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Page 1 of 29

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Polybenzimidazole and Polybenzimidazole/MoS <sub>2</sub> Hybrids as an	1
Active Nitrogen Sites: Hydrogen Generation Application	2
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Mohammad Dinari <sup>1</sup> , Afshin Nabiyan <sup>1</sup> , Ali. A. Ensafi <sup>1</sup> , Mehdi Jafari-Asl <sup>1</sup>	4
<sup>1</sup> Department of Chemistry, Isfahan University of Technology, Isfahan 84156–83111, Islamic	5
Republic of Iran	6
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Abstract: Development free metals or non-noble-metal catalysts for electrode materials with	8
both excellent activity and high stability is essential for hydrogen production. In this work,	9
high rich nitrogen polybenzimidazole (PBI) networks was synthesized through a one-step	10
polycondensation of 1,2,4,5-tetraaminobenzene with 4,4',4"-((1,3,5-triazine-2,4,6-	11
triyl)tris(azanediyl))tribenzoic acid. Then, organic/inorganic nanohybrids of PBI with	12
amorphous $MoS_2$ nanoplates (PBI-MoS <sub>2</sub> ) were prepared. The structural characterization and	13
morphological of these novel hybrids were studies using FT-IR, <sup>1</sup> H NMR, elemental analysis,	14
thermogravimetry, transmission electron microscopy, field-emission scanning electron	15
microscopy and X-ray diffraction techniques. Electrochemical studies revealed the onset	16
potential of only (-160 mV vs. RHE) with a small Tafel slope of 50.6 mV dec <sup>-1</sup> for hydrogen	17
generation reaction in 0.5 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> . Stability tests through long term potential cycles	18
confirm the excellent durability of $PBI-MoS_2$ in acid media. The outstanding hydrogen	19
generation activity is derived from the electronic penetration effect and $\boldsymbol{H}^{\!\!+}$ absorption of	20
pyridinic-N and/or pyrrolic-N as active sites at per repeat of the PBI matrix. It is worth noting	21

<sup>1</sup> - Corresponding author. Tel.: +98 3133913270; fax: +98 3133912351.

E-mail address: dinari@cc.iut.ac.ir; mdinary@gmail.com

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Page 2 of 29

that pure PBI and PBI-MoS<sub>2</sub> hybrids, for the first time, were used as both anode and cathode
in two-electrode system open up new possibilities for exploring overall hydrogen generation
technology catalysts in acidic electrolyte. This development offers an attractive
electrocatalyst for large-scale hydrogen generation.

**Keywords:** Hydrogen generation; Polybenzimidazole; pyridinic-N; Pyrrolic-N molybdenum disulfide.

#### 1. Introduction

The rapid growth of global energy consumption and the associated environmental 31 issues have triggered the urgent demand for renewable and clean energy sources. 32 Electrochemical water splitting driven by solar energy has been considered as an attractive 33 approach to produce hydrogen  $(H_2)$  fuel, a sustainable, secure and environmentally benign 34 energy vector. Efficient water splitting requires high-performance electrocatalysts to promote 35 the hydrogen generation reaction.<sup>1-3</sup> The catalysts are cornerstone of this type of reaction.<sup>4</sup> 36 There is now enormous interest to design and develop efficient and inexpensive catalysts to 37 generate hydrogen.<sup>5</sup> According to the information, which provided by the previous reports 38 only a few synthetic catalysts are known to operate in water and they were able to give a high 39 current density at a low overpotential  $(\Pi)$ .<sup>6-9</sup> To date, the most effective hydrogen generation 40 catalyst are Pt group metals, whose huge scale application has been severely limited by their 41 low abundance and high cost.<sup>7-10</sup> Therefore, finding an inexpensive catalyst still is a serious 42 challenge for hydrogen generation. In earlier works, scientific researches in catalyst areas 43 achieve new approaches, which are used from metal-free catalysts for hydrogen generation 44 such as 4,4'-bipyridine, nitrogen doped reduce graphene oxide, metal-free polymeric 45 photocatalyst, and etc.<sup>11-13</sup> A large proportion of metal-free catalysts like 4,4'-bipyridine and 46

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of nitrogen doped reduces graphene oxide, the pivotal role of the nitrogen element is 47 inevitable and it has crucial junction in most catalyst mechanism of hydrogen generation 48 reaction. Therefore, a metal-free catalyst that is able to incorporate by nitrogen with hydrogen 49 generation mechanism like Volmer, Tafel or Heyrovsky reaction is among the most 50 outstanding catalyst for hydrogen generation.<sup>11</sup> 51

Polybenzimidazole (PBI) PBI is a basic polymer with good thermal and chemical 52 stability, which belongs to the class of heterocyclic polymers that contain benzimidazole 53 units.<sup>14</sup> PBI is the most promising candidate polymer to use as a hydrogen generation 54 catalyst. There have been a numerous reasons why PBI consider or offer as a catalyst in 55 hydrogen generation reaction and it would explore only a few most important properties for 56 hydrogen generation once here. First of all, PBI has considerable proton conductivity as long 57 as doped or hybrid with conductive materials such as graphene and phosphoric acid.<sup>15,16</sup> In 58 some studies, the enhanced electrocatalytic activity of hydrogen generation catalyst is 59 attributed to pyridinic-N and/or pyrrolic-N. Therefore, PBI which is used as a membrane 60 materials for fuel cells, can repeat the pyridinic-N and/or pyrrolic-N in every per repeat 61 unit.<sup>13,17-19</sup> PBI show high surface areas with porous materials to enhance fast mass transport 62 of reagents. Therefore, the high surface area is able to accept PBI as eligible catalyst.<sup>20-22</sup> This 63 vital information can be confirmed that PBI as is a good catalyst candidate for hydrogen 64 generation. 65

In the past years, organic/inorganic hybrid nanocomposites (NCs) as long as the 66 organic part is the polymer matrix and the inorganic part is nanosized fillers have been 67 advanced widely since their specific properties and particular application of NCs achieve 68 after hybridization.<sup>23-25</sup> Polymer/layered inorganic NCs have attracted great consideration for 69 their potential in improving polymer properties such as mechanical, thermal, and physical 70 properties.<sup>23-25</sup> Molybdenum disulfide (MoS<sub>2</sub>) nanosheets are expected to become one kind of 71

Page 4 of 29

useful fillers for improving the properties of polymers.<sup>26</sup> MoS<sub>2</sub> has attracted considerable 72 interest over the last few years due to its extraordinary optical, thermal, and mechanical 73 properties arising from its exceptional structure.<sup>27,28</sup> The unique sandwich structure has 74 potential applications in many technological fields, such as super lubricant, sensors, batteries, 75 photocatalyst, hydrogen storage and NCs.<sup>29-31</sup> where MoS<sub>2</sub>-based polymer composites are a 76 novel class of materials that combine the attractive functional properties of  $MoS_2$  (electrical, 77 optical, thermal, mechanical properties, etc) with the advantages of polymers, such as low 78 cost and good processability.<sup>32</sup> 79

Motivated by these results, in this work, we sought to explore a facile and efficient 80 route for preparing PBI/MoS<sub>2</sub> NCs. First, 4,4',4"-((1,3,5-triazine-2,4,6-triyl) tris (azanediyl)) 81 tribenzoic acid (TCA) was prepared from reaction between cyanuric chloride and para-82 aminobenzoic acid in glacial acetic acid. Then, PBI networks was synthesized through a 83 facile one step polycondensation reaction of 1,2,4,5-tetraaminobenzene and TCA using 84 methane sulfonic acid and phosphorus pentoxide mixture as a reaction medium.  $MoS_2$  plate 85 was synthesized by hydrothermal method and the PBI-MoS<sub>2</sub> NCs was achieved by ultrasonic 86 irradiation methods. Although there are numerous reports in the literature for  $MoS_2$  as 87 electrocatalyst for hydrogen generation, to the best of our knowledge, there is no report which 88 addresses PBI as well as PBI-MoS<sub>2</sub> hybrid as hydrogen generation electrocatalysts. The 89 electrocatalytic analysis results such as onset potentials, Tafel slopes and current densities 90 exhibited infinitely superior and favorable catalytic activities of PBI and PBI-MoS<sub>2</sub> hybrids 91 electrocatalyst for hydrogen generation. 92

#### 2. Experimental

#### 2.1. Reagents

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Cyanuric chloride, methanesulfonic acid, and phosphorus pentoxide were purchased 95 from Merck chemical Co. and 1,2,4,5-benzenetetramine tetrahydrochloride, L-cysteine, 96

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Nafion solution (5.0 wt. % in lower aliphatic alcohols and water), 4-aminobenzoic acid and 97 ammonium molybdate tetrahydrate, ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>. 4H<sub>2</sub>O) were purchased from Sigma 98 Aldrich. All other chemicals used in this investigation were of analytical grade and were 99 purchased from Merck. Deionization water (DI) was used for preparation of all of solution. 100

#### 2.2. Instrumentation

Fourier-Transform Infrared (FT-IR) spectrums of the materials were recorded using a 102 JASCO 680 (Japan) spectrophotometer over the wavenumber range of 400–4000 cm<sup>-1</sup>. <sup>1</sup>H 103 NMR spectra was recorded on Bruker Avance 400 MHz spectrometer operating on polymer 104 solution in dimethyl sulfoxide-d6 (DMSO-d6). Chemical shifts are given in the  $\delta$  scale in 105 parts per million (ppm). Thermal properties of the compounds was performed with a STA503 106 win TA (Bahr-Thermoanalyse GmbH, Hüllhorst, Germany) at a heating rate of 10 °C/min 107 from 25 to 800 °C under nitrogen atmosphere. The composition of the polymer (C, H, and N) 108 was analyzed by elemental analysis (LECO, CHNS-932). The X-ray diffraction (XRD) was 109 used to characterize the crystalline structure of the polymer and NCs. XRD patterns were 110 collected on a Bruker, D8ADVANCE (Germany). Transmission electron microscopy (TEM) 111 was performed using a Philips CM120. Morphology was observed using field-emission 112 scanning electron microscopy (FE-SEM, MIRA FE-SEM | TESCAN, Mira 3-XMU). 113

#### 2.3. Electrochemical characterizations

The electrochemical measurements were performed in 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> solution at 115 room temperature (RT). The electrode potential was controlled by an Autolab electrochemical 116 analyzer, Model PGSTAT 30 potentiostat /galvanostat (Eco-Chemie, The Netherlands). Data 117 were acquired and processed (background correction) using the GPSE and FARA computrace 118 software 4.9.007. A standard three-electrode cell containing a platinum wire auxiliary 119 electrode, a saturated Ag/AgCl reference electrode and PBI/MoS<sub>2</sub> and/or PBI modified glasy 120 carbon electrode as a working electrode. 121

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## 2.4. Preparation of the working electrodes

The glassy carbon electrode (GCE) was polished to a mirror finish using alumina 124 powder. After that, the electrode was washed several times with DI water and ethanol. Then, 125 10 mL of catalyst ink (PBI/MoS<sub>2</sub> and PBI, that prepared by dispersing of 2.5 mg of the as 126 prepared catalysts in 1 mL of ethanol/water (1:1)) was drop-coated on the polished GCE 127 electrode surface. After drying, 5 mL of 5.0 wt. % Nafion solution in lower aliphatic alcohols 128 and water was coated on the catalyst layer to ensure better adhesion of the catalyst on the 129 glassy carbon substrate. This electrode was then dried under room temperature. 130

# 2.5. Preparation of 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tribenzoic acid

4,4',4"-((1,3,5-triazine-2,4,6-triyl) tris(azanediyl))tribenzoic acid (TCA) as a three 132 acid monomer was prepared according to the reported procedure.<sup>33</sup> Briefly, cyanuric chloride 133 (3.68 g, 20 mmol) was added in one portion to a stirred solution of a 4-aminobenzoic acid (33 134 mmol) in 150 mL of glacial acetic acid and the mixture was refluxed for 12 h. The products 135 were precipitated from the mixture as white solids and were recovered by filtration. The solid 136 products were washed with boiling water to neutral pH and dried at 90°C in air. 137

### 2.6. Preparation of star polybenzimidazole

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Star PBI was synthesized by polycondensation method. In a typical procedure, a 139 three-necked flask equipped with a mechanical stirrer and  $N_2$  inlet, was charged with 3.0 g of 140 phosphorus pentoxide and 20 mL of methanesulfonic acid. The mixture was stirred at 50 °C 141 under a nitrogen flow until phosphorus pentoxide dissolved. Then, TCA (0.69 g) and 1,2,4,5-142 tetraaminobenzene (0.29 g) were added and the temperature was increased and the mixture 143 was allowed to polymerize at 80 °C for 2 h, 100 °C for 1 h, 120 °C for 1 h ,and 140 °C for 3 h. 144 The resulting mixture was poured into ice water and then collected by filtration. The solid 145 was washed with ammonia solution and then with deionized water to neutrality and remove 146

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Page 7 of 29

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the possibly unreacted monomers. Final, the perception was dried at 100 °C under vacuum to constant weight. Yield: 90%.

#### 2.7. Preparation of molybdenum disulfide

MoS<sub>2</sub> was synthesized according to the reported procedure.<sup>34</sup> Briefly, 1.5 mmol of 150 ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> 4H<sub>2</sub>O was dissolved in 30 ml deionized water, and then a given amount of L-151 cysteine was added into the solution under violent stirring. After stirring for 10 min, 152 approximately, 12 mol/L HCl was added into the above solution mixture drop by drop under 153 stirring to adjust the pH value to less than 1. Finally, the solution was transferred into a 100 154 ml Teflon-lined stainless steel autoclave and heated at 240 °C for 24 h. After cooled to room 155 temperature naturally, the black precipitates of  $MoS_2$  were collected, washed with distilled 156 water and absolute ethanol for several times, and then dried in vacuum at 60 °C for 12 h. 157

#### 2.8. Preparation of polybenzimidazole/molybdenum disulfide (PBI/MoS<sub>2</sub>) hybrids

For preparations of PBI-MoS<sub>2</sub> hybrid, 0.1 g of the PBI was dispersed in 10 mL of 159 DMSO and a uniform colloidal dispersion was obtained after sonication for 2h at room 160 temperature. Then the suspension was mixed with the different amounts of MoS<sub>2</sub> (1, 5 and 161 10%wt) to produced electrocatalyst followed by sonication for 2 h and stirred for 3 day at 110 162 °C. The solvent was removed and the powders obtained were dried under vacuum for 24 h at 163 60 °C. The NCs are named as PBI/MoS<sub>2</sub> NC1%, PBI/MoS<sub>2</sub> NC5% and PBI/MoS<sub>2</sub> NC10%, 164 where the percentage given in the genetic abbreviations is the weight percentage. 165

#### 3. Results and discussion

#### 3.1 Synthesis, structural characterization and morphological investigation

The synthesis of the triazine based monomer is presented in Fig 1. TCA was prepared 169 through a successive procedure of aryl amination of cyanuric chloride with paraaminobenzoic acid in glacial acetic acid. The synthesis route to polybenzimidazole networks 171

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is outlined in Fig. 1. PBI was respectively prepared by TCA and 1,2,4,5-tetraaminobenzene 172 *via* a one-step polycondensation in a solution of phosphorus pentoxide in methanesulfonic 173 acid *i.e.* Eaton's reagent. Eaton's reagent has been reported for the preparation of linear PBIs, 174 and it has been found that the polymerization system has, a high reaction temperature and a 175 low viscosity, less reaction time and high catalytic efficiency.<sup>35</sup> To clarify, it was observed 176 here that the target polymerizations proceeded clearly and could be completed within several 177 hours at a temperature below 140 °C. The obtained light brown products are insoluble in 178 many common solvents. "Figure 1 Here" 179

Fig.2 shows FTIR spectra of the triazine based monomer (TCA), MoS<sub>2</sub>, neat PBI and 180 PBI NCs with different amount of MoS<sub>2</sub>. For TCA monomer, the FTIR spectrum shows the 181 broad bond around 2600-3500 cm<sup>-1</sup> for acid functional groups. Absorbance of the NH group 182 was appeared around 3550 cm<sup>-1</sup>. Peaks correspond to C=N in cyanuric ring is shown at 1500-183 1600 cm<sup>-1</sup>. Also, the carbonyl groups of TCA appeared around 1706 cm<sup>-1</sup> (Fig. 2a). After 184 polymerization of TCA with tetraamine monomer, new absorbance bond corresponded to the 185 PBI was appearing and broad bond in the range of 2600-3500 cm<sup>-1</sup> was disappeared to 186 confirm the formation of the polymer (Fig. 2b). The board band from 3450 to 3400 cm<sup>-1</sup> is 187 attributed to the isolated N-H stretching of the imidazole, whereas the broad band near 3250-188 2900 cm<sup>-1</sup> is assigned to the self-associated N-H bond. This band is broader in the presence of 189 moisture (-OH). The C=C and C=N stretching appear in the region of 1630-1500 cm<sup>-1</sup>. A 190 strong band at 1400-1390 cm<sup>-1</sup> must be attributed to the deformation of benzimidazole rings 191 and inplane C-H deformations appear at 1235-1225 cm<sup>-1</sup> in PBI.<sup>36,37</sup> Moreover, it is clear that 192 the FTIR spectrum of PBI/MoS<sub>2</sub> NCs shows the same characteristic signals with pure PBI. 193 All characteristic peaks related to the PBI such as NH, C=N, C=C, C-N, C-C and C-H were 194 appearing in the FTIR spectra of the NC materials. The FTIR results indicate that PBI/MoS<sub>2</sub> 195 NCs have been prepared successfully. "Figure 2 Here" 196 Published on 18 November 2015. Downloaded by University of California - Santa Barbara on 23/11/2015 08:06:59

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The formation of PBI polymer was confirmed by the <sup>1</sup>H NMR spectra as shown in 197 Fig. 3. In this Fig., the peak of the imidazole proton was observed at 12.74 ppm, and 198 secondary amine (aromatic N-H) was observed at 9.75 ppm as well as all of the aromatic 199 protons were appeared at 7-9 ppm and confirmed the formation of the PBI.<sup>38</sup> 200

#### "Figure 3 Here

The composition of the C, H, and N in the PBI structure was analyzed by elemental 202 analysis, as shown in Table 1. It is known that PBI is very hygroscopic. During the sample 203 preparation and handling for elemental analysis, the PBI absorbed water from air. The 204 residual percentage due to the oxygen element in the structure is caused by absorbed water 205 throughout the analysis. This absorption justifies decrease in the C and N percentages and 206 also increase in the H percentage of the experimental results. The elemental analysis on dry 207 base was performed several times and the same percentages values were obtained for each 208 experiment.<sup>39</sup> "Table 1 Here" 209

Thermal properties of the pure PBI and PBI/MoS<sub>2</sub> were studied by means of TGA at a 210 heating rate of 20 °C/min under a nitrogen atmosphere. The PBI network exhibited 211 remarkably high thermal stability. TGA data for PBI and all the PBI-MoS<sub>2</sub> with different 212 percentage loadings of MoS<sub>2</sub> are shown in Fig. 4. All samples show weight loss at around 213 530-600 °C. These weight losses are due to the degradation of the polymer backbone. Table 2 214 summarizes the corresponding thermoanalysis data, including the temperatures at which 5% 215  $(T_5)$  as well as 10%  $(T_{10})$  degradation occurs. Char yield is at 800 °C and also limiting oxygen 216 index (LOI) is based on Van Krevelen and Hoftyzer equation.<sup>40</sup> 217

$$LOI = 17.5 + 0.4 CR$$
 218

Where CR = char yield. From these data, it is clear that neat PBI and its NCs are stable at 219 about 530 °C, owing to the existence of heterocyclic benzimidazole ring. All samples had 220

Page 10 of 29

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LOI values higher than 40, calculated based on their char yield at 800 °C. On the basis of 221 LOI values, such NCs can be classified as self-extinguishing materials. The obtained TGA 222 data clearly indicates that the thermal stability of the PBI improved significantly after NCs 223 formation with MoS<sub>2</sub> and the stability increased with increasing loading of MoS<sub>2</sub> nanoplates 224 in PBI matrix. Interfacial interaction between PBI and MoS<sub>2</sub> has a very significant function in 225 the thermal degradation of polymeric NCs. A suitable interfacial interaction permits  $MoS_2$ 226 nanoplates to act as a thermal barrier in the PBI matrix. The shielding ability depends on the 227 dispersion patterns of the  $MoS_2$  nanoplates in the polymer matrix. This aspect is related to 228 both the nature and morphological features of the MoS<sub>2</sub> nanoplates in the PBI matrix. Since, 229 in the current NCs, the morphological and structural feature changes with the MoS<sub>2</sub> loading 230 (as seen in Fig. 4), we obtained a different level of thermal stability. This clearly proves the 231 effect of morphologies in the thermal stability. In addition, as a typical layered inorganic 232 material,  $MoS_2$  is expected to disperse and exfoliate in the polymers and results in the 233 physical barrier effects, which inhibit the diffusion of heat and the decomposition products of 234 the polymer. Moreover, the transition metal element, Mo, promotes the formation of the 235 charred layer acting as a physical barrier, which could slow down heat and mass transfer 236 during the burning. So it is reasonable that  $MoS_2$  may improve the thermal stability and fire 237 resistance of polymer-based composites just like MMT, LDHs and grapheme.<sup>26,41</sup> 238

#### "Figure 4 and Table 2 Here"

The morphological information of  $MoS_2$ , PBI, and PBI-MoS\_2 with 5 and 10% w/w of 240 the MoS\_2 characterized by FE-SEM are show in Fig. 5. According to the previous study,<sup>6</sup> in 241 the MoS\_2 nanoplate, Mo atoms are covalently bonded to S atoms in two adjacent S layers; the 242 electroneutral MoS\_2 slabs are held together by van der Waals interactions. Due to the weak 243 interaction between the S-Mo-S layers, the slabs can be easily separated from each other, 244 leading to a plate-like morphology with visible edges.<sup>6</sup> In this study, as shown in Figs. 5a and 245 Published on 18 November 2015. Downloaded by University of California - Santa Barbara on 23/11/2015 08:06:59

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5b, MoS<sub>2</sub> that obtained using L-cysteine in the layered structure, show plate-like morphology. 246 In the other word, MoS<sub>2</sub> obtained through the proposed method consists of large-scale sheets 247 that are tightly stacked together. Pure PBI shows two different types of morphology such as 248 semi plate-like morphology and nanorod (Figs. 5, b and f). From these FE-SEM images (b 249 and f), it is clearly observed that synthesized PBI is matrix with different distribution for 250 morphology's elements. The obtained FE-SEM images, beside two different percent of PBI-251  $MoS_2$  (5 and 10 % w/w), are shown in Fig. 5 (c-h). According to these images in the PBI-252  $MoS_2$  hybrids, the micrograph exhibits a good dispersion of  $MoS_2$  into polymer matrix. It 253 seems that the particles are distributed uniformly in the polymer matrix with both of the 254 plate-like and nanorod morphology. "Figure 5 Here" 255

The hybrid structure were further characterized using transmission electron 256 microscopy (TEM) and TEM images of MoS<sub>2</sub> sheets beside PBI-MoS<sub>2</sub> (5% w/w) with two 257 different magnifications are shown in Fig. 6. As shown in Figs. 6a and 6b, for  $MoS_2$ , the 258 nanoparticles are actually in the form of irregularly sized nanopltate, and each  $MoS_2$ 259 nanosheet is well stacked to other plate-like  $MoS_2$ . On the other hand, in the case of PBI-260  $MoS_2$  (5% w/w), a mixture of PBI and  $MoS_2$  nanosheets can be observed, in which the PBI 261 simply serve as surface with uniform hole and MoS<sub>2</sub> nanosheets displays themselves by 262 discrete connection. "Figure 6 Here" 263

XRD analysis of the synthesized samples (PBI,  $MoS_2$ , and PBI- $MoS_2$ ) is presented in 264 Fig. 7. Figure 7 also shows XRD patterns of commercial  $MoS_2$  and the synthesized  $MoS_2$  265 nanoparticles. It appears that the commercial  $MoS_2$  has strong crystallinity and a layered 266 structure with an interlamellar distance of 6.15 Å (0.615 nm), as seen from the high order 267 diffraction peaks (004), (006) and (008) as shown in Fig. 7. This highly crystalline material is 268 very difficult to exfoliate and disperse in polymer matrices without special procedures 269 However,  $MoS_2$ , synthesized by the above described method is unambiguously amorphous as 270

Page 12 of 29

shown by the lack of crystalline or high-order basal peaks in the XRD diffractograms and is 271 therefore presumably very dispersible in various polymer matrices. The absence of the (002)272 reflection at 6.15 Å ( $2\theta$ =14.5°) and a broad feature indicating the absence of crystalline long-273 range order, strongly suggests a large extent of destacking in the synthesized MoS<sub>2</sub>. Fig. 7 274 also shows the XRD pattern of PBI-MoS<sub>2</sub> NCs with 1% and 10 w/w of MoS<sub>2</sub> as compared to 275 the MoS<sub>2</sub> and pure PBI. For neat PBI, several crystalline peaks were observed, indicating that 276 this polymer is member of the crystal polymers. The XRD patterns of the PBI-MoS<sub>2</sub> NCs 277 with 1% and 10 w/w of  $MoS_2$  are characterized. AS shown in this figure, because of the low 278 amounts of  $MoS_2$ , the peaks of amorphous  $MoS_2$  could not be find. This complete 279 disappearance of MoS<sub>2</sub> peaks may be due to the partial exfoliated structures. 280

#### "Figure 7 Here"

#### 3.2. Electrochemical measurements

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Electrochemical measurements were performed in a conventional three-electrode 283 single cell at room temperature. A glassy carbon electrode (GCE) with a geometric surface 284 area of 0.0314 cm<sup>2</sup> was used to prepare the modified working electrode. A Pt wire and 285 Ag/AgCl were used as the counter and reference electrodes, respectively. Cyclic 286 voltammograms (CVs) and liner sweep voltammetry (LSV) of the electrocatalysts were 287 measured in a 0.5 M  $H_2SO_4$  aqueous solution, to determine the hydrogen generation activity. 288

#### 3.3 Electrocatalytic Activity of PBI and PBI-MoS<sub>2</sub>

The catalytic activities of the PBI and PBI-MoS<sub>2</sub> with different percentage of MoS<sub>2</sub> 291 (1%, 5%, and 10% w/w) for hydrogen generation were studied by electrochemical methods. 292 The electrochemical activities of PBI and PBI-MoS<sub>2</sub>, and MoS<sub>2</sub> were also studied and 293 compared. Generally, an optimal hydrogen generation catalyst is a material that could give 294 the highest current at the lowest overpotential, as well as a low hydrogen generation onset 295

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potential (*i.e.*, the potential at which hydrogen generation activity begins) comparable to that 296 of Pt catalyst. The Tafel slope, which can be deduced from Tafel equation ( $\eta = b \log (j) + a$ , 297 where  $\eta$  is the overpotential, j is the current density and b is the Tafel slope), is always 298 correlated with reaction pathway and the adsorption type. 299

First of all, the electrochemical activity of PBI was studied and compared with MoS<sub>2</sub> 300 (Fig. 8A). The LSV curve of PBI shows an onset potential of -40 mV, while the curve of 301  $MoS_2$  is more positive with a higher onset potential of about -60 mV. Moreover, PBI exhibits 302 a current density of 10 mA cm<sup>-2</sup> at overpotential of -40 mV, which is much smaller than 303  $MoS_2$  (-8 mA cm<sup>-2</sup> at -1.0 V). Possible reasons for different hydrogen generation activities of 304 PBI and MoS<sub>2</sub> can be deduced from the morphological difference (TEM and FE-SEM) and 305 hydrogen generation active sites. PBI has much more active sites (such as pyridinic-N and 306 pyrrolic-N) than MoS<sub>2</sub> and according to the morphological analysis, PBI has several less 307 aggregates than  $MoS_2$ , which cause the open structure for easy electron transfer. In this 308 regard, PBI shows more uniform distribution of nanosheets and nanorods that exposed much 309 more active edges, thus leading to the highest hydrogen generation catalytic activity. 310

In the second part, to developing new electrocatalyst for hydrogen generation, the 311 electrocatalytic activity of the PBI-MoS<sub>2</sub> with different percentage of MoS<sub>2</sub> (1%, 5%, and 312 10% w/w) were investigated. In this regards, liner sweep voltammograms of the 313 electrocatalysts were recorded in a 0.5 M  $H_2SO_4$  aqueous solution, to determine the hydrogen 314 generation activity. The results of LSV studied of PBI-MoS<sub>2</sub> (1%, 5%, and 10% w/w) 315 catalysts are shown in Fig. 8B. As can be seen in the polarization curves, the different 316 percentage of  $MoS_2$  exhibits almost favorable hydrogen generation activity, particularly for 317 10% w/w PBI-MoS<sub>2</sub>. However, when only 10% w/w of MoS<sub>2</sub> nanosheets is added to pure 318 PBI, the onset potential of hybrid catalyst shifts to ~240 mV. Especially, upon the addition of 319 10% w/w of MoS<sub>2</sub>, the overpotential value is close to  $\sim$ 160 mV. Thus, it demonstrates that 320

Page 14 of 29

 $MoS_2$  nanosheets are the core catalyst with abundant active edges for hydrogen generation, 321 while  $MoS_2$  sheets provide a conductive active sites and smaller sizes substrate affording 322 more active edge sites for them. Moreover, with the further addition of  $MoS_2$ , the current 323 density also is improved. "Figure 8 Here". 324

Undoubtedly, identifying the most active site(s) is critical to design and developed 325 improved catalytic materials. In this study, electrocatalytic behaviors suggest that PBI has 326 already carried an adequate load of active MoS<sub>2</sub> nanosheets. According to pervious study,<sup>6</sup> 327 although bulk form of  $MoS_2$  has a poor activity as a hydrogen generation catalyst, but 328 nanoparticulate  $MoS_2$  has high activity for this purpose. Due to achieving the excellent 329 nanoparticulate properties of MoS<sub>2</sub> in PBI matrix, PBI-MoS<sub>2</sub> hybrid catalysts improved 330 electronic contact between the active sites MoS<sub>2</sub> with PBI, thus exhibiting an enhanced their 331 hydrogen generation activities. To clarify, PBI matrix contribute the MoS<sub>2</sub> sheets and 332 nanoparticulates to reach their own exfoliated properties. 333

As an intrinsic properties of the electrocatalyst materials, the Tafel slopes, which is 334 associated with the rate-limiting step of the hydrogen generation, have also been driven from 335 the Tafel plots where their linear portions are fit well with the Tafel equations. For the PBI-336 MoS<sub>2</sub> 10% w/w, the Tafel slope is 50.6 mV dec<sup>-1</sup> which is better than for pure PBI (54 mV 337 dec<sup>-1</sup>). This is due to the fact that the conductivity of pure PBI is very small and it will be 338 activated and increased its catalytic when the active sites and conductive sheets of  $MoS_2$ 339 incorporated with pure PBI's active edges. This result is well consistent with the polarization 340 curves. When the dosage of  $MoS_2$  nanosheets is increased to 10% w/w, as mentioned before, 341 the Tafel slope shifts to 50.6 mV dec<sup>-1</sup> which is comparable to the other  $MoS_2$  catalysts. The 342 hydrogen generation activities data for the proposed nanocomposites and for several recently 343 reported electrocatalysts are compared in Table 3. "Table 3 Here" 344

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#### 3.4. Stability in the long-run

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High durability was another important parameter for a good electrocatalyst. To assess 346 the hydrogen generation stability of the catalysts, long-term potential cycling of PBI-MoS<sub>2</sub> 347 10% w/w catalysts is better than the other synthetic electrocatalysts, when its tested in 0.5 M 348  $H_2SO_4$  at room temperature by taking a potential scan at a scan rate of 20 mV/s, continuously 349 for 1000 cycles. After the end of the cycles, not only any slight loss in the cathodic current 350 was not observed for the PBI-MoS<sub>2</sub> 10% w/w, but also the good stability of the catalysts and 351 rising current density as well as reducing overpotentials was observed in acidic medium. In 352 other words, the almost identical curve (Fig. 9) indicates high stability of PBI-MoS<sub>2</sub> 10%353 w/w in a long-term electrochemical process. Hence these materials can be excellent 354 electrocatalyst for hydrogen generation reaction. "Figure 9 Here" 355

#### 3.5. Electrochemical impedance spectroscopy analysis

To understand the electrochemical behavior of the modified electrodes for hydrogen 357 generation operating circumstance, electrochemical impedance spectroscopy (EIS) tests were 358 conducted for pure PBI and PBI-MoS<sub>2</sub> hybrid (10% w/w). The Nyquist plots of PBI and PBI-359  $MoS_2$  hybrid measured at various negative potentials within the region corresponding to the 360 LSV curves, as shown in Fig. 10. The best fitting was achieved using the Randles circuit ( $R_{s}$ , 361 CPE and R<sub>ct</sub>), and according to the solution resistance (R<sub>s</sub>) in series with two parallel 362 components, the charge-transfer resistance (R<sup>ct</sup>) and a constant phase element (CPE), which 363 is associated with the double layer capacitance. It can be seen that the sequence of the values 364 of R<sub>ct</sub> for the different modified-GCEs are as PBI-MoS<sub>2</sub> < PBI. "Figure 10 Here" 365

#### 4. Conclusions

In summary, we synthesized a polycarboxyl aromatic monomers, 4,4',4''-((1,3,5-367 triazine-2,4,6-triyl)tris(azanediyl))tribenzoic acid, which was utilized to polymerize with 368 1,2,4,5-tetraaminobenzene to achieve a rich nitrogen polybenzimidazole network. The 369 polycondensations could be completed in one-step within a short reaction time and at a 370

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moderately low temperature, using a methane sulfonic acid-phosphorus pentoxide mixture as 371 a medium. Their chemical structures were confirmed by FT-IR, <sup>1</sup>H NMR spectra, elemental 372 analysis, and TGA. TGA results showed that PBI possess excellent thermal stability. Then, a 373 series of organic/inorganic nanohybrid materials consisting of PBI with amorphous MoS<sub>2</sub> 374 nanopalates are prepared by sonochemichal method. FT-IR, XRD, TEM, TGA, and FE-SEM 375 experiments are carried out to characterize the morphologies and properties of the 376 nanohybrids. Finally, the electrochemical behavior of the synthesized PBI and MoS<sub>2</sub> hybrids 377 were evaluated for electrochemical hydrogen generation. By further  $MoS_2$  in PBI matrix, the 378 catalysts improved electronic contact between the active sites MoS<sub>2</sub> with PBI, thus exhibiting 379 an enhanced their hydrogen generation activities. In this regards, the electrochemical studies 380 showed that the obtained nanoelectrocatalys exhibited excellent hydrogen generation 381 activities with an onset potential -160 mV vs. RHE. Large current densities, small Tafel 382 slopes as well as prominent electrochemical durabilities are the main characteristic of these 383 compounds. As the results, the newly proposed protocol opens a potential avenue for the 384 development of high-performance Pt-free hydrogen generation catalysts. 385 Acknowledgements 386 We gratefully acknowledge the partial financial support from the Research Affairs 387 division Isfahan University of Technology (IUT), Isfahan. 388 **Reference:** 389

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Elements	Theoretical	Experimental	Theoretical+16H <sub>2</sub> O
С	65.6	48.90	48.64
Ν	30.6	21.10	22.69
Н	3.6	5.30	5.62
0	0	24.7	23.04

Table 1: The elemental analysis of the PBI

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Table 2: Thermal properties of the PBI and different PBI/MoS<sub>2</sub> hybrids.

	Decom	position	Char	0
Samples	temperature (°C)		yield	LOI
	$T_5^{a}$	$T_{10}^{\ a}$	(%) <sup>b</sup>	
PBI	541	556	71	46
NC1%	566	576	73	46.7
NC5%	574	587	75	47.5
NC10%	581	600	77	48.0

<sup>a</sup> Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 20  $^{\circ}$ C min<sup>-1</sup> in an N<sub>2</sub> atmosphere.

 $^{\rm b}$  Weight percent of the material left undecomposed after TGA at maximum temperature 800  $^{\rm o}C$  in an  $N_2$  atmosphere.

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<sup>c</sup> Limiting oxygen index (LOI) evaluated at char yield at 800 °C.

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 Table 3: Collected hydrogen activity data.

Catalyst	Overpotential (mV versus RHE)	Exchange current density (mA cm <sup>-2</sup> )	Tafel slope (mV decade <sup>-1</sup> )	Reference
MoS <sub>2</sub> /SnO <sub>2</sub>	-187	10	43	42
Exfoliated MoS <sub>2</sub>	>-500	10	70	43
FeS <sub>2</sub> /CNT	-120	20	46	44
MoSe <sub>2</sub> /rGO	-115	10	69	45
PBI	-400	10	54	This work
PBI-MoS <sub>2</sub>	~-160	10	50.6	This work

	495
Legends for the Figures:	496
Fig. 1 Synthesis route to the TCA monomer and PBI networks.	497
Fig. 2 FT-IR of (a): 4,4',4"-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tribenzoic acid (TCA),	498
(b): neat PBI, (c): PBI-MoS <sub>2</sub> 1%w/w, (d): PBI-MoS <sub>2</sub> 5%w/w, (e): PBI-MoS <sub>2</sub> 10%w/w and	499
(f): pure $MoS_{2}$ .	500
Fig. 3 <sup>1</sup> H NMR spectra of PBI. Numbers (1-26) indicate peaks arising from spinning side	501
bands.	502
Fig. 4 TGA curves of PBI, PBI-MoS <sub>2</sub> 1%w/w, PBI-MoS <sub>2</sub> 5%w/w and PBI-MoS <sub>2</sub> 10%w/w.	503
Fig. 5 FE-SEM images of (a and e): MoS <sub>2</sub> , (b and f): PBI,(c and g): PBI-MoS <sub>2</sub> 5%w/w, (d	504
and h): PBI-MoS <sub>2</sub> 10%w/w.	505
Fig. 6 TEM images of (a and b): $MoS_2$ sheets and (c and d): PBI-MoS <sub>2</sub> (5% w/w).	506
Fig.7 XRD pattern of: Commercial MoS <sub>2</sub> , MoS <sub>2</sub> Synthesized, PBI, PBI-MoS <sub>2</sub> 1% w/w, and	507
PBI-MoS <sub>2</sub> 10% w/w.	508
Fig. 8 Linear sweep voltammograms for hydrogen evaluation reaction in 0.5 mol $L^{-1}$ H <sub>2</sub> SO <sub>4</sub>	509
at (A): (a): PBI, (b): amorphous MoS <sub>2</sub> , (B): Linear sweep voltammograms for hydrogen	510
evaluation reaction in 0.5 mol L-1 H <sub>2</sub> SO <sub>4</sub> at (a): PBI-MoS <sub>2</sub> 10% w/w, (b): PBI-MoS <sub>2</sub> 5%	511
,and w/w, (c): PBI-MoS <sub>2</sub> 1% w/w.	512
Fig. 9 Linear sweep voltammograms for long-term electrochemical stability test of PBI-MoS $_2$	513
10% w/w in 0.5 mol $L^{-1}$ H <sub>2</sub> SO <sub>4</sub> at (A): 1th, 200th, 400th, 600th, 800th, 1000th cycles, with a	514
scan rate of 20 mV $s^{-1}$ .	515
Fig. 10 Nyquist plots (from electrochemical impedance spectroscopy data) at (A): PBI	516
modified GCE in different potential vs. Ag/AgCl. Conditions: electrolyte, 0.5 mol $L^{-1}$ H <sub>2</sub> SO <sub>4</sub> .	517
B): Nyquist plots of PBI-MoS <sub>2</sub> (10%w/w) modified GCE in different potential vs. Ag/AgCl.	518
Conditions: electrolyte, 0.5 mol $L^{-1}$ H <sub>2</sub> SO <sub>4</sub> .	519

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530

Page 24 of 29 View Article Online

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Fig. 2

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Fig. 3



Fig. 4

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Fig. 5



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Fig. 8

-0.50

-0.40

-0.30

-0.20

E /V vs. RHE

-0.10

0.00

0.10

-0.7

-1.1

-0.9

-0.5

E /V vs. RHE

-0.3

-0.1

0.1

# Page 28 of 29





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Fig. 10

Graphical Abstract with text	567
High active nitrogen site polybenzimidazole network was synthesized through polycondensation and it was modified	568
with amorphous $MoS_2$ for hydrogen generation.	569

