

# Aggregation-induced Improvement of Catalytic Activity of Metal-fullerene-based Surfactants used in Water Splitting Reaction

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**ABSTRACT:** An inherent paradigm of molecular compounds used in homogeneous catalysis is that maximum performance requires maximum dispersion, and that any form of aggregation results in a loss of activity. We here present a new concept based on surfactants with functional heads, which become better catalysts when they aggregate. The head group of the surfactants is composed of a diethylenetriamine-functionalized fullerene, which coordinates Co<sup>II</sup> ions. This system is applied as an electrocatalyst for the water-splitting reaction. Detailed electrochemistry studies were performed at concentrations below and above the critical aggregation concentration (cac), when 150 nm sized vesicles are formed. While isolated surfactant molecules represent only moderately active catalysts, drastic improvement in the hydrogen evolution (HER) as well as in the oxygen evolution reactions (OER) were detected for the vesicular structures. Self-organization of the surfactants leads to an increase in turnover frequencies of up to 1300% (HER). We show that the strongly beneficial effect of aggregation arises from the favorable alignment of individual molecules, thus facilitating intermolecular charge transfer processes in the vesicles.

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The limited availability of fossil fuels and the energy demands of growing economies, besides many other good reasons, make the provision of alternative resources inevitable. A crucial advantage of chemical fuels over electricity from solar or wind power is that they can be stored better and distributed using the existing infrastructure. Hydrogen is commonly considered the best among the various candidates as fuels, since hydrogen fuel-cells have reached a high level of development and hydrogen consumption does not produce any undesired waste. Moreover, hydrogen is highly abundant in the earth crust, dominantly in the form of water. As a consequence, huge efforts during the last decades were directed at exploring and developing different realizations of the water splitting reaction, resulting in H<sub>2</sub> (hydrogen evolution reaction; HER) and O<sub>2</sub> (oxygen evolution reaction; OER).<sup>1-3</sup> Electrolysis of H<sub>2</sub>O, while being capable to effect water splitting on an industrial level, is energy-intensive due to the underlying thermodynamics. One crucial task is to minimize overpotentials. It is therefore very important to develop suitable electrocatalytic systems that address this issue.<sup>4-7</sup> The present paradigm is that maximum dispersion is critical for achieving high activity, no matter if the investigated system is a molecular catalyst operating in the homogeneous phase or a heterogeneous catalyst operating in the solid phase. For almost any known catalytic system, aggregation is detrimental to performance

as it diminishes a catalyst's activity. We here present a new concept that builds on a surfactant-based system, which defies this paradigm by showing substantial increase of activity on aggregation.

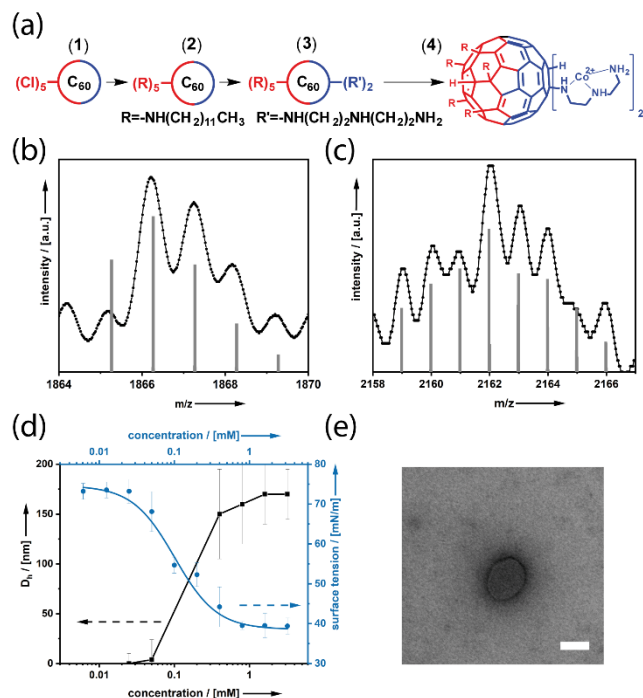
Surfactants are molecular compounds with amphiphilic properties, which form well-defined aggregates. Depending on concentration, individual surfactant molecules self-assemble into micelles, vesicles or liquid crystals. Recently, more and more papers describe advanced surfactants with properties reaching beyond simple amphiphilic properties.<sup>8-9</sup> Surfactant systems possessing catalytic properties are good examples,<sup>10-13</sup> and the potential of improving catalysis in micellar media was discussed in 2015 by La Sorella *et al.*<sup>14</sup> Our group has specialized in the synthesis of surfactants equipped with functional, metal-containing head groups,<sup>15-18</sup> and several examples of catalytically active surfactants have already been published by us.<sup>19-20</sup> Important preliminary work of relevance to the current work is centered on fullerene-based surfactants.<sup>21-23</sup> Fullerenols are multiply hydroxylated fullerenes (C<sub>60</sub> in most cases), which are soluble in water.<sup>24-26</sup> We use an approach, which allows one to modify only one hemisphere of C<sub>60</sub> with OH groups, whereas hydrophobic groups are attached to the other hemisphere; this gives rise to surfactant properties. For instance, in ref. 23 we have attached five dye-molecules, and the resulting compounds were active in the photocatalytic conversion of CO<sub>2</sub>.

In the current work, we aimed at developing a new system, which is equipped with moieties that are capable of effecting electrocatalytic water splitting,<sup>27-28</sup> but with a fullerene-based surfactant design. Particular focus is on the role of self-assembly on catalytic activity.

The major synthesis steps leading to our target system are depicted in **Fig. 1a**. The asymmetrical, pentachlorinated C<sub>60</sub><sup>29</sup> (**1**) is reacted with dodecylamine to obtain the penta-alkylated compound (**2**). Diethylenetriamine is then attached to the remaining hemisphere to obtain the ligand modified species (**3**). It is used as a ligand for complexation of cobalt(II)chloride to obtain the final product (**4**) (see Supporting Information for detailed synthesis procedure and characterization, **Fig S1**). **Fig. 1b,c** shows the characteristic signals for the organic ligand before (**3**) and after coordination to cobalt (**4**) in electrospray ionization time of flight mass spectrometry (ESI-TOF MS) data of characteristic signals for the organic ligand before (**3**) and after coordination to cobalt (**4**). Successful coordination of Co<sup>II</sup> ions was also proven by UV/Vis spectroscopy, which, in addition to the absorption of the fullerene core, showed the d-d transition band of a Co(II) triamine chelate with a maximum at 480 nm (**Fig. S1**).

The amphiphilic properties of (**4**) were investigated by recording concentration dependent surface tension  $\gamma(c)$ . The corresponding

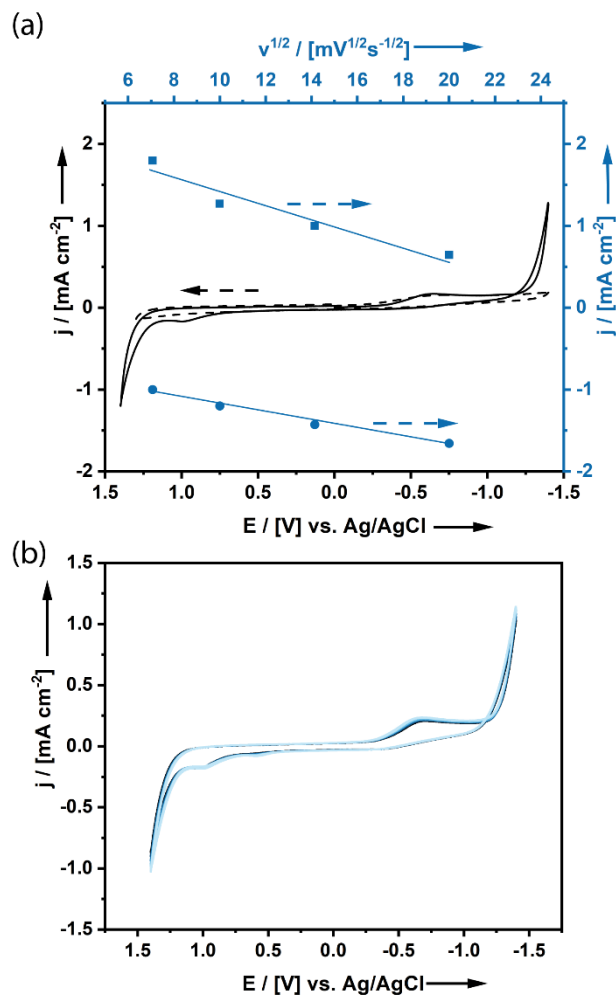
plot shows a shape, (see **Fig. 1d**), which is typical of surfactants. The position of the kink in the  $\gamma(c)$  curve indicates that aggregation commences at a concentration  $c_{ac}$  of approximately 0.2 mM. Aggregation has also been confirmed by dynamic light scattering (DLS). The aggregate sizes determined from DLS are shown in **Fig. 1d**. There were no aggregates found at low concentration, and above  $c_{ac}$  aggregates with a hydrodynamic diameter  $D_H = 150$  nm appear (**Fig. S2**). Analysis of these aggregates using transmission electron microscopy (TEM; **Fig. 1e**) confirms that surfactant (**4**) forms vesicular structures rather than micelles, which is common for fullerene-based surfactants.<sup>21, 23</sup>



**Figure 1.** (a) Synthesis scheme for amphiphilic metal-fullerene-based catalyst (**4**). (b) ESI-TOF MS data of the organic ligand (**3**; black dots) and simulation of the molecular ion peak  $[M]-(H^+)+(H_2O)=1866.23$  g/mol (grey bars) and (c) of the surfactant (**4**; black dots) and simulation of the molecular ion peak  $[M]+(Cl^-)+(H_2O)=2161.98$  g/mol (grey bars). (d) Concentration-dependent aggregate size (black) and surface tension (blue). (e) TEM micrograph of a vesicle formed by (**4**) above the  $c_{ac}$ ; scalebar = 100 nm.

Detailed cyclic voltammetry (CV) measurements were performed to evaluate the redox properties and the electrocatalytic activity of surfactant (**4**) in the water-splitting reaction. First studies were performed at concentrations below  $c_{ac}$  as the reference state ( $c = 0.025$  mM; pH = 7) (**Fig. 2a**). The pure organic compound (**3**) is, as expected, catalytically inactive. The redox behavior of the solution in the presence of the Co-containing surfactant (**4**) is significantly different. There are strongly increased currents at onset potentials of +1180 mV for OER and -1260 mV for HER, which are both accompanied by strong gas formation. The voltammogram of (**4**) displays a partially reversible reduction signal at a half-wave potential  $E_{1/2} = -460$  mV, which is a feature belonging to the fullerene-based ligand. Furthermore, it contains a partially reversible oxidation at  $E_{1/2} = +870$  mV which can be assigned to the Co(II) to Co(III) oxidation. Current densities remain unchanged on repetitive cycling, thus confirming the stability of the system and that the incomplete reversibility of the waves is due to the initiation of OER or HER, respectively, but not to catalyst degradation on oxidation or reduction (**Fig. 2b**). In order to quantify the catalyst's properties in more detail, we calculated the turnover frequency (TOF), assuming a

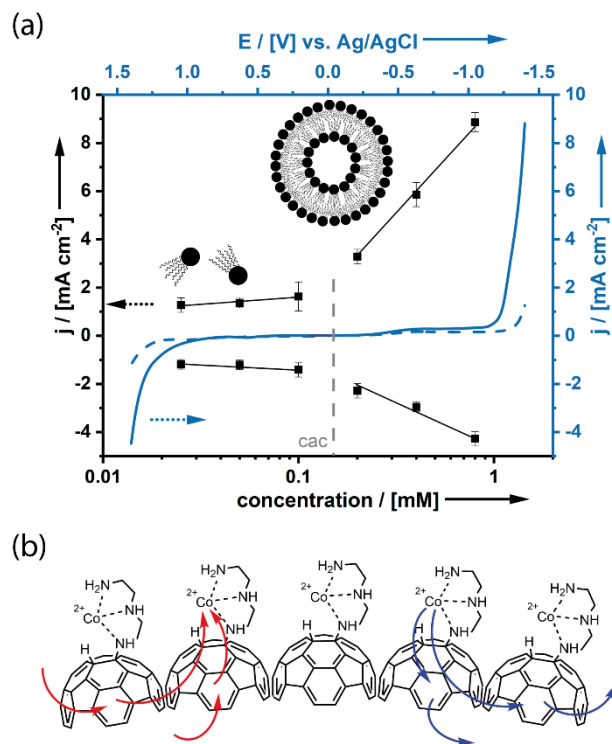
pseudo-first-order catalytic model (**Fig. S3**).<sup>30-32</sup> Evaluation of the data results in  $TOF(OER)_{1400mV} = 57 \pm 10$  s<sup>-1</sup> and  $TOF(HER)_{1400mV} = 25 \pm 10$  s<sup>-1</sup>, which indicates an only medium activity compared to other electrocatalysts known in the literature. The Randles-Sevcik plot depicted in **Fig. 2a** shows a linear increase of the current density with the square root of the scan rate  $\nu$  for OER, indicating a diffusion controlled process. However, the value of current density for HER decreases with increasing  $\nu$ , which indicates that the catalytic process is kinetically slow. As the cyclic voltammograms of (**4**) do not show a wave for cobalt(II) to cobalt(I) reduction, which would be expected at ca. -1000 mV, but solely a ligand reduction, one must assume that the fullerene-DETA ligand acts as a non-innocent ligand, similar to the compounds presented by Haddad et al.<sup>33-34</sup> In a metal centered, ligand assisted mechanism the ligand serves as electron reservoir whereas the catalytic reaction itself takes place at the metal ion (**Fig. S4**).



**Figure 2.** (a) CV measurement (black) and Randles-Sevcik plot (blue; OER = circles; HER = squares) of (**4**) at 0.025 mM compared to the CV of the organic ligand (**3**; dashed line). (b) CV scan over 20 cycles (dark blue = start; light blue = cycle 20).

The central issue of this work is unravelling the dependency of the catalytic properties on the level of aggregation. Consequently, we performed analogous electrochemical investigations at various concentrations, including  $c > c_{ac}$  (**Fig. 3a**). As long as the surfactant concentration remains below  $c_{ac}$ , there is only an insignificant change in HER and OER-related current density at 1400 mV or -1400 mV, respectively. There is, however, a tremendous increase of current density for  $c > c_{ac}$ . The slope of OER changes by a factor

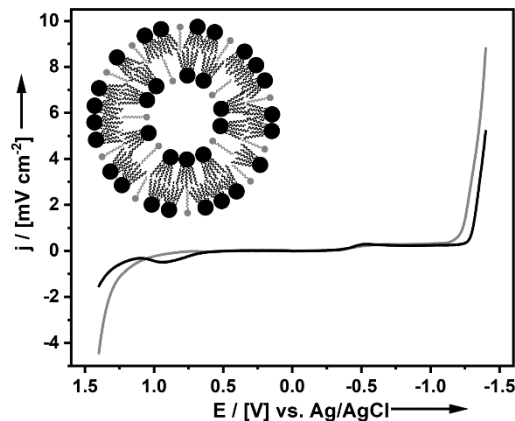
of 7, whereas the slope for HER even changes by more than factor 13. The TOF at -1400 mV is now up to  $346 \pm 10 \text{ s}^{-1}$  (Fig. S5). The observed increase of 1300 % compared to the TOF determined for  $c < c_{ac}$  obviously correlates with the self-assembly of the surfactant into vesicles (Fig. 1d,e). This result is very astonishing considering that the mobility and accessibility of the catalytic centers should be lower in the aggregates, and, accordingly, activity should rather decrease at  $c > c_{ac}$ . This effect can only be explained, if there is a cooperative effect between the individual surfactant molecules in the aggregate. Our hypothesis (Fig. 3b) is, that the vicinity and distinct orientation of the surfactant molecules with respect to each other in vesicle wall renders electron transfer from the ligand to the metal and vice versa more efficient and allows for intermolecular charge transfer processes. Indeed, the ligand reduction potential shifts from  $E_{1/2} = -460$  to  $E_{1/2} = -430$  mV according to linear sweep voltammograms. In the same vein, the onset potential for OER decreases to from +1180 to +1040 mV, while the onset potential for HER shifts from -1260 to -1170 mV (Fig. 3a; Fig. S5).



**Figure 3.** (a) Concentration-dependency of current density (black) for OER (circles) and HER (squares). The grey dashed line marks the cac, when single surfactant molecules (left) assemble to vesicular aggregates (right). Linear sweep measurements (blue) of surfactant (4) below (0.025 mM) (dashed line) and above (0.8mM) (solid line) cac. (b) Cartoon showing the molecular structure of the vesicle surface and the proposed intra- and intermolecular charge transfer processes; (red arrows: reduction process; blue arrows: oxidation process).

Intermolecular charge transfer is thus held responsible for improving electrocatalytic activity of the surfactant aggregates with respect that of dispersed surfactant molecules. If this hypothesis is correct, one would expect that a diminishing content of molecules (4) in the vesicle walls should also decrease its catalytic activity. It is known that sodium dodecyl sulfate (SDS) can also form vesicular structures<sup>35-36</sup> and it is totally inactive in the water splitting reaction. We therefore tried to use SDS as a co-surfactant in a mixture with surfactant (4); see Fig. 4 insert. According to DLS, no SDS micelles are present in such mixtures and the size of the vesicles

( $D_H = 143\text{nm}$ ) changes only insignificantly with respect to pure (4) (Fig. S6a). Upon adding SDS to the catalytic system, the current at +1400 mV and -1400 mV is lowered by approximately 30 % (see Fig. 4). This interpretation is also in line with the observed anodic shift of the onset potential of 45 mV for OER and a cathodic shift of 40 mV for HER (Fig. S6b). In the mixed aggregates fewer molecules (4) are adjacent to each other and, therefore intermolecular electronic communication as initiated by aggregation is rendered less efficient.



**Figure 4.** CV of (4) at  $c = 0.8 \text{ mM}$  (grey) as a reference compare to the (4)/SDS mixed aggregates (black). Insert shows schematic illustration of a vesicle of (4) diluted with SDS.

According to the common sense, aggregation of a catalyst is an undesired event in catalytic reactions, slowing down the rate of the catalytic process. In this work, we were able to show that aggregation can turn into a beneficial feature and increase system's performance, using the water splitting reaction as an example. We present an amphiphilic cobalt-fullerene catalyst, which at concentrations below its cac shows an only medium catalytic activity in OER and HER at neutral pH in aqueous solution. The compound's catalytic activity, especially for HER increases tremendously at concentrations above cac, at which vesicular aggregates form. The onset potentials and current densities are improved and the TOF increases by up to 1300 %. Aggregation allows for intermolecular electron transfer and improves electronic communication within the system, leading to more efficient water splitting.

## ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and methods are included in the supporting information. This material is available free of charge via the internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

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