, where K_{app} is the kinetic rate constant, C_0 is the

338   initial concentration of *p*-nitrophenol, and C_t is the concentration of *p*-nitrophenol at

339   time t. Linear relationships between ln (C_t/C_0) and reaction time are displayed in

340   Figure 9D, which match well with the first-order reaction kinetics. The kinetic rate

341   constant K_{app} is calculated to be 2.58 min^{-1} for Fe$_3$O$_4$@Pt/MIL-100 (Fe) (Figure S6),

342   which is superior to other noble metallic-based catalysts [33, 48-49]. This means that the

343   nanocomposites show excellent catalytic activity for the reduction of *p*-nitrophenol.

344   The catalytic activity of the as-synthesized Fe$_3$O$_4$@Pt/MIL-100 (Fe) catalyst for

345   the reduction of other nitrobenzene analogs including nitrophenol, nitroaniline and

346   nitrophenylhydrazine were also investigated (Table 2). Figure S9 clearly shows the

347   typical changes of UV-Vis absorption spectra of these nitrobenzene compounds

348   during   the   reduction   processes,   demonstrating   that   the   reduction   of   these

349   nitrobenzenes indeed occur in the presence of a small amount of catalyst. Additionally,

350   as shown in Table 2, the catalyst exhibits good catalytic activity (high TOF values)

351   with excellent yields toward a series of nitrobenzene compounds regardless of the

352   types and position of the substituents (the turnover frequency (TOF) is defined as

353   moles (or numbers) of the product molecules generated per moles (or numbers) of

354   catalyst surface atoms per hour [12]). Moreover, the catalysts Fe$_3$O$_4$@Au/MIL-100 (Fe)

355   and Fe$_3$O$_4$@Pd/MIL-100 (Fe) also show high catalytic activity toward the reduction

356 of these nitrobenzene compounds, as illustrated in Table S2 and Table S3. These

357 results indicate the generality and the efficacy of the new catalysts toward the

358 reduction of the series of nitrobenzenes.

359 It will be significant to compare the catalytic performance of

360 Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) with previous reported analogous catalysts.

361 As shown in Table 3, the TOF value can reach 3094 h^{-1} for Fe_3O_4@Pt/MIL-100 (Fe),

362 which is significantly higher than those reported in previous studies [49-53]. From Table

363 3 we can conclude that the as-synthesized catalysts in the present work have a higher

364 catalytic activity than those of most other catalysts. Thus, a simple and efficient

365 preparation of a Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) catalyst with high catalytic

366 efficiency was presented in our work.

367 It should be pointed out that the catalytic performance of the as-prepared

368 Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres with different assembly cycles

369 are also studied (Figure S7). Although more Pt NPs are embedded in the porous as the

370 MOF shell grows (Figure S8), the percentages of the elements in MIL-100(Fe) (C, H

371 and Fe) increase significantly, leading to a decrease of the metallic content (Table S1).

372 Based on the relative changes in the contents of the C, H, Fe, Pt observed in Table S1

373 and the corresponding different catalytic performance, we conclude that the intensities

374 of the noble metallic NPs plays a key role in the catalysis.

375   In addition to catalytic activity, the stability is a very important property for the

376   reusability of catalysts. Recyclability of the as-prepared catalyst is tested. The

377   catalytic activity remains stable even after running for 10 cycles for

378   Fe_3O_4@M/MIL-100 (Fe) (M= Pt, Pd) and the conversion of each cycle remains nearly

379   100%. After reused for 8 cycles, the catalyst Fe_3O_4@Au/MIL-100 (Fe) gradually

380   loses its catalytic activity. However, the conversion of upon 85% is maintained

381   (Figure 10). The high stability can be attributed to the core-shell porous architecture

382   of the as-prepared microspheres, which provides both docking sites for *p*-nitrophenol

383   (the MOF shell) and a super-paramagnetic core allowing easy manipulation by a

384   magnet. In addition, there's no change for adsorption spectra of the solutions after

385   given reduction cycles (Figure S10), which further confirms the long-term stability of

386   the catalysts. Leaching test with the catalyst Fe_3O_4@Pt/MIL-100 (Fe) was also carried

387   out under reaction conditions. The solid catalyst was magnetically separated from the

388   reactant mixture after each catalytic cycle. The residual solution was collected and

389   measured by ICP-AES to determine the lost amount of Pt and Fe. No Fe element was

390   found in the residual solution, suggesting that the Fe_3O_4 NPs were well protected by

391   the MOFs shell. Besides, only trace amount of Pt element was detected in the residual

392   solution. As shown in Figure S11, nearly 80% of Pt content was maintained on the

393   catalyst even after 10 runs, which proved the good stability of the catalyst. Together

394   with the high recyclability of the catalyst (Figure 10), these results clearly

395   demonstrate the stability of the noble metallic NPs in Fe_3O_4@MIL-100 (Fe).

396   The interactions between noble metallic NPs and the support directly affect the

397   catalytic activity of the catalyst, which could mostly explain the different catalytic

398   activities of noble metallic NPs in different reports. In this work, a magnetic MOF

399   was used as support for Au, Pt and Pd NPs with superior catalytic activity. Scheme 2

400   depicts the performance of the Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres

401   as catalysts in the reduction of p-nitrophenol to p-aminophenol by $NaBH_4$. Possible

402   mechanism of excellent catalytic activity may be explained as follows: given that

403   p-nitrophenol is π-rich in nature, it is expected that p-nitrophenol can be adsorbed

404   onto the porous MOFs shell by means of π–π stacking interactions between the

405   aromatic rings of p-nitrophenol and the organic units of the framework, and

406   coordination effects between phenolic hydroxy of p-nitrophenol and metal center of

407   the framework [48, 54]. The mesoporous of MOFs serve as millions of nanoreactors,

408   where the reduction actions take place *via* relaying electrons from the donor BH_4^- to

409   the acceptor p-nitrophenol. In aqueous medium BH_4^- is adsorbed onto the surface of

410   catalyst. The hydrogen atom, which is formed from the hydride, after electron transfer

411   to the noble metallic NPs, attacks p-nitrophenol molecules to reduce it [55]. The

412   adsorption over the porous MOFs shell provides a high concentration of p-nitrophenol

413   near to the noble metallic NPs embedded in the MOFs cavities, leading to highly

414   efficient contact between them. Thus enhancement of the catalytic efficiency for

415   p-nitrophenol reduction is achieved. It is worthwhile to note that more experimental

21

416   or theoretical evidences are still needed to get the exact mechanism of the enhanced

417   activity.

4. Conclusions

419   In summary, we have developed an environmentally friendly method to prepare

420   cauliflower-like magnetic Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres and

421   investigated their superior catalytic properties in the effective reduction of

422   nitrobenzenes compounds. The microspheres show unique structural features such as

423   magnetic core, porous MOFs shell and monodispersed small noble metallic NPs. The

424   contents of noble metallic NPs and the thickness of MOFs shell can be easily

425   controlled by varying the assembly cycles on MOFs coating. The magnetic MOFs

426   support not only enhances the catalytic activity, but lends the catalyst easiness of

427   separation and recovery. The Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd) microspheres

428   maintain high catalytic activity over several reduction cycles. Therefore, this

429   functional nanostructure holds great promise as novel noble metallic-based catalysts

430   for various catalytic reactions. Additionally, the fundamental concept for the

431   multifunctional magnetic MOFs can be extended to the fabrication of multicomponent

432   nanosystem with integrated and enhanced properties for various advanced

433   applications, such as chemical/biosensor, biological molecule separation, drug

434   delivery, and so on.

435

436   **Acknowledgements**

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440   **References**

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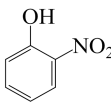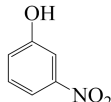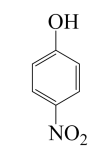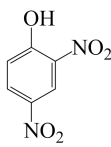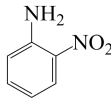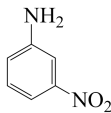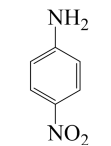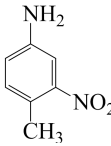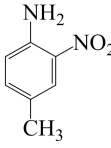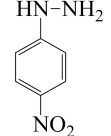
539   **Table 1.** Elemental and ICP analyses for the samples with 20 assembly cycles.

Sample	Found (%)
Fe_3O_4@Au/MIL-100 (Fe)	C, 9.33; H, 1.554; Fe, 44.34; Au, 5.09
Fe_3O_4@Pt/MIL-100 (Fe)	C, 10.06; H, 1.386; Fe, 43.99; Pt, 4.29
Fe_3O_4@Pd/MIL-100 (Fe)	C, 9.23; H, 1.488; Fe, 44.23; Pd, 3.88

540

541

Table 2 Reduction of various nitrobenzenes using Fe_3O_4@Pt/MIL-100 (Fe) catalyst.[a]

Entry	Compound	Structure	Time/s	Conversion (%)	TOF (h^{-1})
1	*o*-Nitrophenol		50	90.8	2973
2	*m*-Nitrophenol		45	98.2	3573
3	*p*-Nitrophenol		50	94.5	3094
4	2,4-Dinitrophenol		450	93.4	340
5	*o*-Nitroaniline		100	95.3	1560
6	*m*-Nitroaniline		75	95.8	2091
7	*p*-Nitroaniline		120	95.1	1297
8	4-Methyl-3-nitroaniline		100	91	1490
9	4-Methyl-2-nitroaniline		180	92.7	843
10	*p*-Nitrophenylhydrazine		270	92.8	563

[a] Reaction condition: 25 μL of 10 mM nitrobenzene, 25 μL of 1.0 mg/mL catalyst, and 200 μL of

100 mM fresh $NaBH_4$.

545

546   **Table 3.** Comparison of various catalysts for the reduction of *p*-nitrophenol.

Catalyst	Au/Pt/Pd content (wt.%)	Size of Au/Pt/Pd (nm)	TOF (h^{-1})	Ref.
Fe$_3$O$_4$@TiO$_2$/Au@Pd@TiO$_2$	0.69 (Au), 0.17 (Pd)	5	891	40
@Au/CeO$_2$	2.97	3~5	240	41
@Pd/CeO$_2$	0.18		1068	
Pt@CeO$_2$/RGO	-^{a}	3~5	90	42
Au/PDDA/NCC	1.45	2.95 ± 0.06	212	43
Pd/CNs	1.06	1–40	880	44
Fe$_3$O$_4$@Au/MIL-100 (Fe)	5.09	2~3	223	This work
Fe$_3$O$_4$@Pt/MIL-100 (Fe)	4.29	2~3	3094	This work
Fe$_3$O$_4$@Pd/MIL-100 (Fe)	3.88	2~3	1343	This work

547   ^{a} No data presented.

548

549

550   **Figure captions**

551   **Figure 1.** TEM and SEM images of (A) Fe$_3$O$_4$ particles, (B, I) Fe$_3$O$_4$@MIL-100 (Fe),

552   (C, J) Fe$_3$O$_4$@Au/MIL-100 (Fe), (D, K) Fe$_3$O$_4$@Pt/MIL-100 (Fe) and (E, L)

553   Fe$_3$O$_4$@Pd/MIL-100 (Fe) microspheres with 20 assembly cycles. (F-H) HRTEM

554   images of the Au, Pt and Pd NPs, respectively. Inset is the SAED pattern recorded on

555   a single particle.

556

557   **Figure 2.** TEM images of individual (A) Fe$_3$O$_4$ and Fe$_3$O$_4$@MIL-100 (Fe) core-shell

558   nanospheres after (B) 15, (C) 20, (D) 30, (E) 40, and (F) 60 assembly cycles. (G) The

559   correlations between the assembly cycles and the resulting diameter (red line) and

560   shell thickness (black line), obtained from the TEM investigations by averaging over

561   50 NPs.

562

563   **Figure 3.** XRD patterns of (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$@MIL-100 (Fe), (c)

564   Fe$_3$O$_4$@Au/MIL-100 (Fe), (d) Fe$_3$O$_4$@Pt/MIL-100 (Fe), (e) Fe$_3$O$_4$@Pd/MIL-100 (Fe)

565   after 20 assembly cycles, (f) MIL-100 (Fe) (simulated). ● represents Fe$_3$O$_4$

566   nanospheres; ★ represents MIL-100 (Fe); ■ represents Au NPs; ▼ represents Pt NPs;

567   ◆ represents Pd NPs.

568

569   **Figure 4.** (A) FT-IR spectra of (a) Fe_3O_4, (b) Fe_3O_4@MIL-100 (Fe) microspheres and

570   Fe_3O_4@MIL-100 (Fe) microspheres with 20 assembly cycles after embedded with (c)

571   Au, (d) Pt, (e) Pd NPs; (B) TGA analyses under air of Fe_3O_4@MIL-100 (Fe)

572   microspheres with 20 assembly cycles before (a) and after embedded with (b) Au, (c)

573   Pt, (d) Pd NPs.

574

575   **Figure 5.** (A) Nitrogen sorption isotherms at -196 ºC and (B) pore size distribution

576   curves for the as-synthesized (a) Fe_3O_4@MIL-100 (Fe), (b) Fe_3O_4@Au/MIL-100 (Fe),

577   (c) Fe_3O_4@Pt/MIL-100 (Fe) and (d) Fe_3O_4@Pd/MIL-100 (Fe) with 20 assembly

578   cycles.

579

580   **Figure 6.** (A) Room-temperature magnetic hysteresis loops of (a) Fe_3O_4, (b)

581   Fe_3O_4@MIL-100 (Fe), (c) Fe_3O_4@Au/MIL-100 (Fe), (d) Fe_3O_4@Pt/MIL-100 (Fe)

582   and (e) Fe_3O_4@Pd/MIL-100 (Fe) with 20 assembly cycles. (B) Magnetic

583   separation−redispersion process of Fe_3O_4@Pt/MIL-100 (Fe) microspheres with 20

584   assembly cycles.

585

586   **Figure 7.** (A) Survey XPS spectra of Fe$_3$O$_4$@M/MIL-100 (Fe) (M=Au, Pt, Pd) with

587   20 assembly cycles. (B) High-resolution Au 4f XPS spectrum of Fe$_3$O$_4$@Au/MIL-100

588   (Fe). (C) High-resolution Pt 4f XPS spectrum of Fe$_3$O$_4$@Pt/MIL-100 (Fe). (D)

589   High-resolution Pd 3d XPS spectrum of Fe$_3$O$_4$@Pd/MIL-100 (Fe).

590

591   **Figure 8.** (A) UV-Vis absorption spectra of *p*-nitrophenol before (a) and after (b)

592   adding NaBH$_4$ solution, (c) UV-Vis spectrum of the resultant reduction solution with

593   the catalyst, (d) UV-Vis spectrum of pure *p*-aminophenol. Inset: photograph of

594   *p*-nitrophenol with (1) and without (2) NaBH$_4$ addition; (B) C_t/C_0 versus reaction time

595   for the reduction of *p*-nitrophenol with (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$@MIL-100 (Fe), (c)

596   Fe$_3$O$_4$@Au/MIL-100 (Fe), (d) Fe$_3$O$_4$@Pt/MIL-100 (Fe) and (e) Fe$_3$O$_4$@Pd/MIL-100

597   (Fe) microspheres with 20 assembly cycles.

598

599   **Figure 9.** Time dependent absorption spectra for the catalytic reduction of

600   *p*-nitrophenol by NaBH$_4$ in presence of 25 μg catalyst: (A) Fe$_3$O$_4$@Au/MIL-100 (Fe),

601   (B) Fe$_3$O$_4$@Pt/MIL-100 (Fe), (C) Fe$_3$O$_4$@Pd/MIL-100 (Fe) with 20 assembly cycles.

602   (D) The relationships of ln(C_t/C_0) *versus* reaction time plot in presence of 25 μg

603   different   catalysts: (a)   No   catalysts,   (b)   Fe$_3$O$_4$@MIL-100   (Fe),   (c)

604   Fe$_3$O$_4$@Au/MIL-100 (Fe), (d) Fe$_3$O$_4$@Pd/MIL-100 (Fe), and (e) Fe$_3$O$_4$@Pt/MIL-100

605   (Fe) with 20 assembly cycles. Conditions: [*p*-nitrophenol] = 0.083 mM; [NaBH$_4$] =

606   6.67 mM, 25 °C.

607

608   **Figure 10.** The reusability of the as-prepared catalysts for the reduction of

609   *p*-nitrophenol with NaBH$_4$: (a) Fe$_3$O$_4$@Au/MIL-100 (Fe), (b) Fe$_3$O$_4$@Pt/MIL-100

610   (Fe), and (c) Fe$_3$O$_4$@Pd/MIL-100 (Fe) with 20 assembly cycles.

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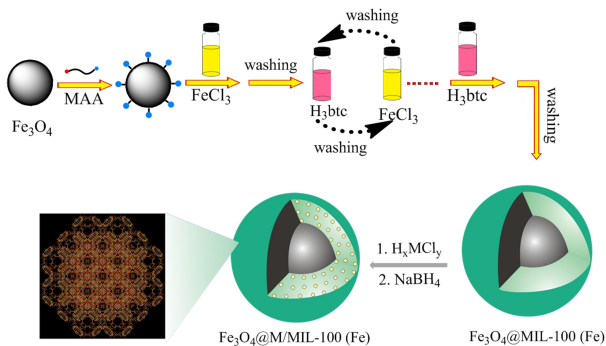
614   **Scheme 1.** Schematic illustration of fabrication of Fe_3O_4@M/MIL-100 (Fe) (M=Au, Pt, Pd)

615   microspheres. MAA: Mercaptoacetic acid; H_3btc: 1,3,5-benzenetricarboxylic acid.

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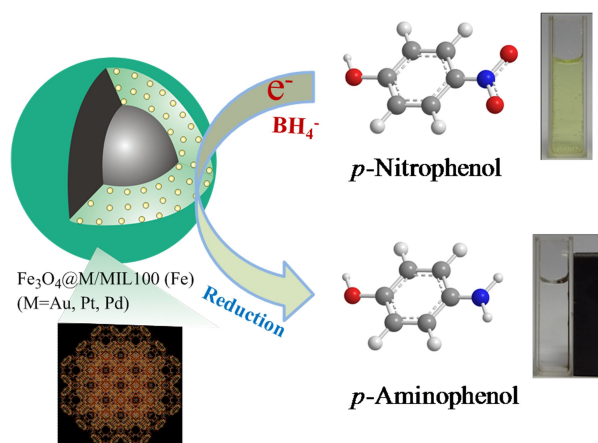
619   **Scheme 2.** Schematic and photographic representation of the performance of Fe_3O_4@M/MIL-100

620   (Fe) (M=Au, Pt, Pd) microspheres as catalysts for the reduction of *p*-nitrophenol.

621

622   **Figure 1**

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625   **Figure 2**

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628 **Figure 3**

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630 **Figure 4**

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634 **Figure 5**

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638   **Figure 6**

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645   **Figure 8**

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650 **Figure 9**

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653 **Figure 10**

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