

Bericht zur Max-Buchner-Forschungsarbeit

“ElectroMagnetOdes”: A Two-Way Bridge Between Heterogeneous and Homogeneous Electrocatalysis (MBFSt-Kennziffer: 3827)

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1. Motivation and Objectives

In a simplified view, electrocatalysts can be divided into two main categories, depending on whether they are located on the electrode, or dispersed in the electrolyte. While the first category is typically composed of (nano)materials deposited directly on the electrode, the second includes mainly molecular catalysts. Recently, attaching molecular catalysts to the surface of supports or electrodes to produce hybrid (electro)catalysts has attracted increasing interest, with the potential to combine the advantages of both approaches.^[1,2] However, despite promising results, this strategy still suffers from serious limitations.^[2] Through this project, we aim at validating a new concept allowing the easy, strong but reversible “attachment” of molecular electrocatalysts on electrodes. In addition, the approach proposed will potentially provide the opportunity to switch in real-time between the heterogeneous and homogeneous modes of electrocatalysis, with potential advantages with regards to catalyst selectivity and product switching. For that, a multidisciplinary project was planned. The objectives include in particular the development of a new generation of electrodes able to accommodate an electromagnet (EM), and the synthesis of well-defined molecular electrocatalysts that can be chemisorbed at the surface of superparamagnetic nanoparticles (NPs). Switching ON/OFF the electromagnet could then potentially allow having the electrochemically active species either at the electrode or in solution, thus achieving either homogeneous or heterogeneous electrocatalysis depending on the needs.

2. Work Plan

The work plan was organized around the following main objectives:

- 1) Building an electromagnet and testing its efficiency for the reversible attraction of iron-based magnetic NPs in aqueous media.
- 2) Design and production of a hollow electrode that can accommodate the electromagnet.
- 3) Synthesis and characterization of TEMPO-based molecular structures, and their chemisorption at the surface of magnetic NPs.
- 4) Testing of the system for the electrochemical oxidation of alcohols as a case study.

3. Results

3.1. Electromagnet and NPs Attraction. The first step of our work consisted in preparing water-dispersible magnetic NPs. For that, citrate-capped Fe_3O_4 NPs were synthesized following a procedure from the literature (Figure 1a).^[3] Briefly, this involved the addition of an aqueous solution of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ to a mixture of trisodium citrate, NaOH, and NaNO_3 in deionized water. After reaction at 100°C for 1 h, the solution was cooled, and the 23 nm Fe_3O_4 NPs (Figure 1b) were purified by magnet-assisted washing. The resulting black powder can be easily redispersed in water, and precipitated by the application of an external permanent magnet (Figure 1c).

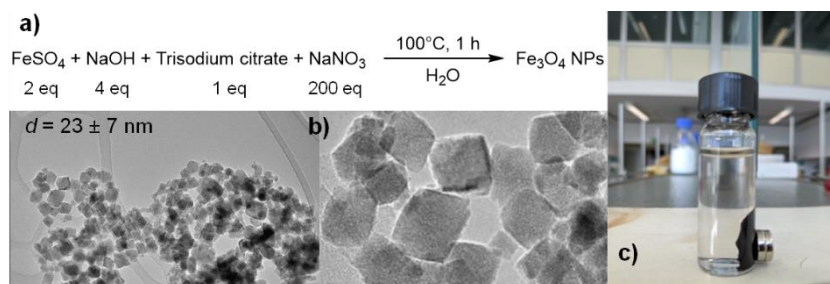


Figure 1. Preparation of Fe_3O_4 NPs. a) Synthesis pathway, b) transmission electron microscopy, c) NPs attraction by a permanent magnet.

From there, an electromagnet needed to be designed and built in order to achieve the reversible attraction of these Fe_3O_4 NPs

in solution. After some tests, a Cu coil delivering 24 V and 8 W was selected together with fitting iron bars and glass vials of different dimensions that were prepared by our mechanical workshop (Figure 2). The attraction test was performed by dispersing Fe_3O_4 NPs in water in a beaker. The tip of the electromagnet (iron bar protected by a glass vial) was immersed in the solution (Figure 3a), and the current was turned ON. After ca. 35 min, all magnetic NPs accumulated at the surface of the glass vial, attracted by the electromagnet, and leaving the solution clear (Figure 3b). Turning OFF the current, the magnetic NPs were released from the electromagnet, and redispersed in solution in less than 2 minutes (Figure 3c).



Figure 2. Electromagnet parts.



Figure 3. Reversibility of the attraction a) => b) and release b) => c) of Fe_3O_4 NPs by the EM.

While the time needed to attract the NPs is relatively long (and can be optimized by using a more powerful EM and/or NPs with better magnetic properties), these results demonstrate the possibility to trap and release magnetic NPs in solution on a material shaped like an electrode.

3.2. Hollow Electrode. Following this successful attempt, a hollow glassy carbon rod was bought and cut to the desired size by our mechanical workshop to serve as electrode. A similar behavior was observed when putting the electromagnet iron tip in the hollow electrode as when using the glass vial, validating this first part of the concept.

3.3. TEMPO-Based Molecular Structures. The synthesis of TEMPO-functionalized ligands for Fe_3O_4 NPs was achieved as shown in Figure 4. The structure of the intermediates and of the final product were confirmed by NMR (^1H , ^{13}C , HSQC, DEPT; as well with reaction with phenylhydrazine to reduce the radical) and by mass spectrometry. The direct silanization of this TEMPO-based ligand at the surface of the Fe_3O_4 NPs was unsuccessful, however. As an alternative, Fe_3O_4 NPs were coated with SiO_2 following a previously reported protocol.^[4] Chemisorption of the TEMPO-based ligand on the resulting $\text{SiO}_2@ \text{Fe}_3\text{O}_4$ NPs succeeded, with a grafting efficiency of ca. 30% which represents 60 mg of ligand for 200 mg of NPs, which is fairly good. Unfortunately, Fe_3O_4 NPs lost most of their magnetic properties upon coating with SiO_2 , resulting

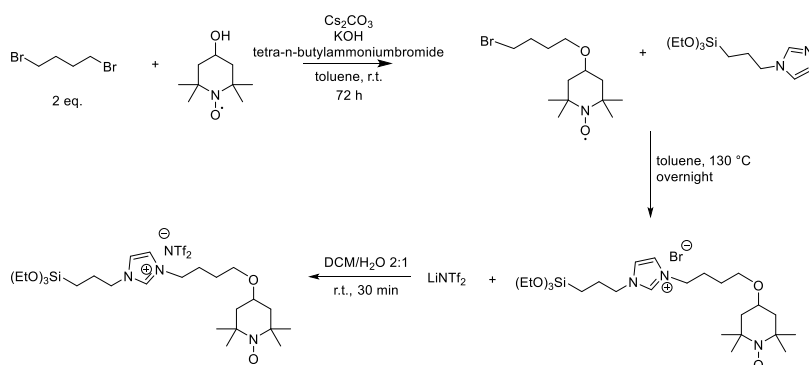


Figure 4. Synthesis pathway for the target TEMPO-functionalized ligand.

are known to bind very strongly to the surface of iron-based NPs.

3.4. Electrochemical Testing. Once the challenges associated to point 3.3. will be tackled, the reactivity of TEMPO-functionalized Fe_3O_4 NPs will be investigated for the electrochemical oxidation of alcohols. An aqueous carbonate buffer will be used as the electrolyte, and a current of 0.55 - 0.7 V will be applied. The electromagnet-containing hollow glassy carbon rod will represent the anode, and a Pt mesh will be used as the cathode (Figure 5).

Interestingly, through investigations related to this project, we also developed a Pickering emulsion system enabling the electrocatalytic hydrogenation of water-insoluble organic substrates at high efficiency. The emulsion can transport electricity and act as extended electrode, and performances are improved by running reactions at the interface of two phases, each containing a necessary reactant. These results were recently published in *Nature Catalysis*,^[5] with acknowledgements to this Forschungsstiftung 3827.

4. Conclusion

In conclusion, the possibility to introduce an electromagnet in a hollow electrode to reversibly attract magnetic NPs in aqueous media was demonstrated. The preparation of TEMPO-functionalized ligands was successful, however their attachment to the surface of iron oxide NPs proved challenging. This issue could be solved by coating Fe_3O_4 NPs with SiO_2 , however at the expense of their magnetic properties. Nevertheless, we are confident that we can tackle this challenge by using a thinner SiO_2 shell, or by replacing the silane linker by catechol functionalities. From there, electrochemical testing and switching experiments will be close at hand.

5. Literature

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in the impossibility to attract them with the EM. Future developments will thus focus on the optimization of the SiO_2 shell thickness to preserve sufficient magnetization. In parallel, other ways to functionalize the surface of Fe_3O_4 NPs without SiO_2 coating will be explored, using for example catechol-type of ligands, that

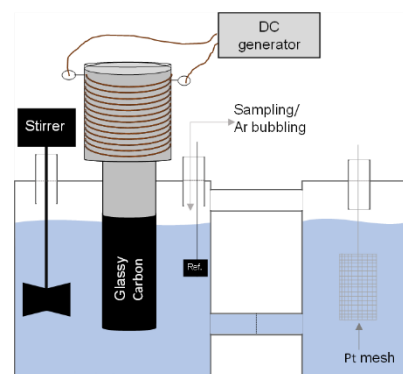


Figure 5. Potential cell design.