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# Self-healing for nanolayered manganese oxides in the presence of cerium(IV) ammonium nitrate: New findings

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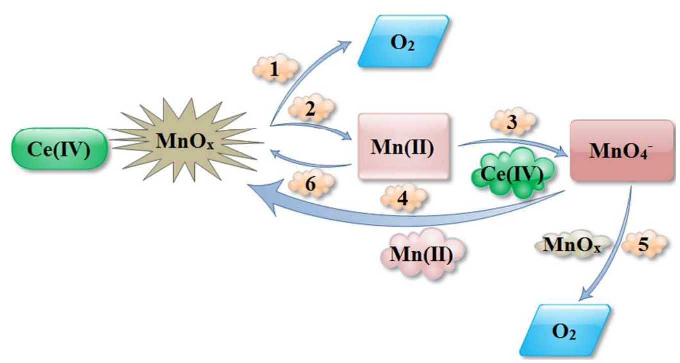
The self-healing reactions for metal oxides are among the most important reactions. For Mn oxides in the presence of cerium(IV) ammonium, Mn(II) and $MnO_4^-$ combine and heal the Mn oxide. In the reaction, Mn(II) is formed from the reductive dissolution of the Mn oxide or by disproportionation of Mn(III) on the surface of oxide. This Mn(II) is then oxidized by cerium(IV) ammonium nitrate to $MnO_4^-$. The $MnO_4^-$ in the presence of Mn oxide oxidizes water or in a second pathway is reduced by Mn(II) to form Mn oxide. Here, we use for the first time multivariate curve resolution-alternative least square to analyze spectroscopic data and obtain concentration profiles of cerium(IV) ammonium and $MnO_4^-$ during the reaction time in different conditions.

## Introduction

The sun provides high amounts of energy at a few hours per day. Thus, storage of energy at unprecedented scales is necessary to use solar energy or any sustainable energy.[1] Water splitting is an important reaction that can store energy in the form of fuel ($H_2$) and oxidant ($O_2$). However, water oxidation to evolve $O_2$ is a bottleneck for the development of water splitting.[2] On the other hand, many compounds are decomposed under water-oxidation conditions.[3]
Heterogeneous metal oxides exhibited efficient catalytic reactivity for water oxidation.[4] Among different ions for water oxidation, Mn is promising regarding low-cost and environmentally friendly.[2,3] However, in addition to efficiency, stability of catalysts is a very important issue.[5-12] Self-healing is defined as self-recovery of the initial properties of a compound following damage caused by the external environment or internal stresses and is a promising strategy to stabilize an efficient catalyst.[5-12] Self-healing reactions for Co[5,7] and Mn[6,8-12] oxides in electrochemical water oxidation were reported by different groups. We also reported the self-healing of a nanolayered Mn oxide in the presence of cerium (IV) ammonium nitrate ($Ce^{4+}$).[8-11] We indicated that the products of decomposition of nanolayered Mn oxide, Mn(II) and $MnO_4^-$, combine to heal damage to the oxide.[11] In the self-healing reaction, Mn(II) arises from reductive dissolution of the nanolayered Mn oxide and by disproportionation of Mn(III).[11b] These Mn(II) ions are then oxidized by $Ce^{4+}$ to $MnO_4^-$ (Scheme 1).




Scheme 1 Self-healing in water oxidation by Mn oxides in the presence of $Ce^{4+}$. **1**: Oxygen evolution was detected by an oxygen meter. **2**: Mn(II) was detected by EPR. **3**: $MnO_4^-$ formation could be detected by UV-Vis in reacting Mn(II) and $Ce^{4+}$. **4**: It is known that in the reaction of Mn(II) and $MnO_4^-$ at different pH values, Mn oxide is produced. **5**: $MnO_4^-$ in the presence of Mn oxide oxidizes water. In the reaction, $MnO_4^-$ reduces to Mn oxide. **6**: Mn(II) in the presence of $Ce^{4+}$ form Mn oxide. In a typical experiment, the reaction of $MnSO_4$ in the presence of $Ce^{4+}$ (1.0 M), forms $MnO_2$ that can be detected by XRD. Caption and image are from ref. 11b.

Here, we use chemometrics method to analyze the self-healing reaction for nanolayered Mn oxide in the presence of $Ce^{4+}$ reaction. The new findings by this method help us to understand more details for the important reaction.

## Experimental section

### Material and methods

We synthesized and characterized nanolayered Mn oxide (Fig. S1, ESI†) by previously reported method.[11] We studied UV-Vis spectra for the reaction of this oxide with different concentrations of $Ce^{4+}$ by

Pharmacia Biotech ultrospec 3100. In each experiment, 10 mg nanolayered Mn oxide and different concentrations of $Ce^{4+}$ (5.0 mL) were mixed in the cell of UV-Vis spectroscopy device with a cap to inhibit solvent evaporation, and UV-Vis spectra was considered after 5, 10 and 15 minutes, and then each one hour for 148 hours.

## Results and Discussion

### Chemometrics methods to study of the self-healing

The self-healing reaction for nanolayered Mn oxides in water oxidation is very important because such nano-sized Mn oxides are fragile toward decomposition reactions. On the other hand, usually catalysts for multi-electron reactions, such as water oxidation, are prone to structural rearrangement and instability during turnover.[5] Thus, self-healing can be necessary over an extended period of time.
We used chemometrics methods to study of the self-healing reaction with more details. Univariate methods, often involve using single wavelength measurement for resolving of the systems. There are some limitations when we use such methods:[11b] Firstly, it is often not easy to find selective wavelength for all components (especially in UV-Vis and NIR spectroscopy, but Raman for example is quite selective). Secondly, it is necessary to know the exact initial concentrations of reactants and finally, the reactions and chemicals involved are highly affected by physical and chemical parameters like temperature or pH.[13-16] However, some chemometrics methods apply multivariate data analysis for completion of resolving spectroscopic information. In these methods, the measured spectra for a chemical reaction can render a two-way data matrix, which contains both the reaction kinetic information (such as rate constants) and the pure spectrum of each component involved in the reaction.[17] Two types of data can be used in multivariate analysis of data matrices: 1) an individual data matrix or a two-way array, 2) augmented data matrices and simultaneous analysis of them.[18-20] Compared to individual data analysis, working with augmented data matrices has some advantages. First, augmentation decreases the uncertainty of the results because of having more information about the system.[12-15] Second, using augmented data rank deficiency can be handled.[14,19-21] Third, employing augmented data uncertainty in the estimated parameters is considerably reduced. Forth, in presence of a minor species in the experimental system, which causes poorly defined spectrum for it, augmentation can improve the detection and resolution of it.
In our previous study,[11b] the reaction of nanolayered Mn oxide in the presence of cerium(IV) ammonium nitrate ($Ce^{4+}$) was monitored and analyzed using singular-value decomposition as a multivariate method[12] and a mechanism was proposed as shown in the following equations:

$$3Ce^{4+} + MnO_2 + 2H_2O \rightarrow 3Ce^{3+} + MnO_4^- + 4H^+ \quad (1)$$

$$4MnO_4^- + 12H^+ \rightarrow 4Mn^{2+} + 6H_2O + 5O_2 \quad (2)$$

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+ \quad (3)$$

In order to precise analysis of the reaction, this reaction is monitored in different concentrations of $Ce^{4+}$ (M) which they were 0.05, 0.1, 0.12, 0.15, 0.18, 0.20, 0.22, 0.50, 0.75 and 1 from $\mathbf{D}_1$ to $\mathbf{D}_{10}$ respectively (Table S1).

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After that, all data matrices were analyzed simultaneously and MCR-ALS method was applied on augmented data matrices. The obtained results in this study confirmed the results in our previous study. In addition, the behavior of $MnO_4^-$ as a function of $[Ce^{4+}]$ was explained.

### Multivariate Curve resolution-Alternative least square (MCR-ALS)

The spectroscopic data were formatted in a data matrix in which the columns were variations in concentrations and the rows were the recorded spectra from each sample. MCR-ALS was based on the bilinear decomposition of the data matrix into the estimated concentration and the spectral profile matrices, which can be explained with the following equation:

$$\mathbf{D} = \mathbf{C}.\mathbf{S}^{\mathrm{T}} + \mathbf{E}$$

Where the **C** is a nt×nc concentration profile matrix of involving species. **D** is nt×nw data matrix and **S** is nc×nw the pure spectral profiles for each of the components. E is a nt×nw residual matrix with contains noise and has not any contribution in **C** and **S** matrices. nt, nw, and nc are the number of recorded time points, wavelengths and the number of components, respectively.
MCR-ALS[23] method is an iterative method, which starts with an initial estimation of **C** (or **S**) matrix obtained from evolving factor analysis (EFA),[24-26] random initial values[18,27,28] or the determination of the purest variables.[29-31] Starting with concentration profiles, pure spectral profiles, $\mathbf{S}^{\mathrm{T}}$, and matrix-componet distribution, **C**, of nc components will be estimated, which can reconstruct experimental data matrix.[18,23,28,32] The main problem in MCR-ALS method is that this method has more than one solution and the results are not unique.[16,32-35] It means that the estimated concentration and spectral profiles are one of the possible solutions for a system.[33] To overcome this problem, in this study ten data matrices were analyzed simultaneously which is called second order globalization in the literatures.[14,19,20] In this study, whole set of experiments were performed in ten different concentrations of $Ce^{4+}$ and were augmented in column wise direction and analyzed based on the extended bilinear model as shown in Fig. 2. In according to this method, the numbers of possible solutions are reduced significantly.[32,33] In this study, the feasible range of concentration profiles and spectral profiles were very narrow and not reported here.

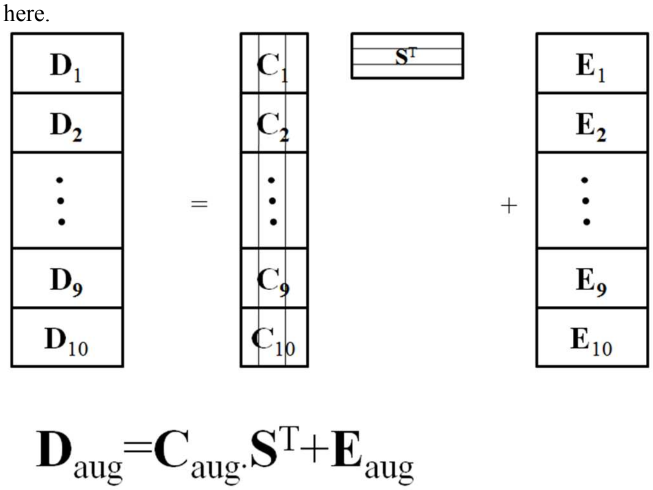
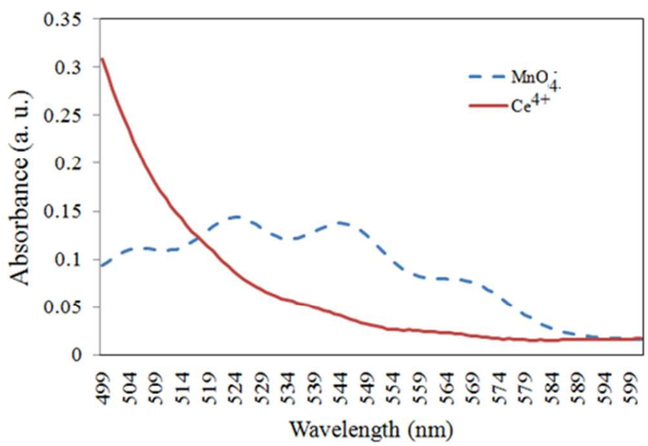



Fig. 2 Schematic the presentation of column wise augmented data and its bilinear decomposition of $\mathbf{D}_{aug}$ applying MCR-ALS method. Three factors were selected in MCR-ALS method.

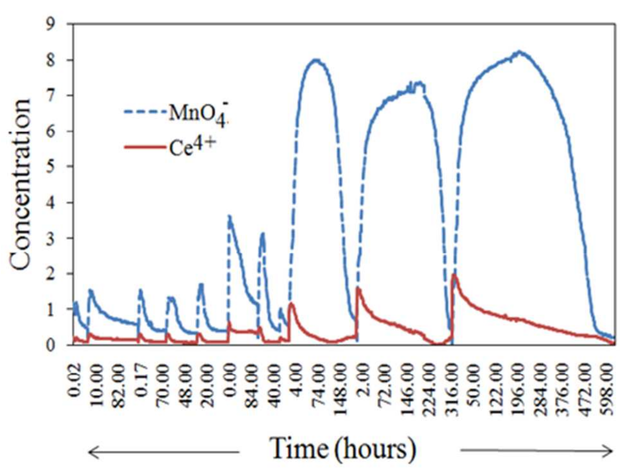
**Estimation of the concentration profiles using MCR-ALS**

The self-healing reaction in this study was investigated in ten different concentrations from $Ce^{4+}$ as shown in Table S1. These data matrices were augmented in column wise as mentioned in previous section and analyzed simultaneously by MCR-ALS method with three factors as described in previous section (MCR-ALS). Two factors were due to $Ce^{4+}$ and $MnO_4^-$ and the third one was due to instrumental drift. The presence of drift is reliable since the time scale of all reactions was very long. The random initial estimates from the concentration profiles were used and pure spectral profiles of $Ce^{4+}$, $MnO_4^-$ and their corresponding concentration profiles were estimated (Fig. 3 (a-c)). From Fig. 3b, it is clear that the concentration profile of $Ce^{4+}$ (red line) is in descending manner and is expected since it is an initial oxidant and is consumed during the reaction times in whole data matrices.

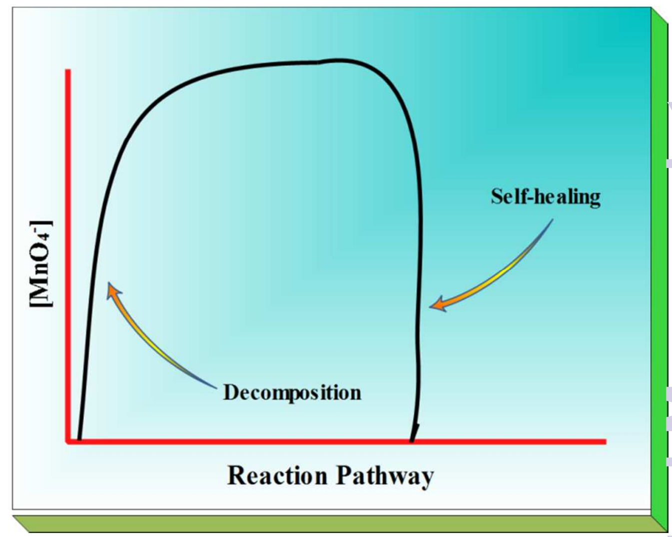
$MnO_4^-$ is produced and consumed during the reaction time. As shown in Fig. 3, the concentration profile of $MnO_4^-$ (blue line) is similar to an intermediate in three last data matrices. From Fig. 3, it is clear that the rate of $MnO_4^-$ formation is decreased when the initial concentration of $Ce^{4+}$ is decreased. It is also observed that when the concentration of $Ce^{4+}$ is low, the concentration of $MnO_4^-$ cannot be clearly observed.




a




b




c

Fig. 3 Measured pure spectral profiles of $Ce^{4+}$ and $MnO_4^-$ (a), estimated concentration profile from ten augmented data matrices (b). Schematic diagram to show decomposition and self-healing reactions for nanolayered Mn oxide in the presence of $Ce^{4+}$ (c).

Thus, low concentration of $Ce^{4+}$ cannot oxidize Mn(II) to $MnO_4^-$. However, in the presence of high concentration of $Ce^{4+}$ (0.6 to 0.8 M), $MnO_4^-$ ions remain in solution a few hours.

## Conclusion

Mn oxides are low cost, and efficient, environmentally friendly and easy to use, synthesis, manufacture catalysts. However, the stability of catalyst is also important. Herein, the stability of Mn oxide in the presence of $Ce^{4+}$ in water-oxidation reaction was considered and MCR-ALS analysis was used to study of self-healing reaction for nanolayered Mn oxide. We found that the $MnO_4^-$, as a decomposed product, is formed in the first seconds of the reaction of Mn oxide with $Ce^{4+}$. Then, the concentration of $MnO_4^-$ remains constant in the solution until that many $Ce^{4+}$ ions is reduced to $Ce^{3+}$. In this condition, the concentration of $MnO_4^-$ decreases. In the presence of high concentration of $Ce^{4+}$, high concentration of $MnO_4^-$ is observed. On the other hand, remaining time of $MnO_4^-$ in the solution is also increased. The findings are important to understand the mechanism of self-healing for Mn oxide and to design new systems by self-healing properties.

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## Notes and references

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