# CHEMISTRY OF MATERIALS

# Multifunctional Nanohybrids by Self-Assembly of Monodisperse Iron Oxide Nanoparticles and Nanolamellar MoS<sub>2</sub> Plates

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# **Supporting Information**

**ABSTRACT:** Here, we report the synthesis, characterization, and properties of novel nanohybrids formed by self-assembly of negatively charged  $MoS_2$  nanoplates and positively charged iron oxide nanoparticles (NPs) of two different sizes, 5.1 and 11.6 nm. Iron oxide NPs were functionalized with an amphiphilic random copolymer, quaternized poly(2-(dimethyl-amino)ethyl metacrylate-*co*-stearyl metacrylate), synthesized for the first time using atom transfer radical polymerization. The influence of the  $MoS_2$  fraction and the iron oxide NP size on the structure of the nanohybrids has been studied. Surprisingly, larger NPs retained a larger fraction of the copolymer, thus requiring more  $MoS_2$  nanoplates for charge



compensation. The nanohybrid based on 11.6 nm NPs was studied in oxidation of sulfide ions. This reaction could be used for removing the dangerous pollutant from wastewater and in the production of hydrogen from water using solar energy. We demonstrated a higher catalytic activity of the NP/MoS<sub>2</sub> nanohybrid than that of merely dispersed MoS<sub>2</sub> in catalytic oxidation of sulfide ions and facile magnetic recovery of the catalyst after the reaction.

**KEYWORDS:** iron oxide nanoparticles, MoS<sub>2</sub> nanoplates, oxidation of sulfide ion

# 1. INTRODUCTION

Molybdenum disulfide based materials received considerable attention due to interesting catalytic properties<sup>1–8</sup> and applications as lubricants.<sup>9–13</sup> Molybdenum disulfide has a layered crystal structure formed by stacking of S–Mo–S monolayers. van der Waals gaps between these layers allow for their separation, leading to crystal exfoliation<sup>14</sup> or formation of inclusion compounds.<sup>15</sup> In the former case, these monolayers can be used for the formation of thin platelets or films of MoS<sub>2</sub> or for the formation of various hybrid structures using organic molecules,<sup>16</sup> metal complexes,<sup>17</sup> hydroxides,<sup>18</sup> and oligocations.<sup>19</sup>

For exfoliation of  $MoS_2$  in aqueous media, dispersion to single layers is used.<sup>14</sup> It includes the steps of the lithium intercalation between  $MoS_2$  layers that is accompanied by a negative charge transfer on these layers, followed by hydration of the lithium cations, leading to exfoliation. It results in formation of the ionic system containing negatively charged  $MoS_2$  layers, lithium cations, and hydroxide anions (eq 1).<sup>18</sup>

$$MoS_{2} \xrightarrow{\text{Li}^{+},e^{-}} \text{Li}^{+}(MoS_{2})^{-}$$
$$\xrightarrow{\text{H}_{2}O} [\text{Li}^{+} + (MoS_{2})^{x-} + (1-x)OH^{-}]_{aq}$$
(1)

It is noteworthy that, in the case of layered MoS<sub>2</sub>-based materials obtained from single-layer MoS<sub>2</sub> dispersions, guest molecules may position themselves between the MoS<sub>2</sub> layers, forming the material with regularly spaced MoS<sub>2</sub> monolayers and guest molecules.<sup>2,16–18,20–25</sup> The distance between layers compared to parent MoS<sub>2</sub>, that is, interlayer expansion,  $\Delta c$ , depends on the guest molecule size. For example, in the case of sufficiently bulky clusters, it reached ~1.5 nm.<sup>17</sup> Even the higher  $\Delta c$  value (2–3 nm) was observed in the case of surfactants that are able to create self-assembled layers in the interlayer space of MoS<sub>2</sub>.<sup>24,25</sup>

Recently, a number of  $MoS_2$ -based nanohybrids have been synthesized using carbon nanotubes,<sup>26,27</sup> TiO<sub>2</sub>,<sup>28</sup> CdS,<sup>29</sup> Ag,<sup>30</sup> Au,<sup>31</sup> Pd,<sup>32</sup> and Pt<sup>32</sup> nanoparticles (NPs) that can be promising

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Figure 1. TEM images of NPs1 (a), NPs2 (b), and exfoliated MoS<sub>2</sub> (c).

for catalytic and optoelectronic applications. It is worth noting that the structure of nanohybrids is dependent on the conditions of the hybrid synthesis and the size of nanoparticles. For example,  $MoS_2$  layers can envelope the carbon nanotube<sup>26</sup> or  $MoS_2$  nanoribbons can be imbedded inside the carbon nanotube.<sup>27</sup> TiO<sub>2</sub> NPs of 1 nm in diameter were perfectly imbedded within the MoS<sub>2</sub> lamellar structure.<sup>28</sup> In ref 29, it was claimed that incorporation of much larger, 6.5 nm CdS, NPs between the MoS<sub>2</sub> layers also preserved the MoS<sub>2</sub> lamellar ordering, but because the distance between the MoS<sub>2</sub> sheets was not estimated, there was no proof of CdS NP incorporation. Exfoliated MoS2 monolayers have been used as substrates for dispersed magnetic materials;<sup>33</sup> however, to the best of our knowledge, there are no examples in the literature where monodisperse magnetic NPs would be used in conjunction with MoS<sub>2</sub>. The incorporation of magnetic nanoparticles in the composite catalysts allows easy catalyst recovery and multiple repeated uses due to facile magnetic separation.34-36

In this paper, we report the synthesis, characterization, and properties of novel nanohybrids formed by  $MoS_2$  nanoplates and iron oxide NPs of two different sizes. Iron oxide NPs were functionalized with an amphiphilic copolymer, quaternized poly(2-(dimethylamino)ethyl metacrylate-*co*-stearyl metacrylate) (poly(DMAEMQ-*co*-SMA), synthesized for the first time for this project. We studied the influence of  $MoS_2$  fraction and iron oxide NP size on the structure of the nanohybrids. We demonstrated promising catalytic activity of these nanohybrids in catalytic oxidation of sulfide ions and facile magnetic recovery of the catalyst after the reaction.

#### 2. EXPERIMENTAL SECTION

Iron oxide NPs prepared by thermal decomposition of iron acetyl acetonate or iron oleate were coated with quaternized (by dimethyl sulfate) poly(DMAEM-*co*-SMA) using a modified procedure describe in ref 37. The NP/MoS<sub>2</sub> nanohybrids have been prepared by mixing aqueous dispersions of both polymer-coated NPs and freshly prepared  $MoS_2$  single layers at different weight ratios of the components. All other experimental details are presented in the Supporting Information.

#### 3. RESULTS AND DISCUSSION

**3.1.** NPs Coated with N-Methylated Poly(DMAEMQco-SMA). To assess the influence of the iron oxide NP size on the NP self-assembly with single-layer  $MoS_2$  nanoplates, two NP samples have been used, NPs1 and NPs2, whose diameters significantly differ:  $5.1 \pm 0.4$  and  $11.6 \pm 0.8$  nm, respectively. In both cases, the NPs synthesized are monodisperse as their standard deviations are below 10% (7.8% for NPs1 and 6.9% for NPs2).

Figure 1 shows TEM images of both NP samples and MoS<sub>2</sub> nanoplates obtained by restacking of exfoliated molybdenum

sulfide layers in the absence of NPs. The histograms of the NP sizes and information on the sizes of  $MoS_2$  nanoplates are presented in the Supporting Information.

It is noteworthy that the as-synthesized iron oxide NPs used in this work are coated with oleic acid and thus are hydrophobic. To make them hydrophilic and water-soluble, they can be functionalized with various amphiphilic molecules, including copolymers.<sup>38–40</sup> In this case, the hydrophobic tails on the iron oxide NP surface are not replaced with functionalizing molecules but rather are employed in the formation of a hydrophobic shell that is connected to the hydrophilic shell in the NP exterior formed by the hydrophilic part of an amphiphilic copolymer. It is noteworthy that, to form composites of NPs with exfoliated MoS<sub>2</sub> nanoplates, the Li cations in LiMoS<sub>2</sub> should be replaced with other cationic species; therefore, the NPs used should be positively charged. In this case, the major advantage of the copolymer coatings compared to surfactants, such as CTAB,<sup>41</sup> is the coating stability due to cooperative interactions of polymer units.

Thus, to form positively charged iron oxide NPs, they were coated with the poly(DMAEMQ-*co*-SMA) copolymer containing cationic groups to allow for ionic interactions with the monolayered  $(MoS_2)^{x^-}$  polyanion. This copolymer was synthesized by atom transfer radical copolymerization<sup>42,43</sup> of hydrophilic DMAEM and hydrophobic SMA to obtain a desirable molecular weight and narrow molecular weight distributions. The amino group of DMAEM was then quaternized by N-methylation with Me<sub>2</sub>SO<sub>4</sub> to convert the amino group to the ammonium group. The copolymer structure is presented in Scheme 1.

# Scheme 1. Structure of the Poly(DMAEMQ-co-SMA) Random Copolymers



The TEM images of coated NPs1c and NPs2c are presented in Figure 2. In both cases, the NPs are well dispersed on the TEM grid. The histograms of the coated NP sizes are presented in Figure S2 in the Supporting Information. They indicate that the particle sizes are  $5.3 \pm 0.5$  and  $12.5 \pm 0.6$  nm for NPs1c and NPs2c, respectively, which are within experimental errors of the initial NPs.

Taking into account NP sizes and magnetite density, we calculated the weight of a single particle, the NP amount in 1 g of the sample, and the number of copolymer macromolecules



Figure 2. TEM images of NPs1c (a) and NPs2c (b) coated with poly(DMAEMQ-co-SMA).

on each NP. The last values are 4.6 and 84.9 for NPs1c and NPs2c, respectively. The difference in the amount of macromolecules on a single NP surface for NPs1c and NPs2c seemed to be striking; however, when we calculated the amount of copolymer macromolecules per 1 nm<sup>2</sup>, these values are 0.056 and 0.201, that is, rather comparable, but indicate a denser coating for the NPs2c sample due to low curvature of NPs2.<sup>44</sup> This is further confirmed by the  $\zeta$ -potential measurements. The  $\zeta$ -potential values for NPs1c and NPs2c are 31.3 and 41.1 mV, respectively, indicating the higher charge density for the latter NPs.

The structure of NPs was assessed using XRD. The XRD profiles of NPs1 before and after coating with the copolymer are presented in Figure 3. According to the literature,<sup>45</sup> the NPs



Figure 3. XRD patterns of NPs1 before (a) and after (b) coating.

prepared by thermal decomposition of  $Fe(acac)_3$  in the conditions described in the Experimental Section should have a magnetite structure. Indeed, the XRD profile presented in Figure 3a shows a typical pattern for  $Fe_3O_4$  NPs.<sup>46</sup> Moreover, transfer of these NPs into water after coating with the copolymer does not change the XRD pattern (Figure 3b). It is noteworthy, however, that, due to line broadening, XRD does not allow one to distinguish between magnetite and maghemite

NPs.<sup>47</sup> In the case of the NPs2 sample, the XRD profile of asprepared NPs (Figure S4a, Supporting Information) demonstrates both wüstite (FeO) and spinel (presumably, magnetite) signals, as was demonstrated in our preceding papers.<sup>48,49</sup> After coating of NPs2 with the copolymer in water (the NPs2c sample), the XRD profile (Figure S4b, Supporting Information) shows more pronounced reflections of the spinel phase, revealing partial NP oxidation in water. We assume that, due to mild conditions of coating, the Fe<sub>3</sub>O<sub>4</sub> (not  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) phase is formed.

3.2. Formation of Nanohybrids of MoS<sub>2</sub> Nanoplates and Iron Oxide NPs Coated with the Copolymer. 3.2.1. The Influence of the NP Size on the Formation of Nanohybrids. To identify the influence of the NP size on the hybrid formation, we compared the hybrids prepared at the equal amounts (by weight) of both components. To estimate whether all NPs are incorporated in the nanohybrid, the reaction solutions, including nanohybrid precipitates and supernatants, were used for TEM studies (Figure 4). Please note that the dark gray areas in the TEM images represent MoS<sub>2</sub> nanoplates, whereas darker circles are iron oxide NPs. TEM images presented in Figure 4a,b show a comparatively uniform distribution of NPs through nanohybrids for both NP sizes. Moreover, in both cases, the majority of NPs are imbedded in the nanohybrid. At the same time, for smaller NPs (Figure 4a), the NP density in the hybrid is higher than that for larger NPs (Figure 4b). Figure 4c, displaying the TEM image of the NPs2c/MoS<sub>2</sub> sample at a higher magnification, shows that formation of multilayer MoS<sub>2</sub> nanoplates in the hybrid also takes place.

The XRD pattern of the NPs1c/MoS<sub>2</sub> nanohybrid is shown in Figure 5. This profile includes the reflections from both dispersed MoS<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>. The position of the (002) reflection, which is characteristic of the distance between the MoS<sub>2</sub> layers, is the same for both NPs1c/MoS<sub>2</sub> and dispersed MoS<sub>2</sub>, indicating the absence of regular insertion of NPs in the interlayer space. In addition, a weak reflection in the small angle region is present, indicated by an arrow in Figure 5, which matches an interplanar distance of ~1.16 nm. It is similar to the interplanar distance of layered MoS<sub>2</sub> compounds with small guests, such as alkyl ammonium cations.<sup>24,25</sup> In this case, the guest thickness  $\Delta c$  is ~0.54 nm. Probably, a small fraction of a copolymer present in the NP solution is incorporated in MoS<sub>2</sub>.

Although XRD does not indicate regular incorporation of NPs in the  $MoS_2$  interlayer voids, we carried out a TEM study using cross sections of the NPs1c/MoS<sub>2</sub> and NPs2c/MoS<sub>2</sub> nanohybrids to take a closer look at the nanohybrid structures (Figure 6). The TEM image of the nanohybrid with 11.6 nm NPs (Figure 6a) shows a few NPs that are imbedded between the MoS<sub>2</sub> layers, as is indicated by red arrows. In the case of the NPs1c/MoS<sub>2</sub> nanohybrid based on 5.1 nm NPs (Figure 6b), numerous NPs are located between the MoS<sub>2</sub> nanoplates.

Although regular penetration of NPs between the adjacent  $MoS_2$  layers does not take place, the layer number in  $MoS_2$  nanoplates is relatively small. To evaluate this value, the mean thickness of the  $MoS_2$  nanoplates in the nanohybrids was calculated from the integral breadth of the  $MoS_2$  (002) reflections in the XRD patterns following the procedure described elsewhere.<sup>50</sup> The thickness amounts to 4.4 nm (seven  $MoS_2$  monolayers) and 4.8 nm (eight monolayers) for nanohybrids with NPs1 and NPs2, respectively. These values are ~2.5 times smaller than those for restacked  $MoS_2$  nanoplates in the absence of iron oxide NPs (see the



Figure 4. TEM images of NPs1c/MoS<sub>2</sub> (a) and NPs2c/MoS<sub>2</sub> (b, c) prepared at the NPs:  $MoS_2$  weight ratio equal to 1:1. Inset shows higher magnification image with a multilayer  $MoS_2$  stacking, indicated by blue arrow.



**Figure 5.** XRD profiles of crystalline  $MoS_2$  (molybdenite) (a), dispersed  $MoS_2$  precipitated from a single-layer dispersion (b), and NPs1c/MoS<sub>2</sub> prepared at equal amounts of the two components (c). Vertical lines show positions of the most intense reflections of Fe<sub>3</sub>O<sub>4</sub>. The arrow indicates a low intensity reflection of the additional phase with the interplanar distance of ~1.16 nm.

Supporting Information) due to self-assembly with positively charged NPs.

In the above experiments, freshly prepared solutions of  $MoS_2$  nanoplates were used in the formation of nanohybrids, because  $MoS_2$  nanoplates are able to lose charge and aggregate upon storage. To ensure that such aggregation did not take place in our case, dispersal of LiMoS<sub>2</sub> was also carried out directly in the

aqueous solution of NPs1c (with equal amounts of the two components) to minimize the time between exfoliation of the  $MoS_2$  nanoplates and their contact with positively charged NPs. The TEM image presented in Figure S5 (Supporting Information) shows the absence of free NPs1c and a much denser nanohybrid structure than that shown in Figure S6a (Supporting Information). Apparently, such exfoliation leads to formation of a multilayer nanohybrid; however, its XRD profile does not differ from that shown in Figure 5, pattern c. The TEM image of the cross section of this nanohybrid (not shown) does not show incorporation of NPs between the  $MoS_2$  nanoplates, unlike the NPs2c/MoS<sub>2</sub> nanohybrid prepared in the regular way and shown in Figure 6a. Apparently, too fast an interaction between exfoliated in situ  $MoS_2$  nanoplatelets and iron oxide NPs leads to a higher degree of disorder.

3.2.2. The Influence of the Component Ratio on the Nanohybrid Formation. We tested the influence of the ratio of the two components, that is, NPs coated with the copolymer and  $MoS_2$  nanoplates, on the nanohybrid formation using a 10-fold and a 5-fold excess of both components along with equal amounts (see discussion above). Note that, in this case, supernatants were also not removed from reaction solutions to estimate the degree of the NP inclusion in nanohybrids. TEM images of the NPs1c/MoS<sub>2</sub> and NPs2c/MoS<sub>2</sub> nanohybrids at different component ratios are shown in Figure S6 (Supporting Information) and Figure 7.

Figure 7 clearly shows that, at the high NP/MoS<sub>2</sub> weight ratios (10:1 and 5:1), a considerable amount of NPs is not incorporated in the nanohybrids, whereas at the low weight ratios (1:5 and 1:10), all NPs are integrated with  $MoS_2$  nanoplates. In the case of equal amounts of NPs and  $MoS_2$ 



Figure 6. TEM images of the NPs2c/MoS<sub>2</sub> (a) and NPs1c/MoS<sub>2</sub> (b) nanohybrid cross sections. Red arrows indicate NPs located in between  $MoS_2$  layers.



Figure 7. TEM images of the NPs2c/MoS<sub>2</sub> nanohybrids at the NP/  $MoS_2$  weight ratios of 10:1 (a), 5:1 (b), 1:5 (c), and 1:10 (d).

(Figure 4b,c), some NPs are not included in the nanohybrid. For the NPs1c/MoS<sub>2</sub> sample formed with smaller NPs, the significant amount of NPs are not incorporated for the NP/ MoS<sub>2</sub> weight ratios of 10:1 and 5:1 (the images are not shown), whereas at the 1:1, 1:5, and 1:10 NP/MoS<sub>2</sub> weight ratios, all NPs are incorporated. This difference between NPs1c/MoS<sub>2</sub> and NPs2c/MoS<sub>2</sub> at equal amounts of the components should be attributed to the ability of negatively charged MoS<sub>2</sub> to compensate the total positive charge of NPs in the reaction solution. Because the NPs2c specimen contains more copolymer than NPs1c (see section 3.1 and the Supporting Information), the former sample comprises more positive charges and requires more MoS<sub>2</sub> nanoplates. This means that the formation of nanohybrids is governed by self-assembly due to electrostatic interactions.

Unlike 1 nm TiO<sub>2</sub> NPs,<sup>28</sup> in our case, the iron oxide NPs do not insert between the individual MoS<sub>2</sub> nanoplates in a regular manner due to large NP sizes (5.1 and 11.6 nm), but consistently attach on the surface of the MoS<sub>2</sub> plates. It is worth noting, however, that, for both NP sizes, at the lowest NP content (1:10), uneven distribution of NPs is observed (Figure 7, curve d, and Figure S6c, Supporting Information), revealing cooperative interaction of NPs between each other on the MoS<sub>2</sub> nanoplate surface, which can be due to magnetic interactions.

**3.3. Catalytic Oxidation of Sulfide Ions Using NPs2-c/ MoS<sub>2</sub>.** Oxidation of sulfide ions in water is a robust way for removing this dangerous pollutant from wastewater.<sup>19</sup> MoS<sub>2</sub>- based materials are known to catalyze this reaction, exhibiting both catalytic and photocatalytic activities that correlate generally with each other.<sup>19</sup> Another photocatalytic property of MoS<sub>2</sub> is production of hydrogen from water using solar energy.<sup>51</sup> In this process, the oxidation of sulfide ions can also play an important role because sodium sulfide is used in some water splitting systems as a sacrificial, hole-consuming reagent.<sup>52</sup>

As a proof of concept that NPs/MoS<sub>2</sub> nanohybrids can be magnetically recoverable catalysts, we carried out sulfide ion oxidation. The NPs2c/MoS<sub>2</sub> nanohybrid for catalytic testing was prepared at equal amounts of the two components similar to that shown in Figure 4b,c, but with removal of supernatants containing nonembedded NPs. The elemental analysis of the nanohybrid is given in the Experimental Section.

For catalytic tests, we used conditions described in ref 19 in the absence of light. We carried out a series of experiments with NPs2c/MoS<sub>2</sub>, taking advantage of a magnetically responsive catalyst and using magnetic separation for the catalyst recovery for repeated uses. Figure S7 (Supporting Information) shows separation of the catalyst with a rare earth magnet in 30 s after sonication, demonstrating a high magnetic response. We compared the catalytic activity of NPs2c/MoS<sub>2</sub> with that of the dispersed and crystalline MoS<sub>2</sub> samples. We also carried out a control experiment with NPs2c to evaluate a possible contribution from iron oxide to catalytic activity. The results of the Na<sub>2</sub>S oxidation are summarized in Table 1. The activities of the catalysts were expressed as initial oxidation rate in mmol/ min, which does not take into account the MoS<sub>2</sub> content in the sample and as turnover frequency (TOF), which does. For NPs2c/MoS<sub>2</sub>, TOF was calculated using the Mo content found from elemental analysis. For NPs2c, TOF was calculated from 38 wt %  $Fe_3O_4$  content in NPs2c. The initial rates were determined from the initial part of the dependences of the oxygen consumption on time (Figure 8) as a result of numerical differentiation of the curve spline approximation at zero time.

Table 1 demonstrates that dispersed  $MoS_2$  exhibits significantly higher activity than that of crystalline  $MoS_2$ , which can be attributed to a much higher specific surface area of exfoliated  $MoS_2$  and improved hydrophilic properties. Indeed, the BET surface areas for crystalline and dispersed  $MoS_2$  are 6.1 and 14.3 m<sup>2</sup>/g, respectively, which is consistent with values published elsewhere.<sup>53</sup> This catalyst also shows the highest initial oxidation rate, yet the catalytic activity of NPs2c/  $MoS_2$  expressed as TOF is noticeably higher compared to that of dispersed  $MoS_2$ . Moreover, the TOF was only slightly reduced (by about 4%) after the first and second reuses, demonstrating stability of the catalyst and easy recovery due to magnetic separation.

Table 1. Results of the Na<sub>2</sub>S Catalytic Oxidation with Oxygen Using NPs2c/MoS<sub>2</sub> and MoS<sub>2</sub> as Catalysts<sup>a</sup>

sample	amount, mg	initial oxidation rate, mmol/min $\times 10^{-3}$	TOF, $sec^{-1} \times 10^{-3}$
NPs2c/MoS <sub>2</sub> <sup>b</sup>	6.4	$2.19 \pm 0.01$	$1.83 \pm 0.01$
First reuse of NPs2c/MoS <sub>2</sub>		$2.12 \pm 0.04$	$1.77 \pm 0.03$
Second reuse of NPs2c/MoS <sub>2</sub>		$2.10 \pm 0.02$	$1.75 \pm 0.02$
crystalline MoS <sub>2</sub>	20.2	$1.13 \pm 0.01$	$0.15 \pm 0.01$
dispersed MoS <sub>2</sub> <sup>c</sup>	7.4	$3.11 \pm 0.03$	$1.12 \pm 0.02$
NPs2c	2.9	$0.22 \pm 0.01$	$0.77 \pm 0.03$

<sup>*a*</sup>0.1 M solution Na<sub>2</sub>S in water, 25 °C. <sup>*b*</sup>MoS<sub>2</sub> content is 50.0% based on the elemental analysis data on Mo (29.95%) <sup>*c*</sup>Obtained by precipitation of MoS<sub>2</sub> single-layer dispersion in the absence of NPs.



Figure 8. Dependences of oxygen consumption on time in the NaS<sub>2</sub> oxidation catalyzed by NPs2c/MoS<sub>2</sub> (a), first reuse of NPs2c/MoS<sub>2</sub> (b), second reuse of NPs2c/MoS<sub>2</sub> (c), crystalline MoS<sub>2</sub> (d), dispersed MoS<sub>2</sub> (e), and NPs2c (f).

The possible cause of the activity enhancement is the influence of iron oxide NPs, and this influence can be 2-fold. As is demonstrated by the control experiment with NPs2c, iron oxide NPs certainly contribute to the catalytic activity. This leads to overestimation of the nanohybrid TOF calculated, taking into account only the  $MoS_2$  contribution. Unfortunately, the exact assessment of the activity contributions from both components in the nanohybrid is hardly possible due to their possible mutual influence. However, we can estimate this influence of each component comparing the joint activity in the nanohybrid with their separate activities. Because the initial rate of the oxygen consumption (V) can be expressed as  $V = TOF \times g$ , where g is the molar amount of the catalyst, then in the case of a simple summation of their activities, the following equation should be valid

$$V_{\rm nh}/(g_{\rm Mo} + g_{\rm NP}) = {\rm TOF}_{\rm Mo} \times f_{\rm Mo} + {\rm TOF}_{\rm NP} \times f_{\rm NP}$$
(2)

where  $V_{\rm nh}$  is the rate of the oxygen consumption in catalysis with the nanohybrid,  $g_{Mo}$  and  $g_{NP}$  are the molar amounts of its components, and  $f_{Mo}$  and  $f_{NP}$  are their molar fractions in the nanohybrid. Thus, the TOF of the nanohybrid should be equal to the sum of contributions of each component. From the elemental analysis data, the molar fraction of MoS<sub>2</sub> in the nanohybrid is  $f_{M_0} = 20.00 \times 10^{-3}/25.25 \times 10^{-3} = 0.792$ . From eq 2, using the TOF values of individual components, the TOF contribution from MoS<sub>2</sub> is  $1.45 \times 10^{-3}$  s<sup>-1</sup>, whereas the TOF contribution from NPs is  $1.05 \times 10^{-3} \text{ s}^{-1}$ . In both cases, the error does not exceed  $0.03 \times 10^{-3}$  s<sup>-1</sup>. Thus, the TOF of the nanohybrid is higher than that of dispersed MoS<sub>2</sub> by nearly a factor of 1.4, revealing synergism between MoS<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>. The catalytic activity enhancement in the presence of iron oxides as supports in photocatalytic processes was observed by others and attributed to a charge transfer.54,55 Thus, the NPs2c/MoS<sub>2</sub> nanohybrid has the higher catalytic activity than merely dispersed MoS<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>, which allows easy catalyst recovery and successful repeated uses.

# 4. CONCLUSION

We developed novel nanohybrids based on positively charged iron oxide NPs and negatively charged exfoliated MoS<sub>2</sub> nanoplatelets. To provide positive charges, hydrophobic iron oxide NPs were functionalized using a specially designed random copolymer of hydrophilic N-methylated DMAEM and hydrophobic SMA units. This copolymer allowed water solubility and positive charges, which were required for selfassembling with  $MoS_2$  nanoplates due to electrostatic interactions. We determined that incorporation of iron oxide NPs into a nanohybrid depends on the NP size and the ratio of two components. The NPs2c/MoS<sub>2</sub> nanohybrid formed at the equal weight ratios of two components showed promising catalytic properties in catalytic oxidation of sulfide ions and facile magnetic recovery of the catalyst after the reaction.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Experimental details, histograms of NP sizes, TGA traces, XRD patterns, TEM images, and a photograph of magnetic separation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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# **Author Contributions**

The manuscript was written through contributions of all authors.

## Notes

The authors declare no competing financial interest.

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