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### **Title**

Microbial engineering of nano-heterostructures; biological synthesis of a magnetically-recoverable palladium nanocatalyst

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### **Author**

Coker, V. S.

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1           **Microbial engineering of nano-heterostructures; biological synthesis of a**  
2                           **magnetically-recoverable palladium nanocatalyst**

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4 Victoria S Coker<sup>1\*</sup>, James A Bennett<sup>2</sup>, Neil Telling<sup>1</sup>, Torsten Henkel<sup>1</sup>, John M Charnock<sup>1</sup>,  
5 Gerrit van der Laan<sup>3,1</sup>, Richard AD Patrick<sup>1</sup>, Carolyn I Pearce<sup>1</sup>, Richard S Cutting<sup>1</sup>,  
6 Ian J Shannon<sup>2</sup>, Joe Wood<sup>4</sup>, Elke Arenholz<sup>5</sup>, Ian C. Lyon<sup>1</sup> & Jonathan R. Lloyd<sup>1</sup>

7  
8           <sup>1</sup>*School of Earth, Atmospheric & Environmental Sciences and Williamson Research*  
9 *Centre for Molecular Environmental Science, University of Manchester, Manchester M13*  
10 *9PL, UK*

11           <sup>2</sup>*School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK*

12           <sup>3</sup>*Diamond Light Source Ltd, Didcot, Oxfordshire, OX11 0DE, UK*

13           <sup>4</sup>*School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK*

14           <sup>5</sup>*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720,*  
15 *USA*

16   \*vicky.coker@manchester.ac.uk

17  
18   **Abstract**

19           Precious metals supported on ferrimagnetic particles form a diverse range of  
20 catalysts. Here we show a novel biotechnological route for the synthesis of a  
21 heterogeneous catalyst consisting of reactive palladium nanoparticles arrayed on a  
22 biomagnetite support. The magnetic support was synthesised at ambient temperature by  
23 the Fe(III)-reducing bacterium, *Geobacter sulfurreducens*, and facilitated ease of

24 recovery of the catalyst with superior performance due to reduced agglomeration. Arrays  
25 of palladium nanoparticles were deposited on the nanomagnetite using a simple one-step  
26 method without the need to modify the biomineral surface most likely due to an organic  
27 coating priming the surface for Pd adsorption. A combination of EXAFS and XPS  
28 showed the particles to be predominantly metallic in nature. The Pd<sup>0</sup>-biomagnetite was  
29 tested for catalytic activity in the Heck Reaction coupling iodobenzene to ethyl acrylate  
30 or styrene and near complete conversion to ethyl cinnamate or stilbene was achieved  
31 within 90 and 180 min, respectively.

32

### 33 **Introduction**

34 Nanoparticles make highly desirable catalysts, often offering unique properties  
35 linked to their very high surface area. Palladium, placed on a suitable support material  
36 makes an exceptional catalyst well known for mild reaction conditions and exhibiting  
37 excellent compatibility with many polar functional groups and a high degree of chemo-,  
38 regio- and even stereoselectivity <sup>1</sup>. Magnetic nanoparticles are particularly useful support  
39 materials for catalysts as they can combine the advantages of high dispersion through a  
40 liquid with ease of recovery <sup>2,3</sup>. Thus, coating magnetic nanoparticles with precious  
41 metals such as palladium results in a highly functional catalyst <sup>4-7</sup>. Conventional chemical  
42 approaches to make these materials have achieved varying degrees of success, as loss of  
43 precious metal during recycling can be a problem, and complicated protocols are often  
44 employed to functionalise the support material surface <sup>3,4,6,8-10</sup>.

45

46 Building on earlier work <sup>11</sup>, recent studies have revealed biosynthetic routes can  
47 be harnessed to make nanoparticles of magnetite (Fe<sub>3</sub>O<sub>4</sub>) efficiently and at low cost with  
48 control over the magnetic properties by substitution of transition metals other than iron  
49 into the spinel ferrite structure <sup>12-14</sup>. Two routes are possible for the biological synthesis  
50 of nanoscale magnetite. In the first, magnetotactic bacteria synthesise intracellular  
51 crystals of single domain magnetite. These are used by the bacteria to orientate the cell  
52 within the Earth's magnetic field, helping the organism to guide itself to the sediment-  
53 water interface, its preferred ecological niche <sup>15,16</sup>. However, for this route growth yields  
54 and indeed, final yields of intracellular magnetite are very low. In the second route,  
55 dissimilatory Fe(III)-reducing bacteria such as *Geobacter* species can produce copious  
56 quantities of extracellular nanoscale magnetite through the respiration of poorly  
57 crystalline Fe(III) oxides and oxyhydroxides <sup>11</sup>. These specialist anaerobic bacteria live in  
58 environments depleted of oxygen and therefore conserve energy for growth by  
59 transferring electrons from the oxidation of simple carbon sources, such as acetate, to  
60 Fe(III) or Mn(IV)-bearing minerals <sup>17</sup>. This mechanism of nano-magnetite formation  
61 involves the extracellular reduction of Fe(III)-oxyhydroxides causing the release of  
62 soluble Fe(II), resulting in complete recrystallisation of the amorphous mineral into the  
63 new, relatively reduced, highly crystalline magnetic phase <sup>18,19</sup>. Especially relevant to  
64 manufacturing, these enzyme-driven reactions take place on the scale of hours, at ambient  
65 pressures and temperatures and use inexpensive feedstocks <sup>18</sup>. Thus, nanoscale  
66 biomagnetite is a potential support material for industrial catalysts, especially if  
67 simplified protocols for functionalising the bionanomineral surface can be developed.  
68

69 Here we describe the bio-production of such a catalyst comprising of  
70 biomagnetite functionalised with palladium nanoparticles and involving a minimal level  
71 of downstream processing. The effectiveness of this catalyst is demonstrated for the Heck  
72 coupling of iodobenzene with styrene or ethyl acrylate. Heck chemistry is of wide-  
73 ranging industrial importance, providing a single step route to the arylation, alkylation or  
74 vinylation of various alkenes<sup>20,21</sup>. Traditionally a palladium-phosphine catalyst is used,  
75 although a large amount of literature is devoted to the study of a variety of different  
76 catalysts for these reactions<sup>20,22</sup>. This work opens the door to the development of an  
77 energy efficient, environmentally friendly route to manufacture novel magnetic  
78 heterostructures which can be employed in a wide range of applications.

79

80 Main text

81 A biogenic nanoscale magnetite support was first produced by anoxic washed cell  
82 suspensions of *Geobacter sulfurreducens* challenged with Fe(III)-oxyhydroxide, an  
83 electron donor (sodium acetate) and a redox mediator [9,10-anthraquinone-2,6-  
84 disulphonate (AQDS)]. After approximately 8 h, the Fe(III)-oxyhydroxide had been  
85 completely converted to magnetite. Production of the functionalised Pd-coated magnetite  
86 was concluded through the addition of a solution of NaPdCl<sub>4</sub> to the water-washed nano-  
87 magnetite suspension under an anoxic atmosphere (N<sub>2</sub>:H<sub>2</sub> = 97%:3%); optimisation  
88 studies revealed that removal of soluble palladium occurred rapidly, within an hour, and  
89 was efficient over a range of Pd(II) concentrations up to 10 mol% Pd.

90

91 Detailed examination was undertaken of a nano-magnetite functionalised with a  
92 ~5 mol% Pd loading, produced by mixing the Pd(II) solution and biomagnetite for 12 h  
93 prior to washing in deionised water. Transmission electron microscope (TEM) images of  
94 the material produced before (Fig 1a) and after (Fig 1b) precipitation of Pd onto the  
95 surface of biomagnetite are shown. Fig. 1(a) shows the magnetite to have a consistent  
96 particle size range of 20 nm to 30 nm. However, after addition of Pd, two sizes of particle  
97 became clearly visible; the high-resolution inset in Fig. 1b shows how smaller particles  
98 (~5 nm) are attached to the larger particles (~20 nm). Energy dispersive X-ray (EDX)  
99 analysis using a relatively unfocussed beam showed the bulk sample (Fig 1b) to contain  
100 ~3.5 at% Pd. Using an EDX spot size of 5-6 nm, analyses (Fig 1b inset, point 1) indicated  
101 that the larger particles contained less than 1 at% Pd whereas analyses centred on the  
102 smaller particles (Fig 1b inset, point 2) suggested that they were enriched for the precious  
103 metal (9-10 at% Pd). These results indicate that the larger particles are the biomagnetite  
104 crystals decorated with small Pd particles. Both small and large particles displayed  
105 continuous lattice fringes, indicative of well-crystalline single crystals. TEM selected  
106 area electron diffraction (SAED) analysis (Fig. 1c) of the particles with supporting data  
107 from powder X-ray diffraction (PXRD) (Fig. 1d) confirmed that the material contained  
108 Bragg reflections consistent with the presence of magnetite with less pronounced  
109 reflections consistent with Pd metal; the latter are broader than those for magnetite owing  
110 to their smaller particle size. Crystallite size was estimated by applying the Scherrer  
111 equation to the (311) peak of magnetite in Fig. 1(d) which resulted in a mean crystallite  
112 size of 27.2 nm consistent with the size estimate from electron microscopy imaging. In  
113 addition, although much weaker it was possible to obtain an estimate of the Pd crystallite

114 size from the Pd (311) peak which gave a value of  $\sim 5$  nm, again in good agreement with  
115 TEM images.

116

117 In most examples of supported Pd catalyst manufacture, an organic ligand or  
118 silica shell is used to aid attachment of the Pd to the support<sup>4,5</sup> for example 3-  
119 aminopropyl triethoxysilane (APTS)<sup>5</sup>. However, in the case of biogenic magnetite no pre-  
120 coating with a ligand was required to aid attachment of Pd. Thus, to characterise the  
121 surface of biogenic magnetite, samples prior to Pd(II) addition were analysed using Time-  
122 of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), as this technique is very  
123 sensitive to both organic and inorganic compounds. Images of different secondary ions  
124 (SI) associated with either Fe, Al or organic material on the surface of a washed biogenic  
125 nanomagnetite (Fig. 2(a)) were compared to the maps from a synthetically produced  
126 nanomagnetite (Alfa Aesar, Heysham, UK) (Fig. 2(b)). Fig. 2 illustrates that there is a  
127 significant quantity of organic material associated with the biogenic magnetite, as the  
128 representative secondary ion images of organic molecules spatially correlate with the Fe  
129 map, whereas the inorganic magnetite showed no significant organic signature  
130 corresponding to the spatial distribution of Fe. Depth profiling of the organic layer using  
131  $C_{60}$  primary ions (PI) indicated that the organic layer is indeed a coating on the  
132 nanomagnetite. One bombardment of  $\sim 10^{15}$  PI/cm<sup>2</sup> resulted in a decrease of the SI-signals  
133 associated with the organic material by a factor of approximately 100 (Fig 2(c)) whereas  
134 the SI-signals associated with the nanomagnetite stayed almost constant. Some of the  
135 secondary ion ratios for the Fe-bearing clusters in Fig 2(c) are below a value of one, as  
136 ionisation efficiencies change slightly with decreasing amounts of organic material. The

137 presence of an organic coating explains the ability of the nanomagnetite to adsorb Pd  
138 without the need to pre-coat the washed nanoparticles prior to introducing the Pd  
139 solution. A likely source of the organic material is extracellular polymeric substance  
140 (EPS), a common product of bacterial pure cultures and communities, as this has  
141 previously been found bound to biogenic uranium nanoparticulate material<sup>23</sup>. We are not,  
142 however, excluding the presence of other cell exudates or constituents released after lysis  
143 of dead cells.

144

145         Using X-ray absorption (XA) spectroscopy, the Fe *K*-edge absorption spectra of  
146 biomagnetite before and after the addition of Pd were collected to provide the extended  
147 X-ray absorption fine structure (EXAFS) [Fig. 3a (i, ii); Table 1] and their corresponding  
148 Fourier transform [Fig. 3b (i, ii); Table 1]. The EXAFS data provided an excellent fit for  
149 a magnetite structure for both samples, with the bond lengths for the tetrahedral ( $T_d$ ) and  
150 octahedral ( $O_h$ ) sites showing slight shortening after addition of Pd from 1.85 to 1.80 Å  
151 and from 2.03 to 2.00 Å, respectively. Incorporating Pd atoms did not improve the fit,  
152 indicating that the nanoparticulate Pd attached directly to the iron cations in magnetite or  
153 via bridging oxygens was below the limit of detection. XA was additionally used to  
154 obtain the Fe  $L_{2,3}$ -edge within a magnetic field and thus provide the X-ray magnetic  
155 circular dichroism (XMCD) difference spectra of these samples (Fig. 4a). The Fe  $L_{2,3}$ -  
156 edge XMCD can distinguish between the three Fe cation environments present in ferrite  
157 spinel structures to a depth of ~65 Å as the intensities of the peaks labelled in Fig. 3a(i)  
158 relate to the amount of  $Fe^{2+} O_h$  (octahedral),  $Fe^{3+} T_d$  (tetrahedral), and  $Fe^{3+} O_h$   
159 respectively (see <sup>24-26</sup> for details). Fig. 4a(i) displays the Fe  $L_{2,3}$ -edge XMCD spectrum for  
160 biomagnetite without addition of Pd that after fitting gave an  $Fe^{2+}/Fe^{3+}$  ratio of 0.64,



161 indicating an excess of  $\text{Fe}^{2+}$  compared to a typical stoichiometric magnetite which would  
162 have a ratio of 0.50, consistent with previous results for biogenic magnetites<sup>27,28</sup>. The  
163 addition of Pd resulted in an increase in the amount of  $\text{Fe}^{2+}$ , forming a spinel with a  
164  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio of 0.70 (Fig. 3b). The reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  in the spinel relates, most  
165 likely, to the ability of  $\text{Pd}^0$  nanoparticles to absorb large quantities of hydrogen which  
166 then interacts with the outer Fe atoms causing reduction to  $\text{Fe}^{2+}$ .

167

168 EXAFS and X-ray photoelectron spectroscopy (XPS) were used to determine the  
169 nature of the Pd particles deposited on the surface of the magnetite. EXAFS and the  
170 related fourier transform from the Pd *K*-edge [Fig. 3(a,b)(iv)] for Pd-biomagnetite could  
171 be fitted with 5 coordination shells of atoms the first shell containing 12 Pd scatterers in  
172 at 2.74 Å and the second shell 6 Pd scatterers at 3.84 Å (see Table 1); these data have an  
173 excellent correspondence to values for Pd metal foil [Fig. 3(a,b)(iii)]. Fitting the Pd *3d*  
174 XPS spectrum (Fig. 4b) indicated that the main Pd peak had a binding energy of 335.3 eV  
175 with a minor peak (6% intensity) at a binding energy of 336.8 eV. These compare well  
176 with literature values that show the main peak to be  $\text{Pd}^0$ <sup>29</sup> and the weak peak to be a  
177 second phase that may be PdO or  $\text{PdO}_2$ <sup>30</sup>. Pd-oxide could be present due to either  
178 oxidation of the surface of the metallic Pd or the Pd nanoparticles could be attaching to  
179 the magnetite via ‘bridging’ oxygens. Additional XPS data (not shown) indicated that the  
180 surface of the nanoparticles had an Fe:Pd ratio of 1.00:0.22. Thus the TEM, XAS and  
181 XPS data are consistent and confirm the presence of  $\text{Pd}^0$  nanoparticles attached to a  
182 biomagnetite support. Samples were kept under anoxic conditions throughout the

183 preparation and measurement when using the surface sensitive techniques XMCD and  
184 XPS to ensure that the samples were not air oxidised.

185

186         The definitive test of the usefulness of the 5 mol% Pd-coated biomagnetite is its  
187 catalytic potential and therefore Heck Reaction coupling of iodobenzene to styrene or  
188 ethyl acrylate was performed. Identical catalytic testing was also carried out on colloid  
189 stabilised nanoparticulate palladium<sup>31-33</sup> as a means of comparing the Pd-coated  
190 biomagnetite to a highly active conventional catalyst. The Pd-coated biomagnetite was  
191 found to be active in the coupling of both olefins, with the complete conversion of the  
192 iodobenzene (plus ethyl acrylate or styrene) to ethyl cinnamate or stilbene within 90 and  
193 180 min, respectively. Rates of reaction were equal or superior to those obtained with an  
194 equimolar amount of Pd from the colloidal palladium catalyst. However, the advantage of  
195 the magnetite-based catalyst was that it could be readily recovered at the end of the  
196 reaction by simply decanting the solution from the reaction vessel while retaining the  
197 solid catalyst by applying a magnetic field to the base of the flask. The solid was washed  
198 and dried before use in subsequent reactions.

199

200         Successive runs were performed for the Heck coupling of iodobenzene and ethyl  
201 acrylate to test the Pd-coated magnetite for recyclability. Although a small decrease in  
202 initial reaction rate was observed in each successive cycle, virtually quantitative  
203 conversions were reached in 120 min for each run, up to a fourth cycle (Fig. 5), an  
204 improvement on some literature values for conventional catalysts<sup>5</sup>. These experiments  
205 were conducted without attempting to exclude air and the decrease in activity is attributed

206 to the loss of a small amount of material due to oxidation of some of the magnetite  
207 support to a non-magnetic phase material which was not recovered between runs, rather  
208 than direct loss of Pd to solution. Indeed, ICP-AES analysis of the supernatant in each  
209 cycle confirmed that there was negligible loss of Pd or indeed Fe to solution (data not  
210 shown). By comparison although the palladium colloids remained catalytically active for  
211 a second cycle of the ethyl acrylate coupling the halide conversion was only 89 %  
212 compared to > 99% for Pd-coated biomagnetite (Fig. 5). In addition more than 75% of  
213 the mass of the catalyst was lost during the recovery step, most likely due to the tertiary  
214 butyl ammonium bromide capping layer dissolving in the solvent. This would lead to the  
215 remaining palladium aggregating, reducing the active surface area substantially. Further  
216 recycling after the second run was unfeasible due to the very low mass of remaining  
217 material.

218

219         These results demonstrate that a novel biomagnetite-supported Pd-nanoparticle  
220 catalyst has several major advantages over conventional colloidal Pd catalysts. First,  
221 recovery and recycling is facile and, second, the biomagnetite support keeps the Pd  
222 dispersed and prevents it from agglomerating and losing vital surface area. The  
223 preparation method, apart from its novelty, provides an organics-coated ferrite particle in  
224 a one-step process, allowing Pd nanoparticles to be attached to the support material  
225 without further processing. Bacterial production is a low cost environmentally-friendly  
226 biotechnological route of manufacture, which opens up a route to the manufacture of  
227 other precious metal nanocatalysts. Recent success at applying gold and platinum derived  
228 materials to biogenic magnetite as supported nanoparticles (unpublished data) indicates

229 the versatility of bacterial production of nanocatalysts, which could be applied to a wide  
230 range of catalytic reactions.

231

232

### 233 **Methods**

234 As previously described, magnetite production was achieved by the reduction of  
235 Fe(III)-oxyhydroxide in the presence of AQDS using *G. sulfurreducens*<sup>13</sup>, under an  
236 atmosphere of N<sub>2</sub>-CO<sub>2</sub> (80:20). Bottles were incubated in the dark at 30°C for two days  
237 after which magnetite had been produced. The resulting magnetite was washed twice in  
238 degassed deionised water and then re-suspended in water using its magnetic properties to  
239 separate the mineral from the supernatant. An aliquot of a solution of sodium  
240 tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>, Sigma-Aldrich CAS no. 13820-53-6) was then added so  
241 that the final concentration of Pd was 5% by mass of the magnetite. The magnetite  
242 suspension was left overnight in a shaking incubator at 150 rpm and 20°C. The sample  
243 was then washed again twice using degassed, distilled deionised water twice before  
244 drying under anoxic conditions.

245

246 The Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) analyses  
247 were carried out using the IDLE instrument<sup>34</sup> which was equipped with a C<sub>60</sub> primary ion  
248 gun<sup>35</sup>. Chemical damage by C<sub>60</sub> primary ions is far less than by any other primary ion  
249 species so that depth profiling of organic samples becomes feasible<sup>36</sup>. Analysis of  
250 inorganic material is also improved<sup>37</sup> enabling comprehensive investigation of mixed  
251 samples. Only a few atomic layers are sputtered during each measurement making TOF-

252 SIMS an ideal method to study thin layers on sample surfaces with sensitivities high  
253 enough to analyze trace element abundances. As the beam is rastered over the measured  
254 area a complete mass spectrum is recorded at each point allowing for comprehensive  
255 offline analysis. Secondary ion distribution images have been reconstructed for all  
256 interesting mass intervals and background-corrected count integrals for all these mass  
257 intervals have been used for quantitative analysis. The magnetite samples have been  
258 mounted on Al stubs in a thick layer of around one hundred micro-metres and analyses  
259 have been carried out with a lateral resolution of  $2\mu\text{m}$  and a field-of-view of  
260  $480\times 365\mu\text{m}^2$ .

261

262 X-ray absorption (XA) spectra were collected for the Fe and Pd *K* edges on  
263 beamline 9.3 at the Synchrotron Radiation Source (SRS), Daresbury Laboratory. A  
264 double crystal Si(311) monochromator was used, detuned to 70% transmission for  
265 harmonic rejection. Pd *K*-edges were collected at 80 K in fluorescence mode using a 9-  
266 element Ge detector. Fe *K*-edges and a standard palladium foil were collected at 80 K in  
267 transmission mode. Background subtracted EXAFS spectra were analyzed in EXCURV98  
268 using full-curved-wave theory as described in Henderson et al. (2007)<sup>38</sup>, which allows the  
269 proportion of metal in each site to be refined as a single parameter. The metallic-phase Pd  
270 *K*-edge spectra were analysed in EXCURV98 using a model based on the crystal  
271 structure of Pd<sup>39</sup> the Fermi energy correction and the absorber-scatterer distances and  
272 Debye-Waller factors were refined to minimise a least squares residual.

273

274 XA spectra for XMCD were collected on beamline 4.0.2 at the Advanced Light  
275 Source (ALS), Berkeley, CA, using the octopole magnet endstation<sup>40</sup>. Powders were  
276 mounted on carbon tape attached to the sample manipulator and kept in O<sub>2</sub>-free  
277 conditions throughout. XA was monitored in total-electron yield mode, which gives an  
278 effective probing depth of ~4.5 nm. At each energy point the XA was measured for the  
279 two opposite magnetisation directions by reversing the applied field of 0.6 T. The XA  
280 spectra of the two magnetisation directions were normalised to the incident beam  
281 intensity and subtracted from each other to give the XMCD spectrum<sup>24</sup>. Spectra were  
282 fitted by means of a non-linear least-squares analysis, using calculations for each of the  
283 Fe sites<sup>24</sup>. In these calculations, as described elsewhere<sup>41</sup>, the Hartree-Fock Slater  
284 integrals for the *3d-3d* and *2p-3d* Coulomb and exchange interactions were scaled to 70%  
285 and 80%, respectively, and the crystal fields for the O<sub>h</sub> and T<sub>d</sub> sites were taken to be  
286  $10Dq = 1.2$  eV and  $-0.6$  eV, respectively. The calculated spectra were convoluted by a  
287 Lorentzian of  $\Gamma = 0.3$  (0.5) eV for the *L*<sub>3</sub> (*L*<sub>2</sub>) edge to account for intrinsic core-hole  
288 lifetime broadening and by a Gaussian of  $\sigma = 0.15$  eV to account for instrumental  
289 broadening.

290

291 TEM was conducted using a Phillips/FEI CM200 equipped with a field emission  
292 Gun, EDX system (Oxford Instruments UTW ISIS) and a Gatan imaging filter. All TEM  
293 images presented here are bright-field images obtained using an operating beam voltage  
294 of 200 keV. Selected area electron diffraction (SAED) patterns were acquired using an  
295 appropriate diffraction aperture. A droplet of washed sample was placed on a carbon grid  
296 (Agar Scientific) and allowed to dry before imaging.

297

298 X-ray photoelectron spectroscopy (XPS) data were recorded using a Kratos Axis  
299 Ultra employing a monochromated Al  $K\alpha$  X-ray source and an analyser pass energy of  
300 20eV, resulting in a total energy resolution of  $\sim 0.9$ eV. Uniform charge neutralisation of  
301 the photoemitting surface was achieved by exposing the surface to low energy electrons  
302 in a magnetic immersion lens system (Kratos Ltd.). The system base pressure was  $5 \times 10^{-}$   
303  $^{10}$  mbar. All samples were dried anaerobically and the resulting powders were loaded into  
304 the spectrometer via a dry nitrogen glove box to avoid exposure to atmospheric oxygen.  
305 Photoelectron binding energies (BE) were referenced to C1s adventitious carbon  
306 contamination peaks set at 285eV BE. The electron energy analyser was calibrated using  
307 elemental references: Au4f $_{7/2}$  (83.98eV BE), Ag3d $_{5/2}$  (368.26eV BE) and Cu2p $_{3/2}$   
308 (932.67eV BE). An appropriate (Shirley) background was removed from all spectra<sup>42</sup>.

309

310 To test the catalytic properties of the Pd-coated biomagnetite dry DMF (15 mL),  
311 5% wt Pd magnetite catalyst (10.6 mg, 0.5 mol %), iodobenzene (204 mg, 1 mmol) and  
312 triethylamine (0.21 mL, 1.5 mmol) were added to a 2-necked round bottomed flask,  
313 equipped with reflux condenser under a nitrogen atmosphere, and the mixture heated to  
314 120 °C with stirring. Olefin substrate (1.5 mmol) was added and the mixture stirred at 120  
315 °C under nitrogen. Samples were taken from the reaction periodically for analysis by high  
316 performance liquid chromatography using a Dionex Summit HPLC (with Chromeleon  
317 software) with a Summit p580 quaternary low pressure gradient pump, Summit UVD  
318 170s UV/VIS multichannel detector with analytical flow cell and a Phenomenex Luna  
319 10u C18 (2) Column, 250 mm x 4.6 id. A flow rate of 1 ml/min was used with a solvent

320 gradient of 100 % water to 100 % MeCN over 40 min, hold for 10 min, and then back to  
321 100 % water for 10 min. At the end of the reaction, the mixture was allowed to cool to  
322 room temperature before decanting the solution from the flask whilst retaining the  
323 catalyst by applying a magnetic field to outside of the flask. The solid was washed (5 mL  
324 DMF followed by 5 mL acetone) and the solid dried for use in the next run.

325

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- 460
- 461

462 **Table Caption**

463

464 **Table 1.** Parameters obtained from fitting the Fe and Pd *K*-edges EXAFS spectra of  
465 biomagnetite samples. *N* is the coordination number, *r* is the interatomic distance and  $2\sigma^2$   
466 is the Debye-Waller factor.

467

468 **Figure captions**

469

470 **Figure 1.** TEM images of, **a**, biomagnetite and, **b**, Pd-coated biomagnetite, inset contains  
471 annotation indicating where EDX spectra were taken. **c**, selected area electron diffraction  
472 (SAED) pattern for Pd-coated biomagnetite with reflections labelled in black (magnetite)  
473 and grey (palladium) and, **d**, X-ray diffraction (XRD) of Pd-coated biomagnetite.

474

475 **Figure 2.** TOF-SIMS images of (a) washed biogenic nanomagnetite produced by  
476 *Geobacter sulfurreducens* and (b) commercially available inorganic nanomagnetite.  
477 Normalised secondary ion ratio of the surface of washed biogenic magnetite before and  
478 after ablation of the surface with a C<sub>60</sub> gun.

479

480 **Figure 3. a**, EXAFS and, **b**, corresponding Fourier transform for the Fe K-edge of (i)  
481 biomagnetite and (ii) Pd-coated bio-magnetite and Pd K-edge of (iii) Pd foil and (iv) Pd-  
482 coated biomagnetite. Data (black lines) and fits (dotted red lines).

483

484 **Figure 4. a**, Fe  $L_{2,3}$ -edge XMCD spectra of (i), biomagnetite and (ii), Pd-coated  
485 biomagnetite and **b**, XPS of the Pd 3d peaks of biogenic Pd-coated magnetite

486

487 **Figure 5.** Rate of conversion during the Heck coupling of iodobenzene and ethyl acrylate  
488 catalysed by Pd-coated biomagnetite (solid lines) or Pd colloids (dashed lines). Fresh  
489 catalyst was used in run 1, runs 2 to 4 used recycled catalyst.

490



	Atom type	<i>N</i>	<i>r</i> (Å)	$2\sigma^2$ (Å <sup>2</sup> )
	<b>Fe K-edge</b>			
<b>Biomagnetite</b>	O	1.3	1.85	0.0394
	O	4	2.03	0.025
	Fe	4	3.00	0.021
	Fe	8	3.50	0.012
	O	4	3.36	0.027
<b>Pd biomagnetite</b>	O	1.3	1.80	0.037
	O	4	2.00	0.024
	Fe	4	2.99	0.024
	Fe	8	3.48	0.012
	O	4	3.28	0.009
	<b>Pd K-edge</b>			
<b>Pd foil standard</b>	Pd	12	2.74	0.012
	Pd	6	3.85	0.020
	Pd	24	4.77	0.020
	Pd	12	5.36	0.012
	Pd	24	6.14	0.029
<b>Pd biomagnetite</b>	Pd	12	2.74	0.014
	Pd	6	3.84	0.018
	Pd	24	4.79	0.030
	Pd	12	5.42	0.016
	Pd	24	6.08	0.030









