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# Tetra-n-butylammonium decatungstate supported on Fe<sub>3</sub>O<sub>4</sub> nanoparticles: a novel nano-catalyst for green synthesis of nitroso compounds

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1 **Tetra-n-butylammonium decatungstate supported on**  
2 **Fe<sub>3</sub>O<sub>4</sub> nanoparticles: a novel nano-catalyst for green**  
3 **synthesis of nitroso compounds**

4  
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12 **Abstract**

13       The aim of this study was to prepare a Fe<sub>3</sub>O<sub>4</sub>/tetra-n-butylammonium decatungstate  
14 (TBADT) catalyst (M-DT) for the selective oxidation of aromatic amine compounds in the  
15 presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The material M-DT, prepared from the interactions  
16 between TBADT and Fe<sub>3</sub>O<sub>4</sub>, was fully characterized by Fourier infrared spectroscopy (FTIR),  
17 X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron  
18 microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and, X-ray photoelectron  
19 spectroscopy (XPS). Electron transfers between H<sub>2</sub>O<sub>2</sub> and TBADT or Fe<sub>3</sub>O<sub>4</sub> or M-DT were  
20 studied by cyclic voltammetry (CV) using carbon-modified electrodes. The optimized  
21 M-DT/H<sub>2</sub>O<sub>2</sub> catalytic system can effectively oxidize sulfapyridine (SPD) to  
22 nitroso-sulfapyridine (N-SPD) in the pH range of 2.5 to 4.6 with an efficient (93%) and  
23 selective conversion (86%). The oxidation rate constant ( $1.20 \times 10^{-2} \text{ min}^{-1}$ ) is much higher  
24 with M-DT than with TBADT ( $2.09 \times 10^{-4} \text{ min}^{-1}$ ) or Fe<sub>3</sub>O<sub>4</sub> ( $4.81 \times 10^{-4} \text{ min}^{-1}$ ) alone using 5  
25 mM H<sub>2</sub>O<sub>2</sub> as a co-catalyst. This M-DT catalyst can be reused 6 times with high efficiency and  
26 selectivity.

27 **Keywords:** TBADT; Fe<sub>3</sub>O<sub>4</sub>; H<sub>2</sub>O<sub>2</sub>; Amine oxidation; Electron transfer process.

## 28 **1. Introduction**

29 Nitroso compounds are known to be highly valuable chemical intermediates, which are  
30 versatile building blocks in polymer, dyes, agrochemicals, and pharmaceutical industries <sup>1</sup>.  
31 Nitroso compounds can be prepared easily from inexpensive starting materials <sup>2</sup>. Among the  
32 preparation methods, catalytic oxidation of primary amines appears to be one of the widely  
33 used methods <sup>3-5</sup>. In the last years, the most popular methodology to prepare nitroso  
34 compounds was the transition metal based catalyzed, with tungsten (W) <sup>2,6</sup>, molybdenum (Mo)  
35 <sup>1,7</sup>, vanadium (V) <sup>7</sup>, zirconium (Zr) <sup>8</sup> and gold (Au) <sup>9</sup> as metals, in combination with H<sub>2</sub>O<sub>2</sub>.  
36 H<sub>2</sub>O<sub>2</sub>, known as a milder oxidant, is widely used in “green synthesis” since H<sub>2</sub>O and O<sub>2</sub>  
37 represent the main reaction products <sup>2,10</sup>. However, the production of products such as azo or  
38 azo derivatives is the main reason for the low selectivity of this catalytic oxidation process <sup>11</sup>.  
39 Nowadays, improving the high activity and selectivity attracts more attention, and  
40 immobilization of transition metal catalysts on solid support became an interesting strategy <sup>6,9</sup>.  
41 Moreover, this catalyst has the potential to be recycled and reused several times. Tungstate  
42 catalysts proved to be efficient catalysts, for example, tungstate-supported silica-coated Fe<sub>3</sub>O<sub>4</sub>  
43 nanoparticles prepared by Jadidi Nejad, et al. can be reused up to 6 times in presence of H<sub>2</sub>O<sub>2</sub>  
44 to prepare nitroso compounds in a yield of roughly 70% <sup>2</sup>.

45 Decatungstate (DT) is a catalyst commonly used for organic selective synthesis, especially  
46 in photo-catalyzed oxidation <sup>12</sup>. A variety of methods have been developed to prepare  
47 heterogeneous DT photocatalysts <sup>12-16</sup>. Considering the selection of the support material, a  
48 previous study proved that the interaction exists between iron oxide and tungstate oxide <sup>17</sup>.  
49 Rakshit et, al. proved that tungsten forms inner-sphere-type bonds on hematite surfaces using

50 in situ ATR-FTIR <sup>18</sup>. In addition, previous studies illustrated that this interaction can make the  
51 electron more easily transfer from W<sup>6+</sup> sites to Fe<sup>3+</sup> <sup>17</sup> and can be affected by pH <sup>19</sup>.

52 Based on the well-comprehension of interaction between these two species, we sed, in the  
53 present study, nanoparticles of Fe<sub>3</sub>O<sub>4</sub> (M) as a support of TBADT to synthesize a  
54 Fe<sub>3</sub>O<sub>4</sub>/TBADT (M-DT) composite material. We used M-DT to obtain a catalytic system to  
55 selectively oxidize sulfapyridine (SPD) to nitroso-sulfapyridine (N-SPD) in the presence of  
56 H<sub>2</sub>O<sub>2</sub>. Compared with tungstate-supported silica-coated Fe<sub>3</sub>O<sub>4</sub> prepared by Jadidi Nejad, et al  
57 <sup>2</sup>, the M-DT catalyst was innovatively prepared by directly linking TBADT on the Fe<sub>3</sub>O<sub>4</sub>  
58 surface via the strong interaction between the W element and Fe element. Therefore, it is not  
59 necessary to coat the Fe<sub>3</sub>O<sub>4</sub> with silica first, and the process of catalyst preparation is  
60 relatively simple. In addition, the mechanism research of this catalytic system is very  
61 interesting, and there are not many studies on the mechanism of this kind of catalytic system.

62 Hence, in this study, i) to investigate the mechanism of the M-DT/H<sub>2</sub>O<sub>2</sub> catalytic system,  
63 the catalytic materials were characterized by XRD, FTIR, TEM, SEM, EDS, and XPS. The  
64 electron transfer between H<sub>2</sub>O<sub>2</sub> and M-DT catalyst was studied by the CV experiment. ii) to  
65 identify the produced species, NMR, HPLC, and HRMs/UHPLC were used. iii) to optimize  
66 the efficiency and selectivity of the oxidation of the substrate to nitroso compound in the  
67 M-DT/H<sub>2</sub>O<sub>2</sub> system, catalytic oxidation of SPD to N-SPD was investigated as a function of  
68 various parameters, such as the ratio of TBADT and Fe<sub>3</sub>O<sub>4</sub> in M-DT, the amount of M-DT, the  
69 pH, and the concentrations of H<sub>2</sub>O<sub>2</sub>.

## 70 **2. Experimental**

### 71 **2.1. Materials**

72 Sulfapyridine (SPD) ( $\geq 99\%$ ), sodium tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ), tetra-n-butylammonium  
73 bromide (TBABr), hydrochloric acid (HCl),  $\text{H}_2\text{O}_2$  (30%), perchloric acid ( $\text{HClO}_4$ ), iron (III)  
74 chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), iron(II) chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and sodium hydroxide (NaOH) were  
75 purchased from Sigma Aldrich and used without any further purifications. Water (Milli-Q)  
76 was purified using a reverse osmosis RIOS 5 and Synergy (Millipore) device. Its resistivity  
77 was  $18\text{ M}\Omega\text{ cm}$  and the dissolved organic carbon (DOC) was estimated to be  $< 0.1\text{ mg L}^{-1}$ .

## 78 **2.2. Preparation of TBADT, $\text{Fe}_3\text{O}_4$ , and M-DT**

79 The preparation of TBADT was performed using the method described elsewhere<sup>20</sup>. A  
80 boiling sodium tungstate solution (8 g of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  dissolved in 100 mL of ultrapure  
81 water) was added into 16.75 mL boiling hydrochloric acid (3.0 M). The temperature was  
82 maintained at  $95\text{ }^\circ\text{C}$  for 5 min till the color of the solution changed from colorless to green.  
83 Then, the addition of an aqueous solution ( $95\text{ }^\circ\text{C}$ ) of tetra-n-butylammonium bromide  
84 (TBABr 6.4 g/10 mL) leads to the immediate formation of a white precipitate. The mixture  
85 was kept under stirring at  $95\text{ }^\circ\text{C}$  for 5 min. This suspension was then filtered after cooling at  
86 ambient temperature. The solid was dissolved into dichloromethane, and then the solution was  
87 filtered to remove the insoluble particles. Finally, the obtained dichloromethane solution was  
88 gently evaporated at  $38\text{ }^\circ\text{C}$  to obtain the yellow-green catalyst. Nanoparticles of  $\text{Fe}_3\text{O}_4$  were  
89 prepared by the procedure reported in the literature<sup>21</sup>.

90  $\text{Fe}_3\text{O}_4$ /TBADT solid, taking M-DT<sub>2-1</sub> as an example, was prepared by the following  
91 procedure. A mixture of 1.0 g TBADT and 2.0 g  $\text{Fe}_3\text{O}_4$  was vigorously stirred in 10.0 mL  
92 acetonitrile. The reaction vessel was then kept in the dark for 20 hours at ambient  
93 temperature. After centrifugation, the solid was washed with Milli-Q water three times and

94 then dried in the oven at 50 °C. Different ratios of Fe<sub>3</sub>O<sub>4</sub>/TBADT (20/1, 10/1, 5/1, 2/1) were  
95 tested to prepare various M-DT using a similar process with an equivalent quantity of Fe<sub>3</sub>O<sub>4</sub>  
96 (2.0 g).

### 97 **2.3. Characterization**

98 To characterize the purity of the synthesized TBADT, the UV-Vis absorption spectra of  
99 TBADT dissolved in acetonitrile (CH<sub>3</sub>CN) were obtained using a Varian Cary 300 UV-vis  
100 spectrophotometer (**Fig. S1**). The X-ray diffraction (XRD) patterns of TBADT, Fe<sub>3</sub>O<sub>4</sub>, and  
101 M-DT<sub>2-1</sub> (before and after the reaction) were collected using an X-ray diffractometer  
102 (PANalytical X'Pert Pro) with a diffracted beam monochromator Cu K $\alpha$  source (40 kV-40  
103 mA). Patterns were recorded from 2 $\theta$  = 5 to 70°, in steps of 0.08° with a count time of 4  
104 seconds. The FTIR spectra of TBADT, Fe<sub>3</sub>O<sub>4</sub>, and M-DT<sub>2-1</sub> were recorded with  
105 Thermo-Nicolet 380 spectrometer with an advanced diamond ATR accessory (Specac-Golden  
106 Gate). For the characterization of the morphology and the size of particles of TBADT, Fe<sub>3</sub>O<sub>4</sub>,  
107 and M-DT<sub>2-1</sub>, the samples were suspended in ethanol and dropped onto a 400-mesh holey  
108 carbon-coated copper grid and dried at room temperature, and then analyzed by transmission  
109 electron microscopy (TEM, Hitachi H-7650) at 80 kV acceleration voltage with  
110 magnifications up to 200×000. With the objective to check whether TBADT is uniformly  
111 covered on the surface of nano-Fe<sub>3</sub>O<sub>4</sub>, an element mapping experiment coupled with scanning  
112 electron microscopy analysis (SEM-EDS) was performed on a JEOL JSM-6490LV  
113 microscope. X-ray Photoelectron Spectroscopy (XPS) was performed on a Physical  
114 Electronics/PHI 5300 X-ray photoelectron spectrometer (S 250 Germany) with a  
115 hemispherical analyzer and a single-channel detector that was operated at 300W (15 kV and

116 20 mA). Mg K $\alpha$  radiation (1253.6 eV) and pass energies of 89.45 eV for survey scans and  
117 17.9 eV for high-resolution scans were used. The BET (Brunauer, Emmett, and Teller)  
118 surface area of the materials was determined by a Quantachrome Nova 3000e Surface Area  
119 Analyzer.

#### 120 **2.4. Catalytic tests: SPD oxidation**

121 The conversion of SPD and the formation yield of its corresponding nitroso compound  
122 were performed in a batch experiment at room temperature (roughly 25°C). 20 mg M-DT was  
123 added into the 50 mL of SPD solution (30  $\mu$ M). The pH of the solution was adjusted to  $3.0 \pm$   
124 0.05 using perchloric acid and sodium hydroxide (0.1 M). H<sub>2</sub>O<sub>2</sub> was added using a known  
125 volume of a concentrated solution, and so with negligible volume, prior to starting the  
126 reaction using the magnetic stirrer at 1100 rpm min<sup>-1</sup> to disperse Fe<sub>3</sub>O<sub>4</sub> particles. Then,  
127 aliquots of the mixture were taken at different time intervals and were immediately filtrated  
128 using PTFE filters of 0.2  $\mu$ m (CHROMAFIL<sup>®</sup> Xtra RC-20/25, 25 mm, Macherey-Nagel).

129 The effect of the ratio of Fe<sub>3</sub>O<sub>4</sub>/TBADT in M-DT (20/1, 10/1, 5/1, and 2/1), pH (1.9, 2.5,  
130 3.0, 4.0, 4.6, 5.2, and 7.2), H<sub>2</sub>O<sub>2</sub> concentration (1, 5, 10, 20, 30, 40, and 50 mM), and M-DT  
131 concentrations (0.1, 0.2, 0.4, and 1.2 g L<sup>-1</sup>) was also investigated.

#### 132 **2.5. Preparative LC, UHPLC-MS, HPLC, and NMR Spectroscopy**

133 Preparative liquid chromatography (LC) was used to separate and purify N-SPD from the  
134 reaction mixture. This separation was obtained using preparative LC (Varian Prep Star 218)  
135 equipped with a Varian Pro Star 335 photodiode array detector and an autosampler. The  
136 column was a C18 Varian Dynamax Microsorb 60-8 column (250 mm  $\times$  41.4 mm, 8  $\mu$ m



137 particle size). The identification of all the byproducts was performed using high-resolution  
138 mass spectrometry (HRMS) constituted of an Orbitrap QExactive (Thermo Scientific)  
139 coupled to an ultra-high performance liquid chromatography (UHPLC) instrument Ultimate  
140 3000 RSLC (Thermo Scientific). Analyses were carried out in both negative and positive  
141 electrospray modes (ESI<sup>+</sup> and ESI<sup>-</sup>). The conversion of SPD and the formation of N-SPD  
142 percentages were obtained by HPLC (Shimadzu NEXERA XR HPL) equipped with a  
143 photodiode array detector and an auto-sampler. The column was a Macherey Nagel EC 150/2  
144 NUCLEODUR C18ec (150 mm × 2 mm, 2 μm particle size). All the elution conditions of  
145 those LC are given in **SI**.

## 146 **2.6. NMR spectroscopy**

147 For the characterization and also quantification of the products, NMR spectroscopy was  
148 used. 100 μL at 5.22 mM of 3-(Trimethylsilyl) propionic acid-d<sub>4</sub> sodium salt (TSPd<sub>4</sub>) in D<sub>2</sub>O  
149 solution as a reference was added in 900 μL concentrated pure N-SPD solution. NMR data  
150 were obtained with a Bruker Advance III 500 MHz Ultrashield™ plus spectrometer (equipped  
151 with 5 mm TCI-13C-15N-2H Prodigy Cryoprobe). All spectra were recorded in 600 μL of  
152 H<sub>2</sub>O (10% D<sub>2</sub>O). Chemical shifts (δ) are expressed in ppm relative to the residual peak of 4.79  
153 (ppm) of water.

## 154 **2.7. Electrochemical measurement**

155 Cyclic voltammetry (CV) experiments were carried out with a potentiostat Autolab  
156 PGSTAT204 controlled by the NOVA software (Metrohm) equipped with a three-electrodes  
157 system. An Ag-AgCl electrode was used as the reference electrode and a platinum wire as the

158 auxiliary electrode. The working electrodes were pyrolytic graphite electrodes (PGE, A =  
159 0.07 cm<sup>2</sup>) modified with a TBADT coating (**TBADT/PGE**), a Fe<sub>3</sub>O<sub>4</sub> coating (**M/PGE**), and  
160 an M-DT<sub>2-1</sub> coating (**M-DT<sub>2-1</sub>/PGE**) prepared by a solvent casting method. Before its use, the  
161 PGE electrode surface was polished with 1 μm diamond paste and washed with acetone and  
162 then it was polished again with 0.04 μm alumina slurry to be finally rinsed with ethanol and  
163 water. To prepare the TBADT/PGE. 10 μL TBADT solution was deposited onto the polished  
164 PGE and then air dried for 120 min. The M/PGE was also prepared using a solvent casting  
165 method<sup>22</sup>. A suspension was prepared with 80 mg of Fe<sub>3</sub>O<sub>4</sub> dispersed in 1.0 mL ethanol by  
166 sonication for approximately 30 minutes. Then 10 μL Nafion solution (5%, Sigma Aldrich)  
167 was added in the 1.0 mL Fe<sub>3</sub>O<sub>4</sub> suspension followed by sonication for more than 15 min. 10  
168 μL of the slurry was deposited onto the polished PGE and then air dried for 120 minutes.  
169 Finally, for the M-DT/PGE, a suspension was prepared in a centrifuge tube with 40.0 mg of  
170 TBADT and 80.0 mg of Fe<sub>3</sub>O<sub>4</sub> (M-DT<sub>2-1</sub>) dispersed in 1.0 mL acetonitrile for 24 hours on a  
171 rotating reactor (45 rpm min<sup>-1</sup>) at ambient temperature. After centrifugation, the solid was  
172 washed with acetonitrile and Milli-Q water three times and then dry in the oven at 50 °C.  
173 After getting the fresh M-DT, 1 mL ethanol was added in this centrifuge tube with sonication  
174 for approximately 30 min, then 10 μL Nafion solution was added in the 1.0 mL M-DT<sub>2-1</sub>  
175 suspension followed by sonication for 30 min more. 10 μL of the slurry was deposited onto  
176 the polished PGE and then air dried for 120 minutes. Cyclic voltammograms were recorded  
177 with the TBADT/PGE, M/PGE or M-DT<sub>2-1</sub>/PGE modified electrodes in a 0.1 M LiClO<sub>4</sub>  
178 electrolyte solution (at pH 3.5) in the presence or absence of H<sub>2</sub>O<sub>2</sub> (5 mM) at a scan rate (ν) of  
179 10 mV s<sup>-1</sup> under inert atmosphere. To avoid interference with O<sub>2</sub> reduction, the electrolyte

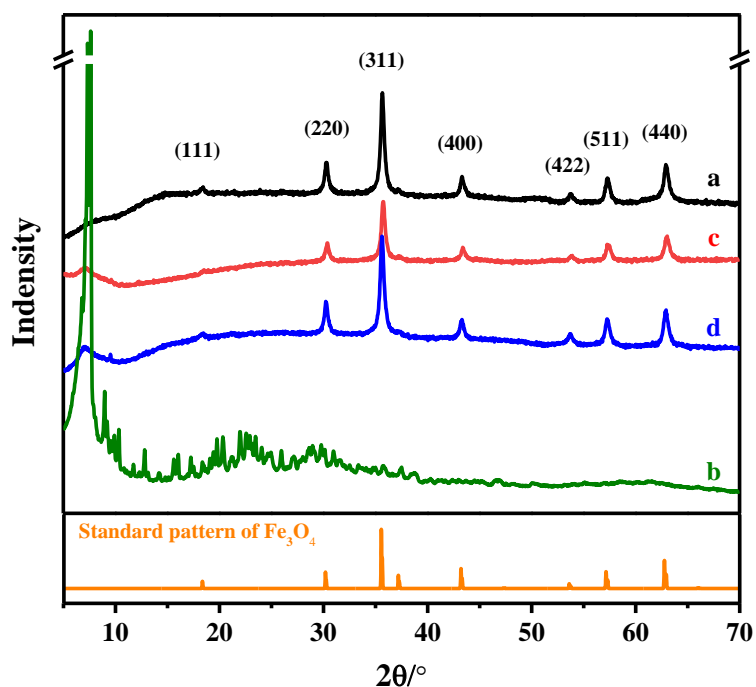
180 solution was bubbling with argon for 30 minutes prior to the CV experiments. The stability of  
181 the modified electrodes was studied during several cycles, and the CVs shown corresponded  
182 to the 10<sup>th</sup> cycle. The recyclability of an M-DT/PGE electrode was also studied under the  
183 same conditions, each time with a fresh LiClO<sub>4</sub> electrolyte solution.

### 184 **3. Results and discussion**

#### 185 **3.1. Characterization of TBADT, Fe<sub>3</sub>O<sub>4</sub>, and M-DT<sub>2-1</sub>**

186 Powder-XRD was used to characterize the solid compounds, Fe<sub>3</sub>O<sub>4</sub>, TBADT, and M-DT<sub>2-1</sub>.  
187 As shown in **Fig. 1**, the XRD pattern of Fe<sub>3</sub>O<sub>4</sub> (**curve a**) presents several diffraction lines at  
188  $2\theta = 18.44^\circ, 30.30^\circ, 35.67^\circ, 37.18^\circ, 43.32^\circ, 53.78^\circ, 57.29^\circ, 62.95^\circ$ . These are in perfect  
189 agreement with those reported in a standard pattern of PDF-#89-6466 (Shown in **Fig. 2**)  
190 leading us to the conclusion that Fe<sub>3</sub>O<sub>4</sub> is successfully synthesized. The **curve b** represents  
191 the XRD pattern of TBADT, which shows two significant peaks at  $7.33^\circ$  and  $7.62^\circ$  and  
192 several small peaks from  $5^\circ$  to  $40^\circ$ , which is quite similar to the previous study<sup>23</sup>. For the  
193 XRD pattern of M-DT<sub>2-1</sub> (**curve c**), the characteristic peaks of Fe<sub>3</sub>O<sub>4</sub> and TBADT can be  
194 observed, which means TBADT is successfully attached to the surface of Fe<sub>3</sub>O<sub>4</sub> particles. In  
195 addition, the intensity of TBADT in M-DT<sub>2-1</sub>, after it has been used as a catalyst in the  
196 oxidation reaction (**curve d**), does not decrease, which seems to indicate that the  
197 immobilization of TBADT is quite stable on the surface of Fe<sub>3</sub>O<sub>4</sub>. While the interaction  
198 between Fe<sub>3</sub>O<sub>4</sub> and TBADT is not shown in XRD patterns, further characterizations by FTIR  
199 and XPS are performed, and the results are presented in the **SI file (Fig S2, S3, Tables S1,**  
200 **S2, and S3)**. These results illustrate that there is a strong interaction between TBADT and

201  $\text{Fe}_3\text{O}_4$ , moreover, the chemical composition of  $\text{Fe}_3\text{O}_4$  has not significantly changed after  
202 M-DT<sub>2-1</sub> synthesis and after the reaction.

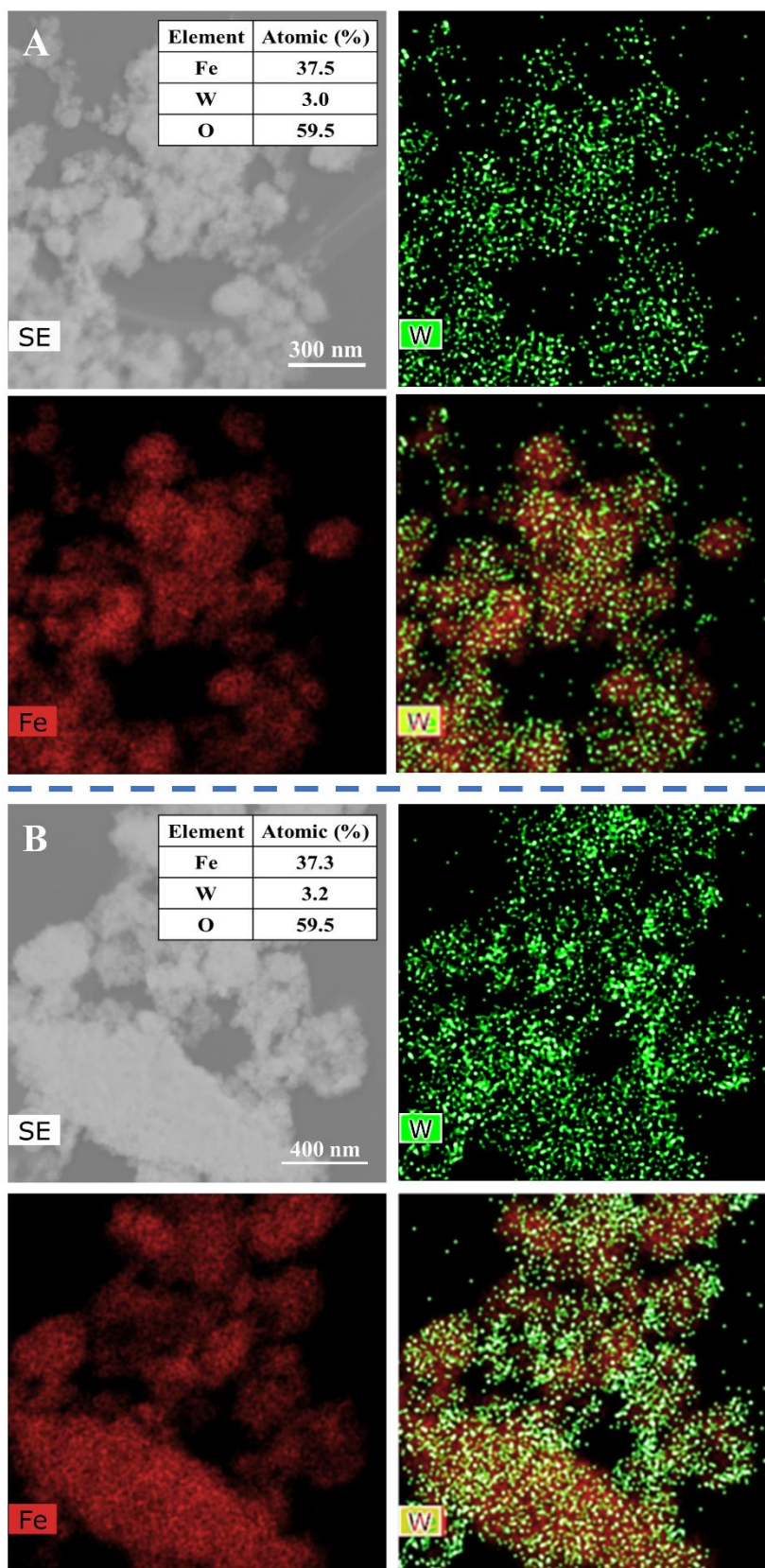


203  
204 **Fig. 1.** XRD patterns of  $\text{Fe}_3\text{O}_4$  (a), TBADT (b), M-DT<sub>2-1</sub> before (c) and after reaction (d)

205 The morphology and particle sizes of those materials were analyzed by TEM. **Fig. S4**  
206 shows the TEM images of  $\text{Fe}_3\text{O}_4$  (a), TBADT (b), and the M-DT<sub>2-1</sub> before (c) and after  
207 reaction (d).  $\text{Fe}_3\text{O}_4$  has a globosity morphology with particle diameters ranging from 20 to 40  
208 nm. This leads us to the conclusion that we are dealing with a nano- $\text{Fe}_3\text{O}_4$  material which  
209 presents more likely a large surface area (BET surface area =  $74 \pm 1 \text{ m}^2 \text{ g}^{-1}$ ). TBADT presents  
210 a short rod-like morphology with a length of 100 nm (**Fig. S4(b)**). The morphology of  
211 M-DT<sub>2-1</sub> is very similar to the morphology of  $\text{Fe}_3\text{O}_4$ , the short rod-like TBADT is not  
212 observed in the M-DT<sub>2-1</sub>. This is because in the preparation process of the M-DT<sub>2-1</sub>, TBADT  
213 is first dissolved in acetonitrile, and then individual clusters of TBADT will be wrapped on  
214 the surface of the  $\text{Fe}_3\text{O}_4$  through an inner-sphere type bond. In addition, the morphology of

215 M-DT<sub>2-1</sub> does not change after the reaction (**Fig. S4(c)**), which confirms that the M-DT<sub>2-1</sub> has  
216 a certain degree of durability.

217 To verify whether TBADT is uniformly covered on the surface of nano-Fe<sub>3</sub>O<sub>4</sub>, SEM-EDS  
218 element mapping technology is used to visually study the distribution of elements. **Fig. 2**  
219 shows the SEM image and SEM-EDS element mapping of M-DT<sub>2-1</sub> before and after the  
220 reaction. The elements such as Fe and W have the same distribution both in the M-DT<sub>2-1</sub>  
221 before and after the reaction, indicating that TBADT is evenly distributed on the surface of  
222 nano-Fe<sub>3</sub>O<sub>4</sub>. After overlapping the W and Fe distribution images, we can infer that M-DT<sub>2-1</sub>  
223 has a core-shell structure with Fe<sub>3</sub>O<sub>4</sub> as the core and TBADT wrapped in the outer layer. In  
224 addition, after the catalytic reaction, the amount of W element does not decrease (about 3  
225 atomic percent, shown in **Fig. 2**), which confirmed the stability of the M-DT<sub>2-1</sub> catalyst.



226

227 **Fig. 2.** SEM image and SEM-EDS element mapping of M-DT<sub>2-1</sub> before (A) and after reaction

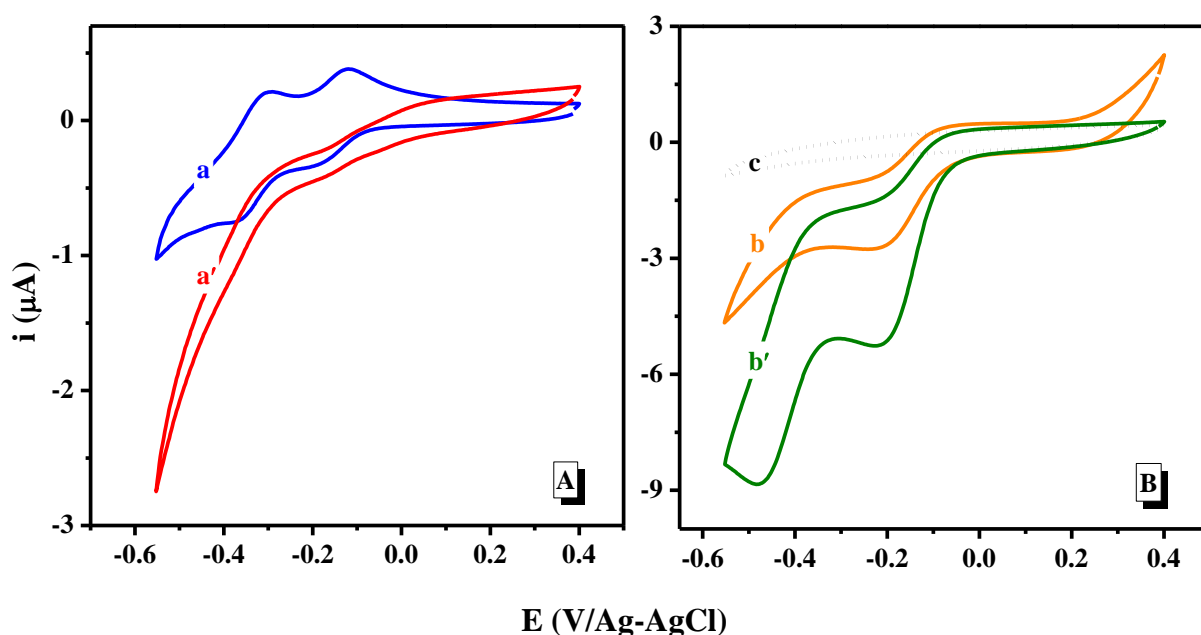
228

(B).

229 **3.2. Electrochemical behavior of TBADT, Fe<sub>3</sub>O<sub>4</sub>, and M-DT<sub>2-1</sub>**

230 To study the possible electron transfer between those materials and H<sub>2</sub>O<sub>2</sub>, we have  
231 compared the electrochemical behavior of TBADT deposited on a pyrolytic carbon electrode  
232 (TBADT/PGE), Fe<sub>3</sub>O<sub>4</sub> modified electrode (M/PGE), and the composite M-DT<sub>2-1</sub> modified  
233 electrode (M-DT<sub>2-1</sub>/PGE) in the absence and the presence of H<sub>2</sub>O<sub>2</sub> by CV experiment.

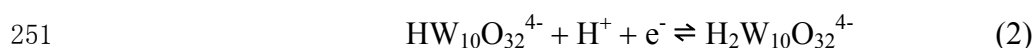
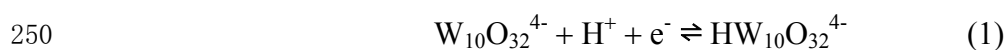
234 **Fig. 3** shows cyclic voltammograms of TBADT/PGE (A) and M-DT<sub>2-1</sub>/PGE (B) in the  
235 absence and presence of H<sub>2</sub>O<sub>2</sub>. The dashed line represents the baseline recorded at the bare  
236 PGE in 0.1 mM LiClO<sub>4</sub> electrolyte at pH 3.5 under argon, showing no interference with  
237 oxygen reduction.



238  
239 **Fig. 3.** Cyclic voltammograms of A) TBADT/PGE and B) M-DT<sub>2-1</sub>/PGE in the absence (a and  
240 b) or presence of 5 mM H<sub>2</sub>O<sub>2</sub> (a', b') in 0.1 M LiClO<sub>4</sub> (pH = 3.5) under Ar,  $\nu = 10 \text{ mV s}^{-1}$ . The  
241 dashed line (curve c) corresponds to the PGE baseline in 0.1 M LiClO<sub>4</sub> pH 3.5 under Ar.

242 The CV of TBADT/PGE (**Fig. 3(A), curve a**) exhibits two reversible signals. The potential

243 of the first cathodic peak ( $E_{p_{c1}} = -0.18$  V/Ag-AgCl) and the second one ( $E_{p_{c2}} = -0.37$   
 244 V/Ag-AgCl) are consistent with the values reported in the literature for sodium decatungstate  
 245 (NaDT) in aqueous solution<sup>24,25</sup>, while Yang, et al reported the first cathodic at 0.06 V/SCE  
 246 for TBADT dissolved in a mixed solvent (10% HCl (12 M) + 90 % CH<sub>3</sub>CN)<sup>26</sup>, which is due  
 247 to the different polarity of the solvent<sup>27</sup>. The peak separation ( $\Delta E = E_{p_c} - E_{p_a}$ ) is 60 mV for the  
 248 first and the second redox couples, showing good reversibility of the electron transfer which  
 249 can be assigned to the following reactions:



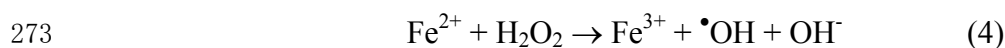
252 **Curve a' in Fig. 3(A)** corresponds to the electrochemical signal of TBADT in the presence  
 253 of 5 mM H<sub>2</sub>O<sub>2</sub>. The shape of the voltammograms changes when H<sub>2</sub>O<sub>2</sub> is added to the  
 254 electrolyte solution. Although the two cathodic peaks are not obvious, the current intensity of  
 255 these two peaks seems to increase slightly (current at  $E_{p_{c1}} = -0.18$ V and  $E_{p_{c1}} = -0.37$ V are  
 256  $-0.43$   $\mu$ A and  $-1.10$   $\mu$ A, respectively), while the corresponding anodic peak current decreases.

257 **Curve b in Fig. 3(B)** represents the CV of the M-DT<sub>2-1</sub>/PGE in 0.1 mM LiClO<sub>4</sub> electrolyte  
 258 at pH 3.5 under argon. A cathodic peak can be observed at  $E_{p_{c1}} = -0.23$  V/Ag-AgCl ( $I_{c1} = -2.77$   
 259  $\mu$ A). The presence of H<sub>2</sub>O<sub>2</sub> in the electrolyte causes an increase of the cathodic current ( $I_{p_{c1}} \times$   
 260 approximately 2 times) and the appearance of a second irreversible peak at  $E_{p_{c2}} = -0.48$   
 261 V/Ag-AgCl (**curve b'**). The shape of those catalytic waves is similar to those we have  
 262 previously reported using M/PGE and NaDT in solution. Even if the peak intensities cannot  
 263 be compared directly, since the same amount of DT was not deposited on both electrode  
 264 surfaces, it was notable that the catalytic current obtained in the presence of H<sub>2</sub>O<sub>2</sub> at



265 M-DT<sub>2-1</sub>/PGE was much higher than the one recorded at the TBADT/PGE. This indicates that  
266 there is an interaction between TBADT and Fe<sub>3</sub>O<sub>4</sub> leading to an enhancement of the  
267 electrocatalytic process.

268 For comparison, **Fig. S5** shows the CVs recorded using a M/PGE with and without 5.0 mM  
269 H<sub>2</sub>O<sub>2</sub> added to the electrolyte solution. With M/PGE, a well-defined cathodic peak is observed  
270 at -0.08 V which is owing to an electro-Fenton process occurring at the Fe<sub>3</sub>O<sub>4</sub> surface<sup>28,29</sup>.  
271 This process can be expressed by equations (3 and 4):



274 However, in this case, the catalytic current ( $I_{p_c} = 2.05 \mu\text{A}$ ) is lower than with  
275 M-DT<sub>2-1</sub>/PGE. This means that with M-DT<sub>2-1</sub> particles on the electrode surface, the  
276 electrocatalytic process for H<sub>2</sub>O<sub>2</sub> reduction is definitively improved. The mechanisms of these  
277 electrocatalytic processes are probably not the same on both types of the electrode (M/PGE  
278 and M-DT<sub>2-1</sub>/PGE), implying in the latter case, iron species from Fe<sub>3</sub>O<sub>4</sub> in interaction with  
279 TBADT, as suggested by Dong and Liu for Dawson-type tungstatephosphonate anion<sup>30</sup>.

280 The current stability of M-DT<sub>2-1</sub>/PGE was investigated in the CVs experiment in the  
281 absence (A) and presence of H<sub>2</sub>O<sub>2</sub> (B) for 10 potential cycles (**Fig. S6**). In absence of H<sub>2</sub>O<sub>2</sub>, a  
282 cathodic peak at -0.18 V/Ag-AgCl ( $I_{p_{c1}} = -7.87 \mu\text{A}$ ) can be observed in the first cycle, and  
283 then the signal is stabilized with the cathodic peak  $E_{p_{c1}}$  at -0.23V/Ag-AgCl and  $I_{p_{c1}} = 2.3\mu\text{A}$ .  
284 The higher current in the first cycle may be due to the reduction of some O<sub>2</sub> molecules  
285 adsorbed on the modified electrode. In the presence of H<sub>2</sub>O<sub>2</sub>, the current stabilized also  
286 rapidly, showing that the M-DT<sub>2-1</sub> coating on the PGE surface is relatively stable. The

287 appearance of the second cathodic peak ( $E_{p_{c2}}$ ) seems to be limited by diffusion restrictions  
288 through the film that seems to be solved after 2 or 3 cycles.

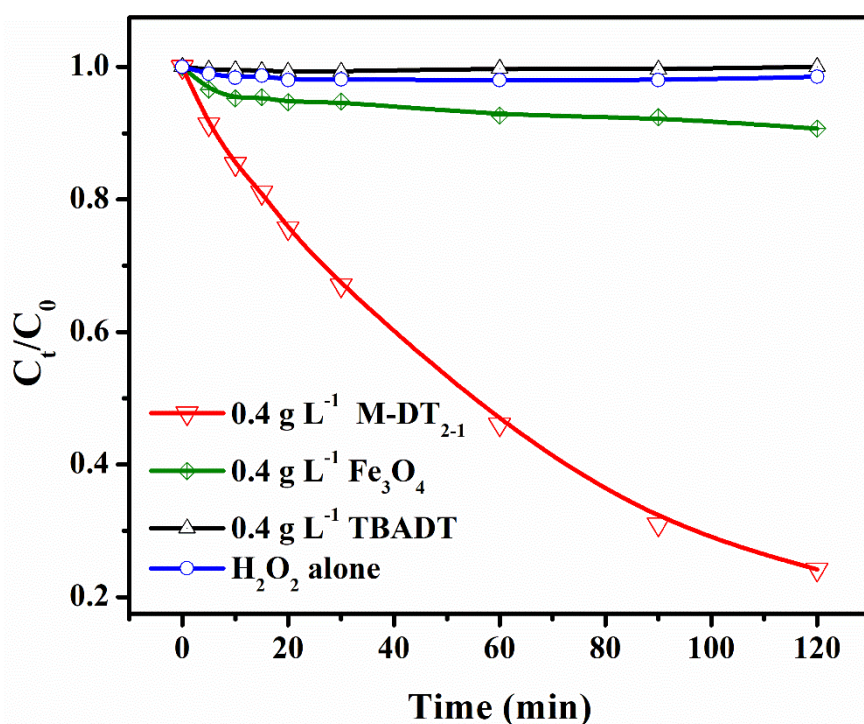
289 To investigate the recycling performance of the M-DT<sub>2-1</sub>, the same M-DT<sub>2-1</sub>/PGE was used  
290 to perform the CVs experiment six times in a fresh electrolyte solution under Ar in the  
291 presence of 5.0 mM H<sub>2</sub>O<sub>2</sub> (**Fig. S7**). The second cathodic peak ( $E_{p_{c2}}$ ) can be seen after the  
292 second use, which is consistent with the above result. Insert shows the evolution of the  
293 cathodic current ( $I_{p_{c1}}$  and  $I_{p_{c2}}$ ) as a function of the electrode uses confirming the good  
294 reproducibility of the electrocatalytic process occurring at the M-DT<sub>2-1</sub>/PGE electrode. This  
295 result indicates that the W element did not decrease after the reaction as well.

### 296 **3.3. Investigation of the catalytic performance**

#### 297 **3.3.1 Comparison of the oxidation process in different systems**

298 The synthesized M-DT composite material associated with H<sub>2</sub>O<sub>2</sub> was used to oxidize SPD  
299 and the efficiency was evaluated. With this objective, an aqueous solution of SPD at a  
300 concentration of 30.0  $\mu$ M was mixed first with M-DT<sub>2-1</sub> and H<sub>2</sub>O<sub>2</sub> (5.0 mM) at pH = 3.0. For  
301 the sake of comparison, experiments were also performed with H<sub>2</sub>O<sub>2</sub> alone, Fe<sub>3</sub>O<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>, and  
302 TBADT/H<sub>2</sub>O<sub>2</sub> under the same experimental conditions. **Fig. 4** shows that in the presence of  
303 H<sub>2</sub>O<sub>2</sub> alone (5.0 mM), almost no oxidation SPD (<1.5% within 2 hours) was obtained under  
304 our experimental conditions. Within the same time, the conversion was estimated to be 0.4 %  
305 with TBADT/H<sub>2</sub>O<sub>2</sub> (0.4 g L<sup>-1</sup>/5.0 mM) and 9.3 % with Fe<sub>3</sub>O<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (0.4 g L<sup>-1</sup>/5.0 mM).  
306 However, in the presence of 0.4 g L<sup>-1</sup> synthesized M-DT<sub>2-1</sub> and 5.0 mM of H<sub>2</sub>O<sub>2</sub>, the  
307 conversion reaches 75.8 % within 120 minutes, demonstrating the important and interesting

308 oxidation ability of the M-DT<sub>2-1</sub>/H<sub>2</sub>O<sub>2</sub> system toward SPD. Under our experimental  
 309 conditions, the conversion appears to follow first-order kinetics and the rate constant is  
 310 estimated to be 1.20×10<sup>-2</sup> min<sup>-1</sup>. While performing the experiments in the absence of H<sub>2</sub>O<sub>2</sub>,  
 311 we can easily evaluate the SPD adsorption ability of the solid support. As shown in **Fig. S8** no  
 312 adsorption of SPD is observed on TBADT, Fe<sub>3</sub>O<sub>4</sub>, and M-DT<sub>2-1</sub> within 2 hours.



313  
 314 **Fig. 4.** Kinetics of SPD disappearance under various experimental conditions, [SPD] = 30 μM;  
 315 H<sub>2</sub>O<sub>2</sub> = 5.0 mM; pH = 3.0

316 The generated products in the M-DT<sub>2-1</sub>/H<sub>2</sub>O<sub>2</sub> systems were analyzed by HRMs/UHPLC and  
 317 NMR. The disappearance of SPD leads to the formation of mainly three products among them  
 318 the N-SPD (m/z<sub>[M+H<sup>+</sup>]</sub> = 264.0435 (**Table S4**) and, the hydroxyl-sulfapyridine (SPD-OH)  
 319 product (**P1**) which is mainly formed in Fe<sub>3</sub>O<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> system, more likely owing the classical  
 320 Fenton and Fenton-like processes<sup>31</sup>. On a contrary, the N-SPD is the main product formed in  
 321 the M-DT<sub>2-1</sub>/H<sub>2</sub>O<sub>2</sub> system leading us to the conclusion that the simultaneous presence of

322  $\text{Fe}_3\text{O}_4$  and TBADT greatly promotes the amino selective oxidation into nitroso compound.  
323 The NMR spectrum confirms this result (**Fig. S9**). The quantification of N-SPD is performed  
324 by using the NMR technique according to the procedure given in **SI**. The average  
325 concentration of N-SPD calculated after quantification by NMR is 52.03  $\mu\text{M}$  (Dropping a  
326 sample with a chemical shift of 7.93 ppm), and the relative standard deviation is (**RSD**) 4.8%  
327 (**Table S5**).

### 328 **3.3.2. The effect of different parameters**

329 To optimize such oxidation process of SPD, the effect of various ratios of  $\text{Fe}_3\text{O}_4$ /TBADT  
330 (**Table S6**), pH (**Table S7**), the concentration of  $\text{H}_2\text{O}_2$  (**Table S8**), and amount of M-DT<sub>2-1</sub>  
331 (**Table S9**) were investigated.

332 The obtained results demonstrate that the SPD conversion percentage increases from 7.8 to  
333 51.5% with the increase of the percentage of TBADT in M-DT from 4.8% to 33.3% (**Fig.**  
334 **S10**). For the coming experiments, M-DT with a ratio of 2/1 which is marked as M-DT<sub>2-1</sub> was  
335 chosen. The pH can affect the conversion of SPD to N-SPD, the efficiency of SPD conversion  
336 decreases with the increase of the solution pH (**Fig. S11**). Meanwhile, the conversion  
337 percentage of SPD decreases also when the pH increases. These are more likely due to the  
338 lower stability of decatungstate at  $\text{pH} > 5.5$ , and also due to the interaction between Fe and W  
339 decreasing when pH increases<sup>18</sup>. As the  $\text{H}_2\text{O}_2$  concentration increases from 0 to 20 mM, the  
340 conversion rate and rate constant of SPD oxidation increase (**Fig. S12**), however those values  
341 both decrease with the  $\text{H}_2\text{O}_2$  concentration increase from 20 to 50 mM. For the amount of  
342 M-DT<sub>2-1</sub>, the conversion rate and rate constant of SPD oxidation increase and reach a plateau

343 when increasing the amount of M-DT<sub>2-1</sub> (**Fig. S13**). The yield of N-SPD increases and reaches  
344 a plateau when H<sub>2</sub>O<sub>2</sub> and the amount of M-DT<sub>2-1</sub> increase.

### 345 **3.3.3. Recycling experiments**

346 To demonstrate that synthesized M-DT<sub>2-1</sub> can be recycled, it was collected after each  
347 reaction and reemployed for the same experiments. **Table 1** shows the conversion of SPD and  
348 selectivity for the formation of N-SPD in this system during repeated experiments. The SPD  
349 conversion and the yield of N-SPD formation remain between 90.5 - 94.5% and 77.6 - 79.4%  
350 in 5 times repeated experiments, respectively. A small decrease in the conversion efficiency  
351 can be observed according to the rate constant and percentage of SPD disappearance which  
352 may be due to the loss of TBADT on the Fe<sub>3</sub>O<sub>4</sub> surface. However, the yield of N-SPD  
353 formation remains at a high level. This indicates that the M-DT<sub>2-1</sub> is a highly efficient catalyst  
354 material that can be reused and is likely to be used in actual production in the future.

355 **Table 1** The conversion and selectivity of SPD in repeated experiments within 2h

Number of cycles	1	2	3	4	5
Rate constant ( $\times 10^{-3} \text{ min}^{-1}$ )	22.5	21.3	21.8	21.3	20.5
Percentage of SPD disappearance (%)	93.4%	94.5%	92.7%	91.6%	90.5%
The yield of N-SPD formation (%)	78.7%	77.9%	79.4%	78.6%	77.6%

356 [M-DT<sub>2-1</sub>] = 0.8 g L<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 5.0 mM; [SPD] = 30  $\mu$ M; pH = 3.0;

### 357 **3.4. Comparison of catalytic performance**

358 To understand the work of selective catalysis more deeply, we have compared  
359 systematically the results of selective oxidation of SPD using sodium decatungstate (NaDT)

360 and TBADT associated with Fe<sub>3</sub>O<sub>4</sub>. **Table 2** shows the SPD selective oxidation reaction  
361 parameters in NaDT/M/H<sub>2</sub>O<sub>2</sub> and M-DT<sub>2-1</sub>/H<sub>2</sub>O<sub>2</sub> systems. It is observed that the catalytic  
362 performance for the selective oxidation of SPD, such as the rate constant of SPD  
363 disappearance ( $\times 10^{-3} \text{ min}^{-1}$ ), the percentage of SPD disappearance (%), and the yield of  
364 N-SPD formation (%) shows no significant difference, when the reaction parameters, such as  
365 the concentration of decatungstate, Fe<sub>3</sub>O<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, SPD, and pH are the same in above  
366 mentioned both systems. In addition, the optimal parameters of the reaction have similarities.  
367 For example, the optimal pH for both systems is in the range of 2.5 - 4.0, and the optimal  
368 concentration of H<sub>2</sub>O<sub>2</sub> is in the range of 5.0 - 20.0. These similarities can let us infer that the  
369 two systems have the same reaction mechanism.

370 However, it should be noted that the amount of catalyst (NaDT and TBADT) that interacted  
371 on the Fe<sub>3</sub>O<sub>4</sub> surface is different, around 15.4  $\mu\text{M g}^{-1}$  of TBADT/M and 74.1  $\mu\text{M g}^{-1}$  of NaDT/  
372 M were adsorbed on the Fe<sub>3</sub>O<sub>4</sub> surface (**Fig. S14**), but the SPD oxidation and N-SPD  
373 formation efficiency are the same. This result indicates that the M-DT<sub>2-1</sub>/H<sub>2</sub>O<sub>2</sub> system is about  
374 5 times more efficient than NaDT/M/H<sub>2</sub>O<sub>2</sub> system.

375 The catalytic performance of M-DT<sub>2-1</sub>/H<sub>2</sub>O<sub>2</sub> systems was also compared with previous  
376 studies in the two dimensions of substrate conversion rate and selectivity. As shown in **Table.**  
377 **S10**, M-DT<sub>2-1</sub>/H<sub>2</sub>O<sub>2</sub> system has good and green catalytic performance in aqueous solution  
378 with high oxidation efficiency (97% conversion rate) and high selectivity (85% yield of  
379 N-SPD).

380 **Table 2.** The comparison of selective oxidation parameters using soluble and insoluble DT

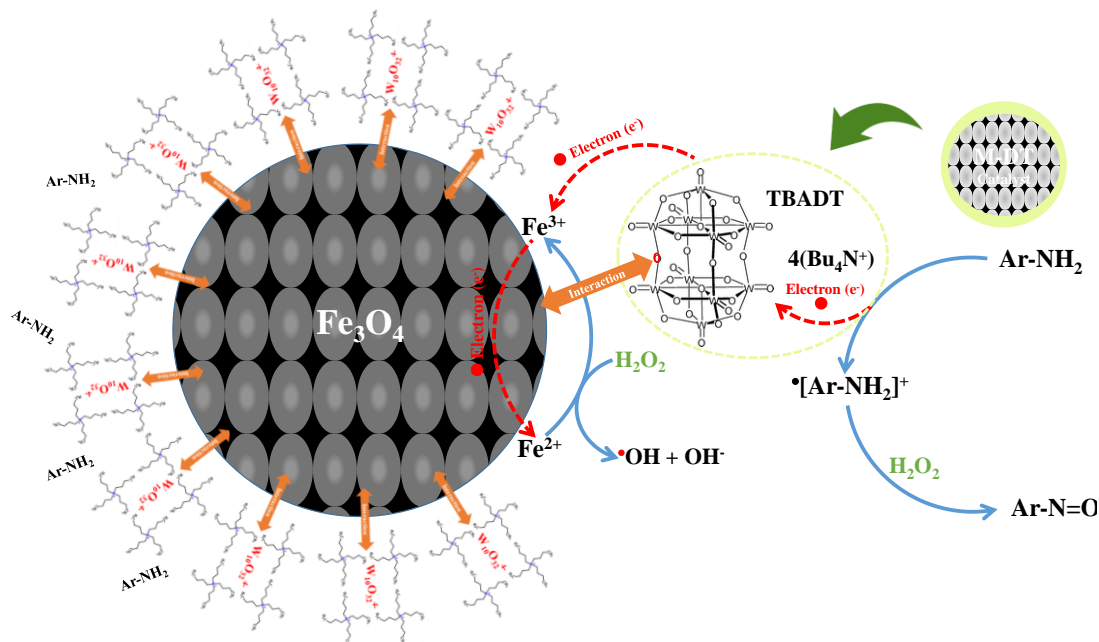
381 Synergistic Fe<sub>3</sub>O<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> Systems

System	NaDT/Fe <sub>3</sub> O <sub>4</sub> /H <sub>2</sub> O <sub>2</sub>	M-DT <sub>2-1</sub> /H <sub>2</sub> O <sub>2</sub>
	System	System
[W <sub>10</sub> O <sub>32</sub> <sup>4-</sup> ] (μM)	41 (NaDT)	40.2 (TBADT)
[W <sub>10</sub> O <sub>32</sub> <sup>4-</sup> ] on the surface (μM g <sup>-1</sup> )	74.1	15.4
[Fe <sub>3</sub> O <sub>4</sub> ] (g L <sup>-1</sup> )	0.264	0.266
[H <sub>2</sub> O <sub>2</sub> ] (mM)	5.0	5.0
[SPD] (μM)	30	30
pH	3.0	3.0
Rate constant (×10 <sup>-3</sup> min <sup>-1</sup> )	11.3	12.0
Percentage of SPD disappearance (%)	75.4	75.8
The yield of N-SPD formation (%)	71.3	73.8

### 382 3.5. Mechanistic study

383 The obtained results demonstrate that the oxidation of SPD into N-SPD is efficient at a pH  
384 lower than 5.0 using an M-DT<sub>2-1</sub>/H<sub>2</sub>O<sub>2</sub> catalyst. The rate constant and the percentage of SPD  
385 disappearance and the yield of N-SPD formation overall increase when concentrations of  
386 M-DT<sub>2-1</sub> and H<sub>2</sub>O<sub>2</sub> increase. The characterization results and CV experiments analysis clearly  
387 show that there is an interaction between Fe<sub>3</sub>O<sub>4</sub> and TBADT. The mechanism in M-DT/H<sub>2</sub>O<sub>2</sub>  
388 system could be explained by an electron transfer from the amine site of SPD to TBADT  
389 giving rise to the formation of the reduced species TBADT with the simultaneous formation  
390 of the radical cation [Ar-NH<sub>2</sub>]<sup>•+</sup>. The radical cation [Ar-NH<sub>2</sub>]<sup>•+</sup> further reacts with H<sub>2</sub>O<sub>2</sub> to  
391 form N-SPD owing to the interaction between W and Fe atom, the electron can efficiently

392 transfer to  $\text{Fe}_3\text{O}_4$ . At the same time, the  $\text{Fe}^{3+}$  on the surface becomes  $\text{Fe}^{2+}$ , and the  
 393 regeneration of  $\text{Fe}^{3+}$  happens in presence of  $\text{H}_2\text{O}_2$  in the solution. The formation of SPD-OH  
 394 is a sign of hydroxyl radical formation. This could be produced via a Fenton reaction. The  
 395 efficiency of the process is mainly owing to the interaction of TBADT with M particles  
 396 (Scheme. 1)



397  
 398 **Scheme 1.** Proposed mechanism for the selective oxidation process of primary aromatic  
 399 amines to nitroso aromatic compounds using the M-DT/ $\text{H}_2\text{O}_2$  catalytic system

#### 400 4. Conclusions

401 The heterogeneous M-DT/ $\text{H}_2\text{O}_2$  system (TBADT/ $\text{Fe}_3\text{O}_4$ / $\text{H}_2\text{O}_2$ ) appears to be a powerful  
 402 system for the efficient (until 93%) and selective conversion (until 85%) of amine substrates  
 403 to their nitroso derivatives. The system consists of a composite material M-DT obtained  
 404 through interaction between  $\text{Fe}_3\text{O}_4$  and TBADT as clearly demonstrated by several  
 405 characterizations and CV experiments. This interaction is without any doubt the driving force



406 for the electron transfer implied in the catalytic process, leading to the formation of the radical  
407 cation on the amine group and the reduced species of TBADT. The regeneration of the  
408  $W_{10}O_{32}^{4-}$  is obtained via a second electron transfer with  $Fe_3O_4$  owing to the interaction. Thus,  
409 in this study, we demonstrated that the system M-DT/ $H_2O_2$  is an innovative and powerful  
410 catalytic system leading to a high yield of transformation for the generation of nitroso  
411 compounds from the amine group. It could be used and implemented easily for the synthesis  
412 of such chemical compounds in different applications.

### 413 **Conflicts of interest**

414 There are no conflicts to declare.

### 415 **Acknowledgement**

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420

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470