

# Visualizing Nanocatalysts in Action from Color Change Reaction to Magnetic Recycling and Reuse

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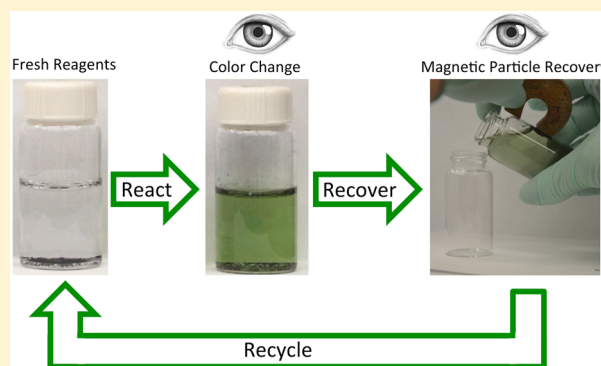
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## Supporting Information

**ABSTRACT:** A demonstration to highlight the utility and ease of handling environmentally benign magnetically recoverable nanoparticle catalysts is described. The demonstration offers two powerful visuals. The first is a color change oxidation of tetramethylbenzidine by hydrogen peroxide catalyzed by Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The second, and more pedagogically relevant to discussion of catalyst recycling, is the retrieval of these nanoparticles from solution with an external magnet and subsequent reuse for further rounds of catalysis. The demonstration, useful to instructors of general chemistry and green chemistry courses or animators of outreach activities, requires a modest time investment of less than 5 min, yet adds striking visual aids to discussions of catalyst recycling and reuse.

**KEYWORDS:** Green Chemistry, Catalysis, First-Year Undergraduate/General, Upper-Division Undergraduate, Demonstrations, Public Understanding/Outreach, Organic Chemistry, Inorganic Chemistry



## INTRODUCTION

An aid to science demonstrators at all levels, magnets provide a tool for the often visually stunning movement of objects. At home, young children link and move paper clips with a magnet. In middle school, students build model magnetic levitation trains. In an undergraduate classroom, instructors demonstrate the triplet nature of dioxygen by manipulating liquid O<sub>2</sub> under a magnetic field.<sup>1</sup> In the research laboratory, chemists for the past 10 years have been retrieving and recycling magnetic nanoparticle catalysts used for various organic transformations.<sup>2–5</sup> Similar particles have been applied in the teaching laboratory for removal of water contaminants,<sup>6</sup> but to the best of our knowledge, no published educational activity or demonstration has showcased their catalytic utility in tandem with their magnetic recoverability. In fact, catalyst recovery and recycling of any kind is relatively uncommon in undergraduate teaching,<sup>7,8</sup> although laboratory exercises focusing on sustainable chemistry topics are becoming more commonplace.<sup>9–12</sup>

Long touted as intermediates between homogeneous catalysts and their bulk heterogeneous counterparts,<sup>13</sup> nanoparticles (NPs) often offer catalytic properties between the two. Under ideal circumstances, they would offer the catalytic efficiency of the former and ease of recovery of the latter. Unfortunately, the catalytic efficiency of many NPs relies on size; smaller NPs offer superior catalytic performance but also more difficult separation schemes such as centrifugation or ultrafiltration.<sup>14</sup> By simply applying an external magnet to draw the particles out of solution, magnetic NPs offer an inexpensive, easy, energy

efficient, and environmentally benign mode for catalyst recovery and recycling.<sup>15</sup>

## ADVANCED AUDIENCE BACKGROUND

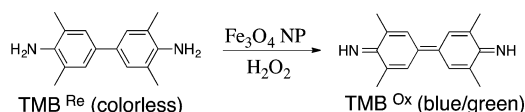
Most strategies for magnetic NP catalysts rely on a pseudohomogeneous species anchored to a heterogeneous particle.<sup>16,17</sup> While such schemes can generate powerful catalysts, the synthetic effort involved in catalyst preparation precludes their use from many industrial applications and almost certainly from simple classroom or laboratory demonstrations. For such applications, simpler metal-coated reduced iron NPs, prepared in two steps, and used for click reactions,<sup>18</sup> cyclopropanations,<sup>19</sup> Suzuki couplings,<sup>20</sup> and transfer hydrogenations,<sup>21</sup> offer a more attractive option to instructors. Simpler still, monometallic reduced,<sup>22</sup> or mostly reduced iron NPs have been used for hydrogenations,<sup>22–24</sup> Grignard-type reactions,<sup>25</sup> dehydrogenation of ammonia borane,<sup>26</sup> and many other reactions. Unfortunately, such reduced particles often readily oxidize, limiting their utility in classroom demonstrations, where inert conditions are infeasible.

Alternatively, iron oxide NPs (Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>) have been used to catalyze a range of oxidation reactions,<sup>27,28</sup> cross-dehydrogenative couplings,<sup>29</sup> and aldehyde–alkyne–amine couplings (A<sup>3</sup>).<sup>30</sup> Similarly, copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) NPs<sup>31</sup> have been used to catalyze similar A<sup>3</sup> coupling reactions,<sup>32</sup> cross-dehydrogenative couplings<sup>33</sup> as well as click reactions,<sup>34,35</sup>

hydrosilylation,<sup>36</sup> in addition to various other cross coupling reactions.<sup>37–41</sup>

Such commercially available, stable, and easily handled iron oxide NPs offer instructors ideal candidates for demonstrations of magnetic nanocatalysts. In search of a reaction catalyzed by simple magnetically recoverable NPs and exhibiting a distinct color change, we adapted an established toxicological colorimetric assay<sup>42</sup> used for the detection of H<sub>2</sub>O<sub>2</sub>, in this case a proxy for specific enzymatic activity. The oxidation of tetramethylbenzidine (TMB) with H<sub>2</sub>O<sub>2</sub> catalyzed by Fe<sub>3</sub>O<sub>4</sub> NPs represents the final step of the assay and is associated with a distinct visible color change (Scheme 1). Since reduced TMB

**Scheme 1. Oxidation of TMB with H<sub>2</sub>O<sub>2</sub> Catalyzed by Fe<sub>3</sub>O<sub>4</sub> NPs**



(TMB<sup>re</sup>: colorless) oxidizes (TMB<sup>ox</sup>: green), the solution quickly takes on a vibrant green color. This NP catalyzed TMB oxidation serves as the basis for the demonstration.

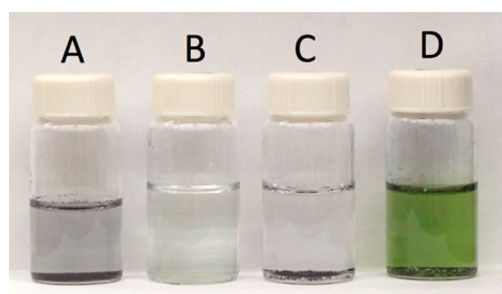
### DEMONSTRATION DETAILS

The instructor should carry out the demonstration in front of a group of general, organic, inorganic, or green chemistry students in a classroom or tutorial<sup>43</sup> setting. Alternatively, the demonstration could be performed as part of a chemistry outreach presentation at which the students guess when the solution will change color. The demonstration requires hydrogen peroxide, water, TMB, Fe<sub>3</sub>O<sub>4</sub> NPs, a magnet, and at least four screw-top vials (or higher volume vessels for larger group sizes). A detailed set of instructor notes and sample lesson plan are available in the [Supporting Information](#).

Start by preparing blank vials that each separately contain two of the three necessary reaction components (H<sub>2</sub>O<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> NPs, and TMB). For the blank without H<sub>2</sub>O<sub>2</sub>, water can be used instead. After the three blanks have been prepared, a fourth vial will be prepared with all the reaction components. Very little TMB (~1–5 mg, either the tip of a spatula or a single 1 mg tablet) is needed to produce a distinct color change. A similar weight of Fe<sub>3</sub>O<sub>4</sub> NPs would suffice to catalyze the reaction, although the instructor may want to add more (~50 mg) for a more dramatic effect when they are pulled from solution. A solvent volume of ~10 mL is appropriate, though if the demonstration is being conducted for a large number of students, the reagent quantities can all easily be scaled. The following vessels should be prepared: (a) H<sub>2</sub>O<sub>2</sub> + Fe<sub>3</sub>O<sub>4</sub> NPs, (b) H<sub>2</sub>O<sub>2</sub> + TMB, (c) Fe<sub>3</sub>O<sub>4</sub> NPs + TMB, and (d) H<sub>2</sub>O<sub>2</sub> + Fe<sub>3</sub>O<sub>4</sub> NPs + TMB (Figure 1). Each vial should be capped and shaken for thorough mixing. The purpose of blanks A–C is to demonstrate to students that all three reaction components are necessary for the reaction to proceed quickly and effectively; no two reagents alone will allow the production a color change in a short time period.

### HAZARDS

TMB is a mild skin, eye, and respiratory irritant. Avoid breathing in dust. It can be disposed of with typical flammable organic waste streams. Fe<sub>3</sub>O<sub>4</sub> NPs can be disposed of in solid or metal waste streams. H<sub>2</sub>O<sub>2</sub> is a powerful oxidant as well as a skin and

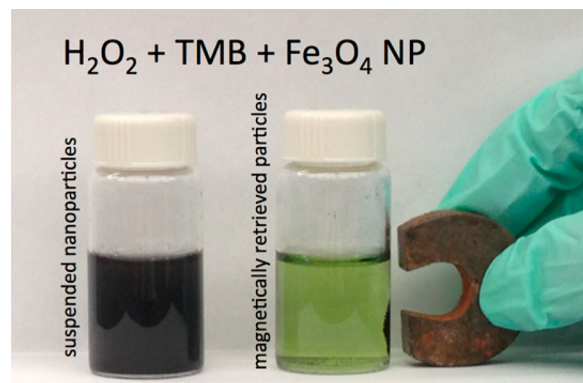


**Figure 1.** Solution colors after 1 min for (a) H<sub>2</sub>O<sub>2</sub> + Fe<sub>3</sub>O<sub>4</sub> NP, (b) H<sub>2</sub>O<sub>2</sub> + TMB, (c) Fe<sub>3</sub>O<sub>4</sub> NP + TMB, and (d) H<sub>2</sub>O<sub>2</sub> + Fe<sub>3</sub>O<sub>4</sub> NP + TMB.

eye irritant; it can cause burns and corrodes skin tissue. Typically, the more benign 3% solution available at a pharmacy will suffice if the water-soluble form of TMB (the HCl salt) is used. Otherwise, the more concentrated, and more dangerous 30% solution available from chemical suppliers may be necessary.<sup>44</sup>

### RESULTS AND DISCUSSION

No color change, or visual evidence of any reaction (bubbling, precipitation, etc.), should be apparent right away in the blank reactions (A–C), but in less than a minute, the TMB in the fourth vial will oxidize, and a distinct color change will be visible. By placing the external magnet against the side of the flask, the instructor can pull the NPs out of suspension (Figure 2), decant



**Figure 2.** Magnetic retrieval of Fe<sub>3</sub>O<sub>4</sub> NPs from a solution of H<sub>2</sub>O<sub>2</sub> + TMB + Fe<sub>3</sub>O<sub>4</sub> NP.

off the liquid, rinse the particles with water, then add more H<sub>2</sub>O<sub>2</sub> and TMB to demonstrate the recyclability of the catalyst. While the NPs are in suspension, the solutions containing them (A, C, D) will appear opaque and black. Upon application of the external magnet, the particles start to move toward the side of the flask and out of suspension. As the particles collect at the side of the flask, the underlying color of the solution is revealed (clear for A and C, but blue/green for D). After decantation of the reaction supernatant, the particles can be easily resuspended in more solvent by simply closing the vial and shaking as before.

The demonstration is best run all at once within the span of about 5 min, rather than drawn out over the course of a lecture period, because some of the blanks will slowly start to change color over time, lessening the contrast between the catalyzed system and the uncatalyzed blanks. Blank B (H<sub>2</sub>O<sub>2</sub> and TMB, but no catalyst) will turn discernably blue/green after ~20 min,

not as vibrant as vial D, but perceptible nonetheless. Likewise, blank C ( $\text{Fe}_3\text{O}_4$  and TMB, but no  $\text{H}_2\text{O}_2$ ) will also turn noticeably blue/green after  $\sim 2$  h unless kept in the dark because visible light can slowly promote the air oxidation of TMB. Instructors can involve students in the activity by having them decide how to run the necessary blanks.

While NPs and microparticles often display drastically different reactivities, we were unsuccessful at elucidating this point with the present demonstration; both NPs ( $\sim 50$  nm) and microparticles ( $< 5$   $\mu\text{m}$ ) successfully catalyzed the reaction. Such a small amount of TMB is required ( $\sim 1$  mg) to elicit a color change that using a substoichiometric amount of catalyst would be operationally difficult and would not allow for the striking visual of catalyst removal (because there would be too little to see). We therefore use an excess of catalyst, thereby obviating one of the benefits of NP catalysts (high surface area to volume ratio meaning many accessible active sites). Since we use an excess of  $\text{Fe}_3\text{O}_4$ , the number of accessible active sites does not limit the reaction in any appreciable way, so both micro- and nano- particles are effective at catalyzing the reaction.

The short time frame required (less than 10 min), largely qualitative results, and absence of common and transferable laboratory techniques make this more suitable as a demonstration for classroom discussion of catalyst recovery and recycling rather than an exercise for a full laboratory period. Nevertheless, the relative ease of the protocol and generally innocuous nature of the reagents make this suitable for a hands-on activity.

## ■ DEMONSTRATION FOR VARIOUS AUDIENCES

Given the accessibility that the color change reaction affords, a wide variety of audiences may find this demonstration interesting and informative, even if the nuances of catalysis and NPs are too advanced. Indeed, the demonstration was well received by a broad range of groups including grade-school students, STEM teachers in training, and advanced organic chemistry students. We taught the grade school students ways to identify when a chemical reaction has taken place, including changes in color, and played a guessing game with them, asking which vials they thought would change color after we added various combinations of reagents (both fresh and recycled). With the STEM teachers in training, we were able to bring up the topic of catalysis and they came away with the understanding that a catalyst should remain unchanged after the reaction, so it theoretically should be recyclable. More importantly, discussion of the development of the demonstration stressed the importance of carefully choosing demo reactions and processes with strong visuals. Feedback solicited from this teachers in training audience included: "The contrast between the rate of reaction in the noncatalyzed reaction versus the nanoparticle vial reaction and its reuse in a second reaction shows its effectiveness as a reusable catalyst." and "Very cool. My favorite part was how you could recycle/reuse the nanoparticles." The advanced organic chemistry students already had a deeper understanding of the role of a catalyst enabling an alternative reaction pathway with a lower energy barrier, so for them we used the demonstration to showcase this point as well as introducing them to green chemistry concepts.

## ■ SUMMARY

The demonstration described offers instructors of general or green chemistry courses a visual example for discussing the

recovery and reusability of magnetic NP catalysts. The demonstration highlights several axioms of sustainable chemistry. First, the mode of catalyst separation requires no extra material input and minimal energy. Second, the reuse of the catalyst for subsequent reactions ensures very little catalyst will ultimately enter the waste stream. The oxidation of TMB, and associated color change, allows students to observe that a reaction has occurred, and it can serve as a visual proxy for reactions perhaps more relevant to the curriculum—alcohol oxidation,  $\text{A}^3$  coupling, or cross-dehydrogenative coupling—but that would otherwise require more time and sophisticated spectroscopic techniques to determine reaction progress. Magnetic retrieval and subsequent reuse of the  $\text{Fe}_3\text{O}_4$  NPs offers a visual example of easy catalyst recycling techniques.

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed materials lists, procedure, and lesson plans. The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00106.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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- (44) Notes: TMB is light sensitive, so it should be stored in a dark location. Additionally, in the absence of a catalyst, the oxidation of TMB can proceed slowly if exposed to visible light. Therefore, blank solutions should be prepared just prior to or during the demonstration, but the reactions do not need to be run in the dark because the visible-light promoted oxidation occurs significantly slower than the catalyzed reaction. The effect of pH is limited to the hue of the color change reaction, but the demonstration was otherwise effective when run under acidic, neutral, and basic conditions.