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Cite this: DOI: 10.1039/x0xx00000x

Nanolayered manganese-calcium oxide as an efficient catalyst toward organic sulfide oxidation

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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We for the first time report that nanolayered Mn-Ca oxide in the presence of H_2O_2 is an efficient catalyst toward sulfide oxidation to sulfoxide. We characterized catalyst by DLS, UV-Vis, diffuse reflectance infrared Fourier transform spectroscopy, SEM, TEM and HRTEM. We also considered different parameters on sulfide-oxidation reaction.

Organic sulfoxides are among important compounds to synthesize various chemically and biologically significant molecules.[1] Among different methods, the oxidation of sulfides is a common method for preparing sulfoxides.[2] There are several reagents for this conversion but many of them have the problem of over oxidation of sulfoxides to sulfones.[1,2] Different solvents, oxidants and catalysts are used in improving the procedure.[1,2] Mn compounds are among the most attractive inorganic materials not only because of their physical and chemical properties but also because they are low cost and environmentally friendly.[3] It was reported that ethyl phenylsulfide (2 mmol) was allowed to react with oxygen/pivalaldehyde (1 eq) in perfluoro-2-butyltetrahydrofuran (2.5 mL, 25°C) in the presence of $Mn(OAc)_3.2H_2O$ (2 mol%) and led to a mixture of ethylphenylsulfoxide and ethylphenylsulfone (67:33) in 1 h.[4] Asymmetric oxidation of sulfides was also examined by using (salen)Mn(III) complexes as catalyst and was found to show high asymmetric induction.[5] Mn oxides are cheap and environmentally friendly compounds and used extensively as bulk, supported, nano-sized with large surface area and colloidal forms. Mn oxides are efficient catalysts for oxidation of both organic[6] and inorganic compounds such as carbon monoxide,[7] nitrogen oxides,[8] and water.[9] Recently, we used layered Mn oxides as efficient catalysts for oxidation of water,[10] alcohols[11] and alkenes.[12] Here, we report nanolayered Mn oxides as efficient catalysts toward organic sulfide oxidation to sulfoxide.

Materials and Methods

All reagents and solvents were purchased from commercial sources (Merck or Sigma-Aldrich) and were used without further purification. MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400 and 4000 cm^{-1}. Diffuse reflectance infrared Fourier transform spectroscopy were recorded on Perkin Elmer -Spectrum one. TEM and SEM were carried out with JEOL JEM 2010 Fas TEM operating at 200 kV and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Kα radiation). Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (10.0 mg metal) was added to 1 mL of concentrated nitric acid and H_2O_2, left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS.

Synthesis of Compound

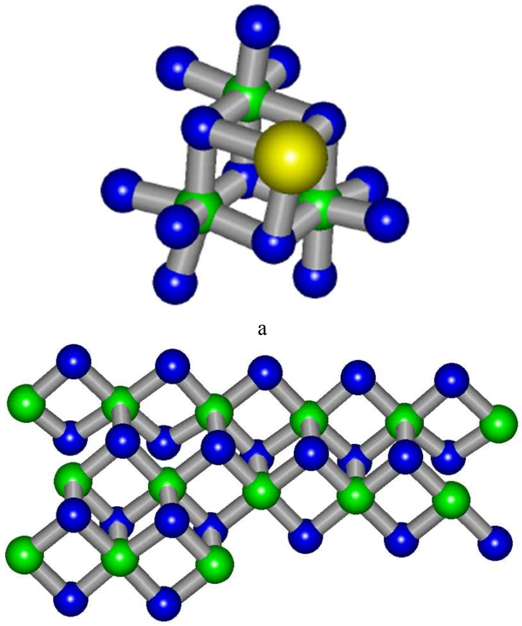
The compound was synthesized by a previously reported method.[13] Briefly, it was synthesized by mixing a solution contain $CaCl_2.4H_2O$ (2.70 mmol, 0.494 g) and $Mn(CH_3COO)_2.4H_2O$ (5.6 mmol, 1372 mg) in water (5 mL) and a solution of $KMnO_4$ (2.4 mmol, 379 mg) and KOH (17.0 g) in 100 mL water. The obtained suspension was filtered and washed with distilled water (3 L) before being allowed to dry for 12 h at 60 °C in an oven. Then the solid was heated to different temperatures (100-400 ^{O}C) for 10 h in air to obtain a brown powder. Yield: > %90; at 400 ^{O}C the oxide could be formulated as $Ca_{0.16}MnO_2.2H_2O$.

Oxidation of sulfides catalyzed by $Ca_{0.16}MnO_2.2H_2O$

To a solution of sulfide (0.5 mmol) and catalyst (10.0 mg) in CH_3CN (1.0 mL), H_2O_2 (1.5 mmol) as oxidant was added. For the analysis of products, after stirring at room temperature for 2 h, the solution was subjected to ether extraction (3 × 10 mL), and the extract was also concentrated down to 1.0 mL by distillation in a rotary evaporator at room temperature. Then, a sample (2 μL) was taken from the solution and analyzed by GC. The retention times of the peaks were compared with those of commercial standards, and chloro benzene was used as an internal standard for GC yield calculation.

Results and Discussion

The procedure to synthesize of the nanolayered Mn oxides was simple, green, easily and cheap by the reaction of $KMnO_4$, Mn(II)$(OAc)_2$ and $CaCl_2$ in the presence of KOH. In reflectance infrared Fourier transform spectra and FTIR spectra of oxide show a broad band at ~ 3200-3500 cm^{-1} related to antisymmetric and symmetric O-H stretchings and at ~ 1630 cm^{-1} related to H-O-H bending are observed.[13] The peaks at ~ 700 cm^{-1} are related to Mn-O-Mn bonds (Fig. S1, ESI†).[13]


a

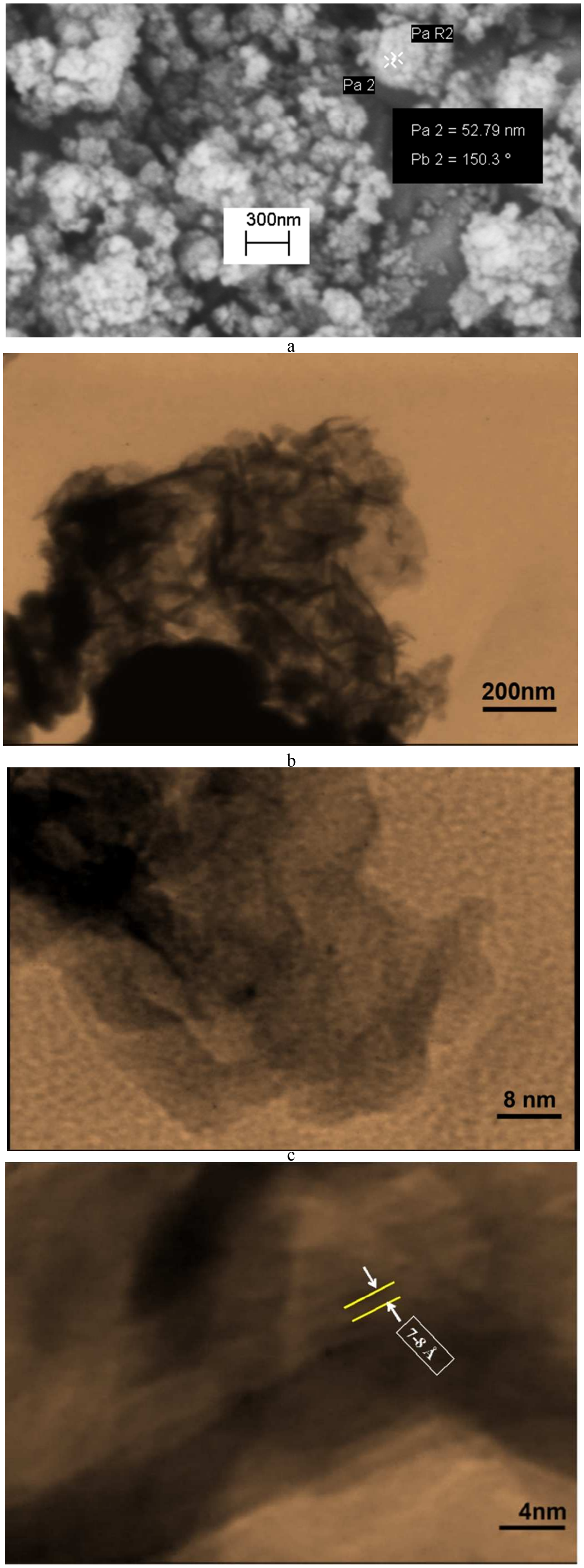
b

Fig. 1 A motif for Mn-Ca cubic in layered Mn oxide (a). Surface area of layered Mn oxide (Ca(II) ions are omitted for clarification) (b).

XRD data for the compound is of very poor resolution and the weak peak in 2θ ~11 related (00l) in layered Mn oxides, reveals the absence of long-range order of the layer stacking (Fig. S2, ESI†).[13]

Using extended-range X-ray absorption spectroscopy (XAS) at the K-edges of both Ca and Mn, two different Ca-containing motifs were identified. One of the motifs was the formation of Mn_3CaO_4 cubes while the other Ca(II) ions probably interconnected oxide-layer fragments (Fig. 1).[14]

SEM images from the catalyst show aggregated nanoparticles from < 100 nm. In TEM images, layers of Mn oxide are clearly detected and showed that the nano-compounds observed by SEM contain nanosheets (Fig. 2 and Fig. S3, ESI†). Only a few short-range orders among layers can be observed in the sample by HRTEM. Such layered Mn oxides without any long-range order among layers are rare. DLS shows that particles are in the range of 100-200 nm (Fig. S4, ESI†). Comparing with SEM (< 100 nm), we found aggregation of particles in solution. Peak at ~ 400 nm in solid state UV-Vis spectrum of oxide is related to Mn(III)/Mn(IV) ions in the structure (Fig. S5, ESI†).



a

b

c

d

Fig. 2 SEM micrographs (a), TEM (b) and HRTEM (c,d) images of nano-size Mn-Ca oxide prepared at 400 °C.

Catalytic performance of $Ca_{0.16}MnO_2.2H_2O$

In order to evaluate the catalytic activities of $Ca_{0.16}MnO_2.2H_2O$ for oxidation reactions, the reactions were optimized according to the oxidation of methyl phenyl sulfide (**MPS**) through the investigation of the influence factors of oxidation, such as the various solvents and oxidants, and the amount of catalyst and oxidant.

In order to understand the effect of catalyst on the catalytic reactivity, the first, **MPS** oxidation reaction was carried out without catalyst. Results indicated that in the absence of catalyst, trace amount of product was generated in presence of H_2O_2 as an oxidant. Various oxidants including TBHP, H_2O_2, NaClO and molecular oxygen were tested for the oxidation of **MPS** over $Ca_{0.16}MnO_2.2H_2O$ at room temperature. Among these oxidants, molecular oxygen and H_2O_2 were much more efficient for the oxidation of **MPS**. The amount of H_2O_2 could also significantly affect the conversion and selectivity for **MPS** oxidation to sulfoxide (selectivity: sulfoxide/(sulfoxide + sulfone))×100) (Table 1). When the amount of H_2O_2 was increased from 0.5 to 1.5 mmol, the conversion of **MPS** increased drastically from 47 to 85%. With a further increasing of H_2O_2 to 2.0 mmol, the selectivity for MPS oxidation to sulfoxide decreases from 92 to 70%. The conversion of **MPS** monotonously increases with the addition of catalyst from 5 to 10 mg. When the amount of catalyst is increased to 20 mg, the selectivity for **MPS** oxidation to sulfoxide reduces from 95 to 70%. Hence, the amount of catalyst can enhance the reaction rate for the selectivity for **MPS** oxidation to sulfoxide. In the next step, a series of reactions was investigated by performing the model reaction in different solvents such as dichloromethane, methanol, acetonitrile, benzene, acetone and n-hexane. Among the solvents examined, acetonitrile was found to be the best for this protocol (Table 1).

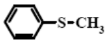
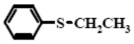
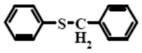
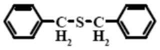
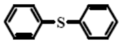
Table 1. The effect of various conditions on the oxidation of **MPS** by $Ca_{0.16}MnO_2.2H_2O$.

Entry	Catalyst amount (mg)	Oxidant	Oxidant amount (mmol)	Solvent	Conversion (%)[a]	Selectivity (%)[b]
1	-	H_2O_2	0.5	CH_3CN	trace	-
2	20	H_2O_2	0.5	CH_3CN	47	100
3	20	TBHP	0.5	CH_3CN	45	94
4	20	NaClO	0.5	CH_3CN	28	100
5	20	O_2	bubbled	CH_3CN	97	41
6	20	H_2O_2	1.0	CH_3CN	63	99
7	20	H_2O_2	1.5	CH_3CN	85	92
8	20	H_2O_2	2.0	CH_3CN	88	70
9	15	H_2O_2	1.5	CH_3CN	83	93
10	10	H_2O_2	1.5	CH_3CN	83	95
11	5	H_2O_2	1.5	CH_3CN	62	99
12	10	H_2O_2	1.5	CH_3OH	75	96
13	10	H_2O_2	1.5	CH_2Cl_2	21	100
14	10	H_2O_2	1.5	C_6H_6	29	100
15	10	H_2O_2	1.5	CH_3COCH_3	33	100
16	10	H_2O_2	1.5	n-hexane	8	100

[a] The GC conversion (%) are measured relative to the starting substrate. [b] Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone))×100.

A series of various types of structurally diverse sulfides were subjected to the oxidation reaction using $Ca_{0.16}MnO_2.2H_2O$ as catalyst and H_2O_2 as oxidant (Table 2). Arylalkyl (Table 2, entries 1,2), arylbenzyl (Table 2, entry 3), dibenzyl (Table 2, entry 4), diaryl (Table 2, entry 5) and dialkyl (Table 2, entries 6-8) sulfides underwent clean and the selectivity for **MPS** oxidation to sulfoxide under air, is high (89-100%). Significantly, the very good conversions of substrates depending on the nature of the sulfide, in the range of 51-100% were obtained for all cases. It was observed that aromatic sulfides undergo oxidation reactions can be oxidized to sulfoxide more easily than aliphatic substrates. These results may indicate that the Mn^V=O intermediate can efficiently transfer oxygen atom to electron-rich sulfides than electron-poor one. The highest and the lowest conversions were obtained for dibenzyl sulfide (100%) and diethyl sulfide (51%), respectively (Table 2, entries 4 and 6).

Table 2. Oxidation of sulfides catalyzed by $Ca_{0.16}MnO_2.2H_2O$ /H_2O_2[a]

Entry	Substrate	Conversion (%)[b]	Selectivity (%)[c]
1		83	95
2		85	91
3		99	91
4		100	89
5		68	98
6	CH_3CH_2-S-CH_2CH_3	51	100
7	$CH_3(CH_2)_2$-S-$(CH_2)_2CH_3$	55	100
8	$CH_3(CH_2)_7$-S-$(CH_2)_7CH_3$	52	100

[a] The molar ratios for substrate: oxidant are 1:3. The reactions were performed in CH_3CN (1 mL) under air at room temperature within 2h. [b] The GC yield (%) are measured relative to the starting sulfide. [c] Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.

The recovery and recyclability of $Ca_{0.16}MnO_2.2H_2O$ have been also examined for the oxidation of **MPS** at room temperature for 2 h and the results have been shown in Fig. 3. The catalyst was separated after each run by filtration, washed 2-3 times with water and diethyl ether repeatedly, and then dried at 50 °C for half an hour. The catalyst could be recycled five times with no significant loss in activity. During reusability studies fifth run provided ~ 79% conversion and 95% selectivity.

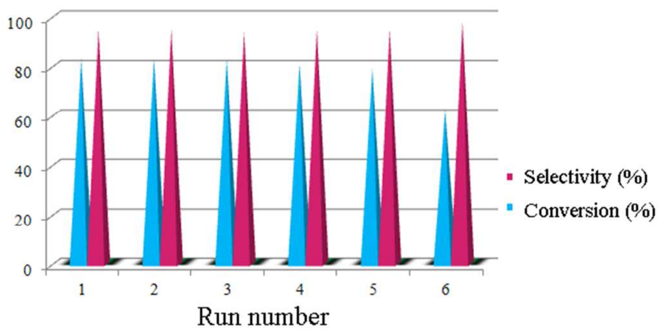


Fig. 3 Recycling studies of the catalyst $Ca_{0.16}MnO_2.2H_2O$ in the oxidation of **MPS**. Condition is similar to table 2.

In order to investigate catalyst leaching in the oxidation of **MPS** as a model reaction, the reaction was stopped at half the reaction time (1 h) and the solid catalyst was completely separated from solution. The rest of the reaction mixture (without catalyst) was allowed to stir for another period of half the reaction time. As seen in Fig. 4, no amount of **MPS** was produced after catalyst separation. After separation of the catalyst, the reaction mixture was analyzed by AAS and no Mn ions were detected. These results show that $Ca_{0.16}MnO_2.2H_2O$ is truly heterogeneous and catalyst leaching is negligible under these conditions.

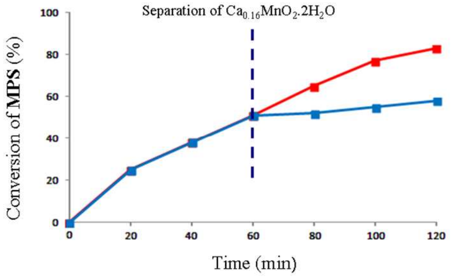


Fig. 4 Leaching experiment; The blue line shows the reaction without $Ca_{0.16}MnO_2.2H_2O$ and the red line shows the reaction with $Ca_{0.16}MnO_2.2H_2O$.

The probable factors of Mn-Ca oxide for activity toward oxidation reactions are:

- The catalyst has a layered structure with considerable thermodynamic stability.[15]
- The oxide has high surface area and many of Mn ions are active sites regarding layered structure. In other words, in contrast to other Mn oxides, in layered Mn oxides many Mn ions are on the surface where can act as active sites.
- Both Mn(III)/Mn(IV) ions are stable in the structure that the factor helps to conversion of Mn(III) and Mn(IV) in the catalytic cycle.[15]

Conclusions

In conclusions, we introduced layered Mn-Ca oxide as efficient catalyst with high selectivity for MPS oxidation to sulfoxide in the presence of H_2O_2. The catalyst is stable and could be recycled five times with no significant loss in activity.

The authors are grateful to Institute for Advanced Studies in Basic Sciences, the National Elite Foundation and University of Maragheh for financial support.

Notes and references

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[c] *Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran*
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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

1 K. Sato, M. Hyodo, M. Aoki, X.-Q. Zheng and R. Noyori, *Tetrahedron*, 2001, **57**, 2469.
2 K. Kaczorowska, Z. Kolarska, K. Mitka and P. Kowalski, *Tetrahedron*, 2005, **61**, 8315.
3 J. H. Albering, in Handbook of Battery Materials, ed. J. O. Besenhard, Wiley-VCH Verlag GmbH, 1999.
4 K. S. Ravikumar, J. Begue and D. Bonnet-Delpon, *Tetrahedron Lett.*, 1998, **39**, 3141.
5 K. Noda, N. Hosoya, R. Irie, Y. Yamashita and T. Katsuki, Tetrahedron, 1994, **50**, 9609.
6 a) G. Cahiez, M. Alami, R. J. K. Taylor, M. Reid and J. S. Foot, (2004), "Mn Dioxide", in Paquette, Leo A., Encyclopedia of Reagents for Organic Synthesis, New York: J. Wiley & Sons; b) B. Dmuchovsky, M. C. Freerks and F. B. Zienty, *J. Catal*., 1965, **4**, 577; c) R. B. Anderson, K. C. Stein, J. J. Feenan and L. J. E. Hofer, *Ind. Eng. Chem*., 1961, **53**, 809; R. Ghosh, X. Shen, J. C. Villegas, Y. Ding, K. Malinger and S. L. Suib, *J. Phys. Chem. B*, 2006, **110**, 7592; d) L. Espinal, S. L. Suib and J. F. Rusling, *J. Am. Chem. Soc*., 2004, **126**, 7676.
7 L. Wang, Q. Liu, X. Huang, Y. Liu, Y. Cao and K. Fan, *Appl. Catal. B: Environ*, 2009, **88**, 204. b) R. Xu, X. Wang, D. Wang, K. Zhou and Y. Li, *J. Catal*., 2006, **237**, 426.
8 T. Yamashita and A. Vannice, *Appl. Catal. B Environ*., 1997, **13**, 141.
9 M. M. Najafpour, F. Rahimi, E. Aro, C. Lee, and S. I. Allakhverdiev, *J. R. Soc. Interface*, 2012, **9**, 2383; A. Iyer, J. Del-Pilar, C. K. King'ondu, E. Kissel, H. F. Garces, H. Huang, A. M. El-Sawy, P. K. Dutta and S. L. Suib, *Phys. Chem. C*., 2012, **116**, 6474; A. Singh, R. K. Hocking, S. L. Y. Chang, B. M. George, M. Fehr, L. Klaus, A. Schnegg and L. Spiccia, *Chem. Mater.*, 2013, **25**, 1098; F. Jiao and H. Frei, *Chem. Commun*., 2010, **46**, 2920; A. Bergmann, I. Zaharieva, H. Dau and P. Strasser, *Energy Environ. Sci*., 2012, **6**, 2745.
10 M. M. Najafpour, M. Abbasi Isaloo, M. Abasi and M. Hołyńska, *New J. Chem*., 2014, **4**, 6375; M. M. Najafpour, B. Haghighi, M. Zarei Ghobadi and D. Jafarian Sedigh, *Chem. Commun*., 2013, **49**, 8824; M. M. Najafpour, B. Haghighi, D. Jafarian Sedigh and M. Zarei, *Dalton Trans*., 2013, **42**, 16683; M. M. Najafpour and D. Jafarian Sedigh, *Dalton Trans*., 2013, **42**, 12173.
11 M. Amini, M. M. Najafpour, H. Naslhajiana and E. Aminib, *submitted manuscript.*
12 M. Amini, M. M. Najafpour, S. Nayeri, B. Pashaei and M. Bagherzadeh, *RSC Adv*., 2012, **2**, 3654; M. M. Najafpour, M. Amini, D. J. Sedigh, F. Rahimi and M. Bagherzadeh, *RSC Adv*., 2013, **3**, 24069.
13 M. M. Najafpour, D. Jafarian Sedigh, B. Pashaei and S. Nayeri, *New J. Chem*., 2013, **37**, 2448; M. M. Najafpour, B. Pashaei and S. Nayeri, *Dalton Trans*., 2012, **41**, 7134.
14 I. Zaharieva, M. M. Najafpour, M. Wiechen, M. Haumann, P. Kurz and H. Dau, *Energy Environ Sci*., 2011, **4**, 2400.
15 N. Birkner, S. Nayeri, B. Pashaei, M. M. Najafpour, W. H. Casey and A. Navrotsky, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 8801.

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4	20	NaClO	0.5	CH_3CN	28	100
5	20	O_2	bubbled	CH_3CN	97	41
6	20	H_2O_2	1.0	CH_3CN	63	99
7	20	H_2O_2	1.5	CH_3CN	85	92
8	20	H_2O_2	2.0	CH_3CN	88	70
9	15	H_2O_2	1.5	CH_3CN	83	93
10	10	H_2O_2	1.5	CH_3CN	83	95
11	5	H_2O_2	1.5	CH_3CN	62	99
12	10	H_2O_2	1.5	CH_3OH	75	96
13	10	H_2O_2	1.5	CH_2Cl_2	21	100
14	10	H_2O_2	1.5	C_6H_6	29	100
15	10	H_2O_2	1.5	CH_3COCH_3	33	100
16	10	H_2O_2	1.5	n-hexane	8	100

[a] The GC conversion (%) are measured relative to the starting substrate. [b] Selectivity to sulphoxide sulfoxide = (sulfoxide/(sulfoxide + sulfone))×100.

Table 2. Oxidation of sulfides catalyzed by $Ca_{0.16}MnO_2.2H_2O$ /H_2O_2[a]

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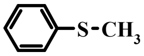
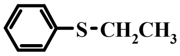
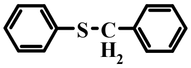
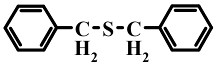
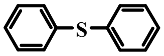
1		83	95
2		85	91
3		99	91
4		100	89
5		68	98
6	CH_3CH_2-S-CH_2CH_3	51	100
7	$CH_3(CH_2)_2$-S-$(CH_2)_2CH_3$	55	100
8	$CH_3(CH_2)_7$-S-$(CH_2)_7CH_3$	52	100

[a] The molar ratios for substrate: oxidant are 1:3. The reactions were performed in CH_3CN (1 mL) under air at room temperature within 2h.[b] The GC yield (%) are measured relative to the starting sulfide. [c] Selectivity to sulfoxide = (sulfoxide/(sulfoxide + sulfone)) × 100.

Electronic Supplementary Information (ESI)

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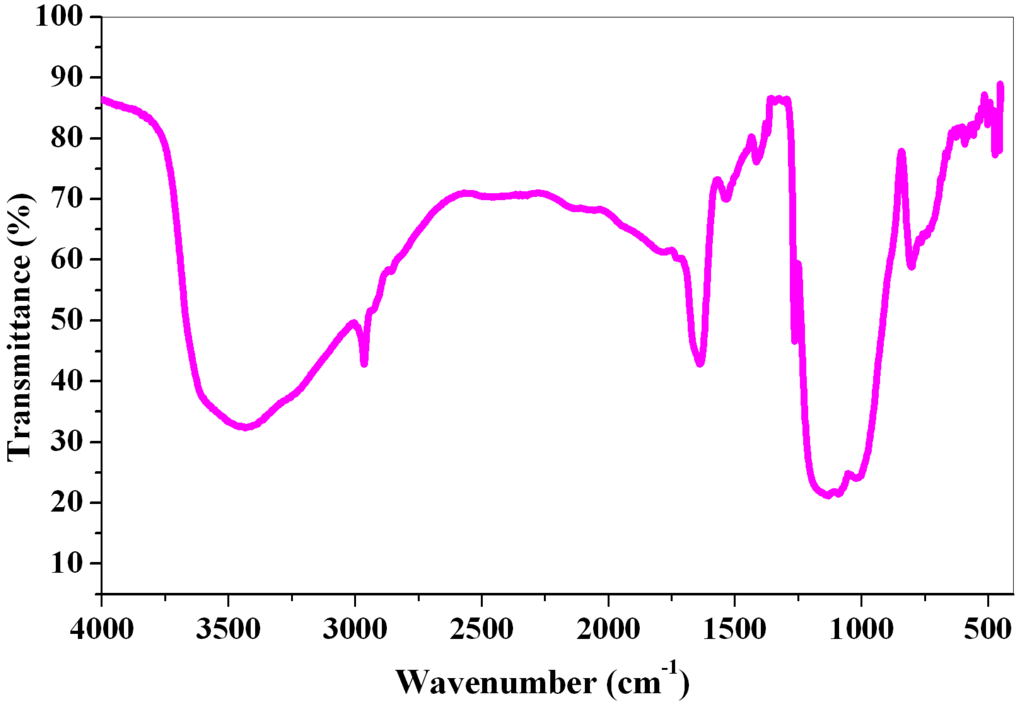


Fig. S1 Reflectance infrared Fourier transform spectra of Mn-Ca oxide.

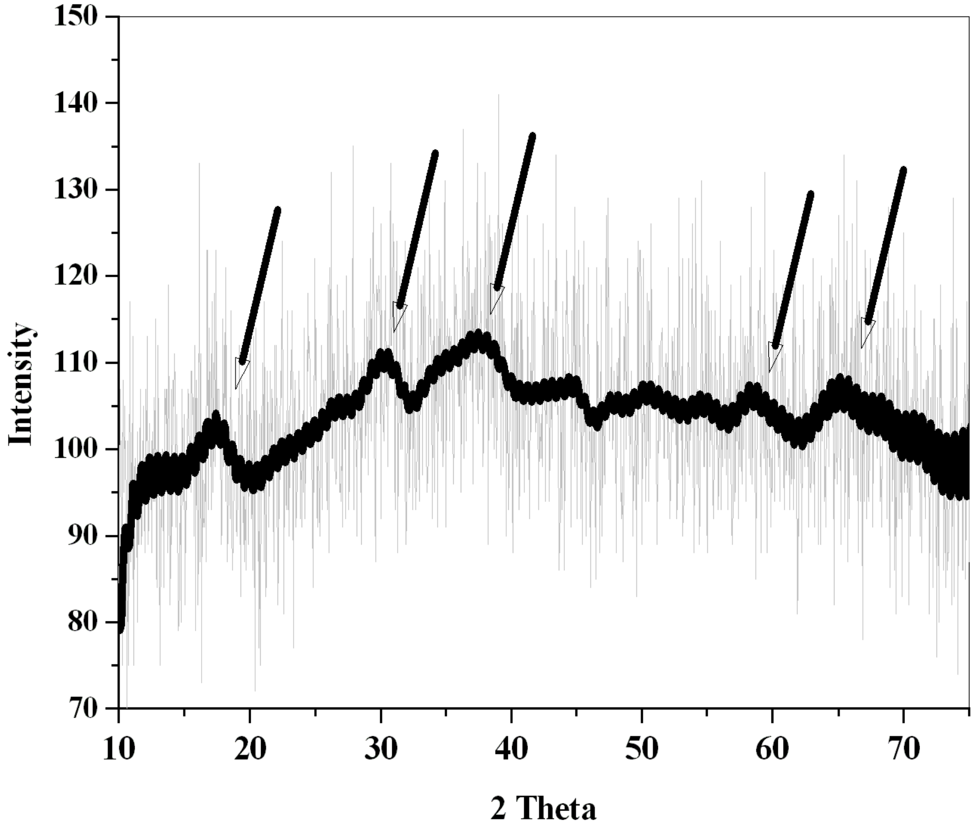
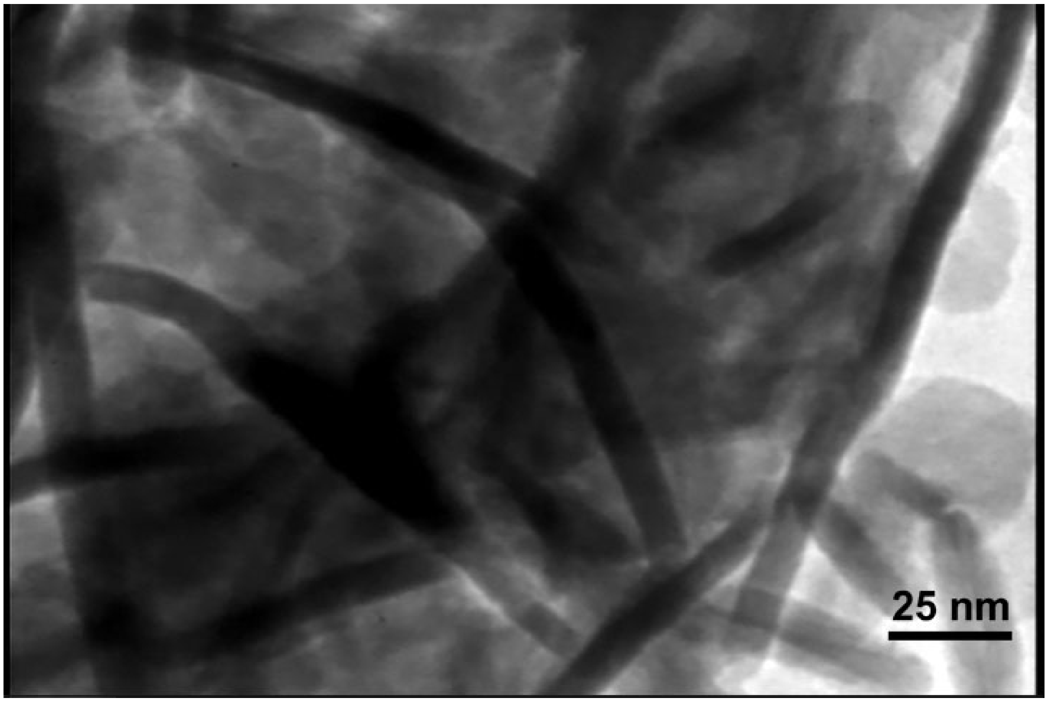
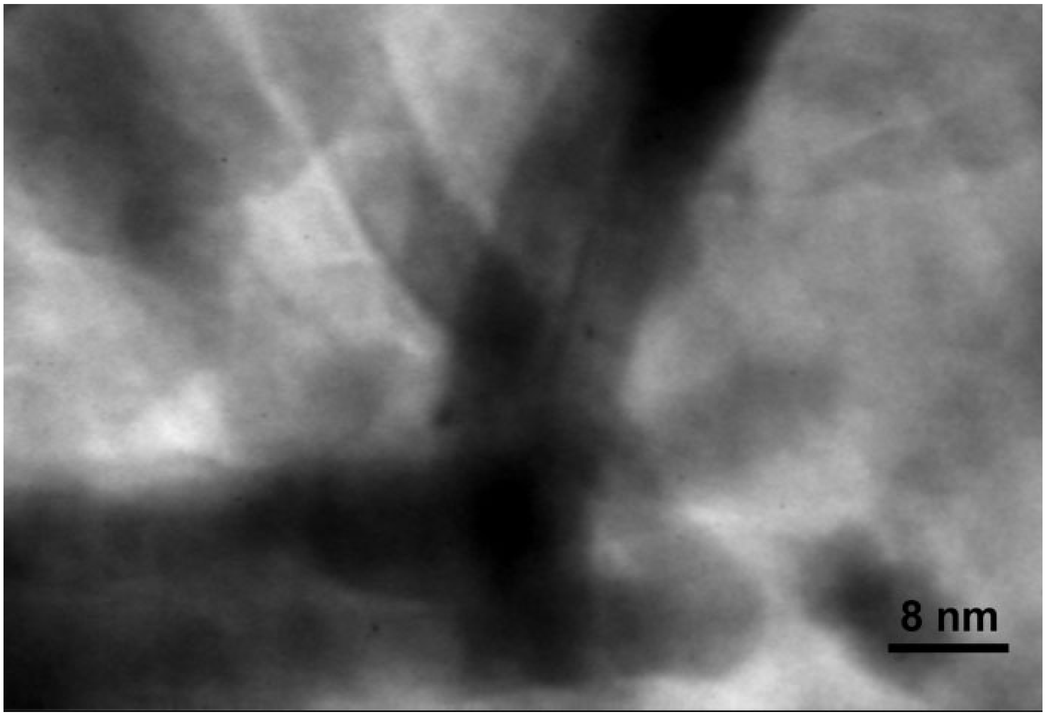


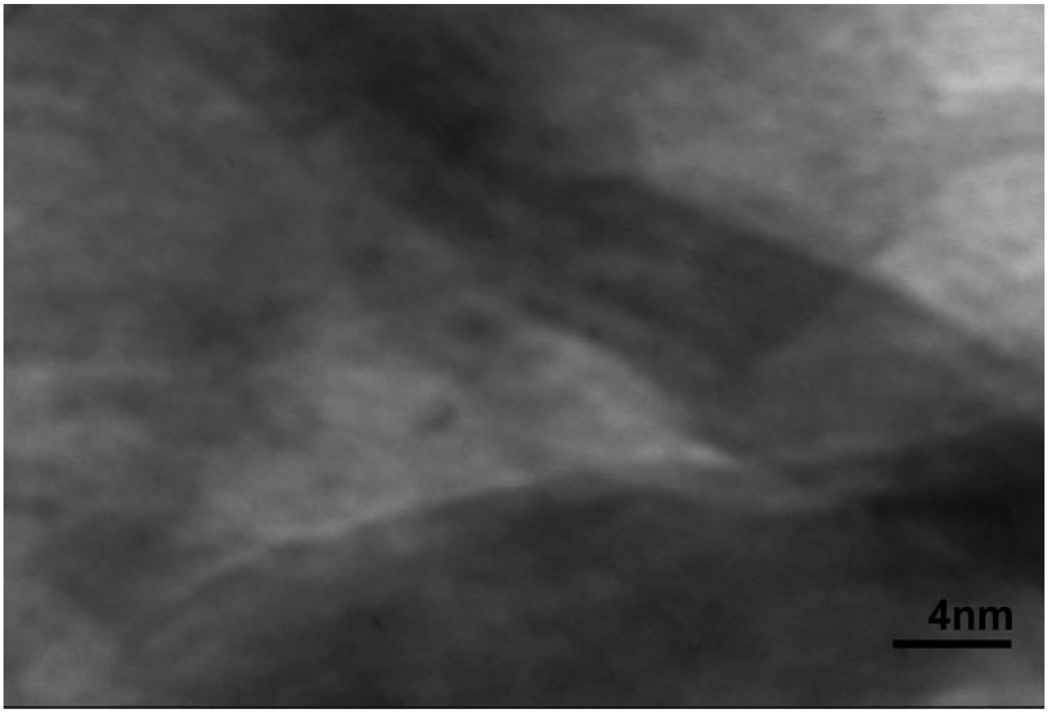
Fig. S2 XRD patterns of the obtained of nanolayered Mn-Ca oxide (grey) and FFT Filter Smoothing (black) of XRD patterns of the compound. FFT Filter Smoothing shows peaks related to layered Mn oxide.



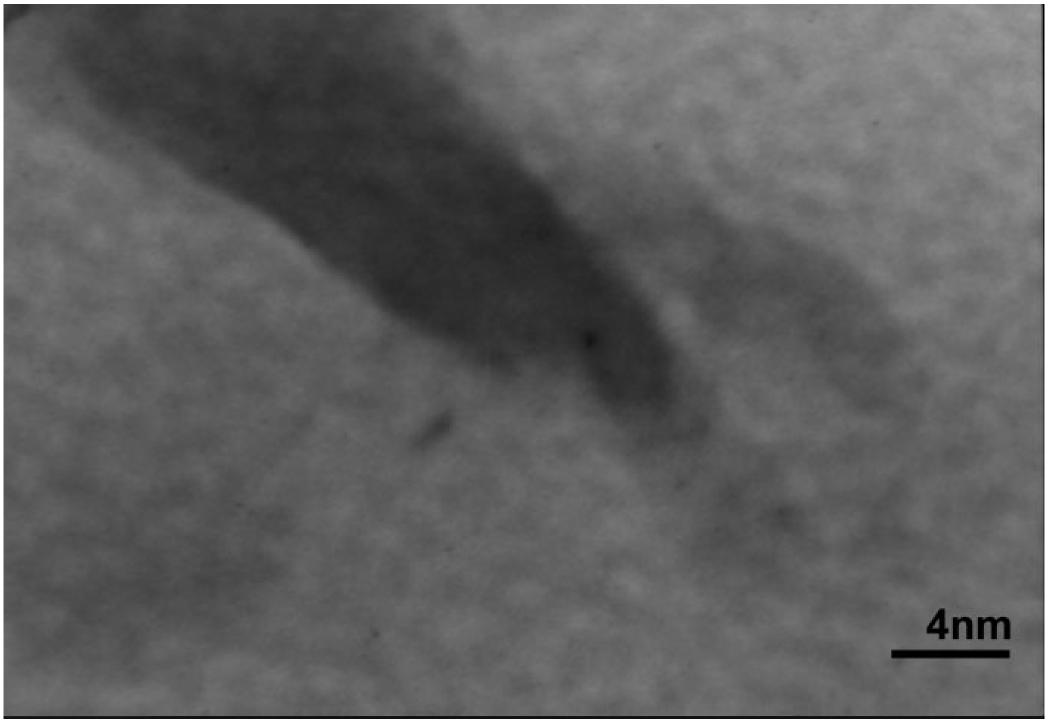
a



b



c



d

Fig. S3 TEM images for the Mn-Ca oxide.

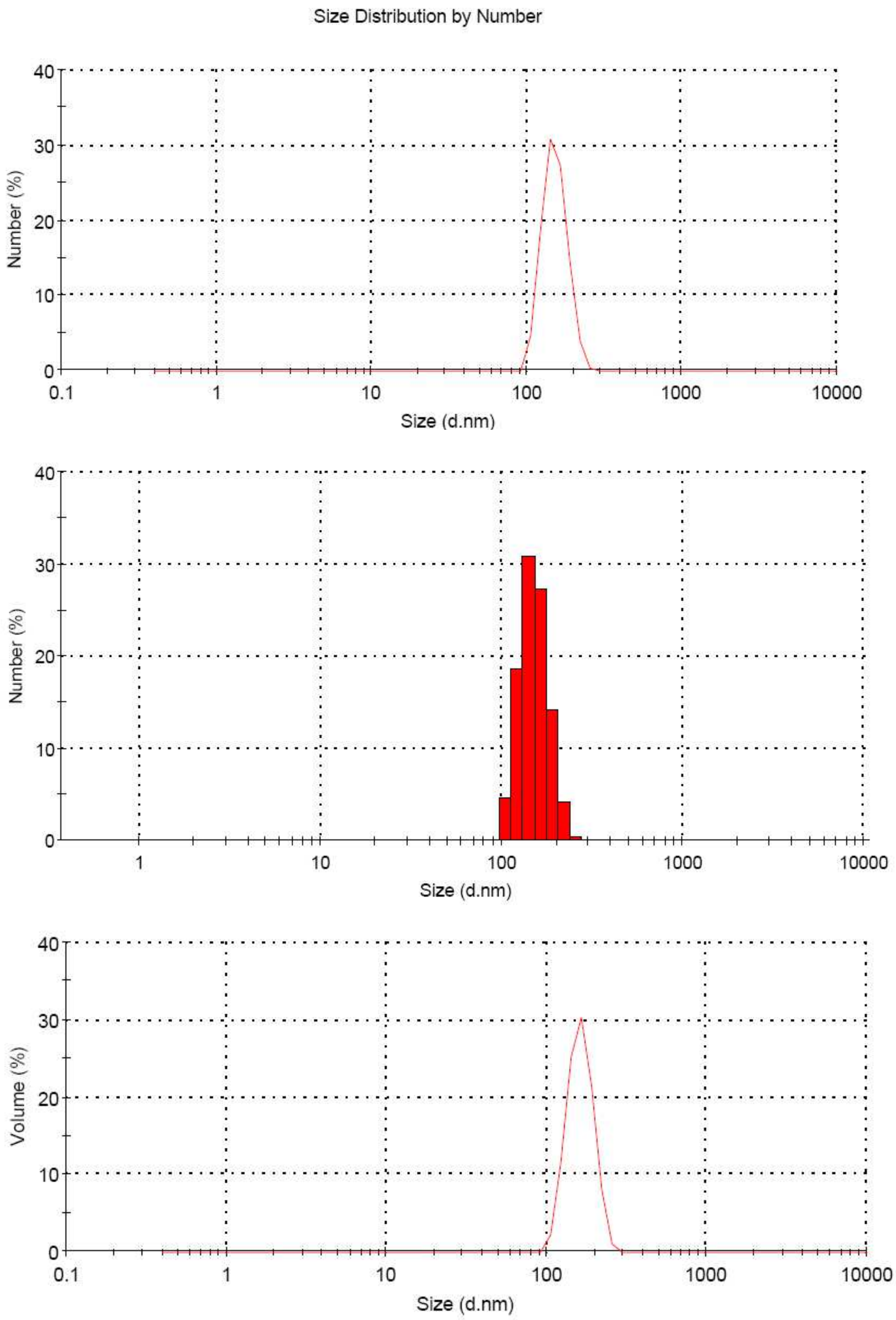


Fig. S4 DLS result for Mn-Ca oxide.

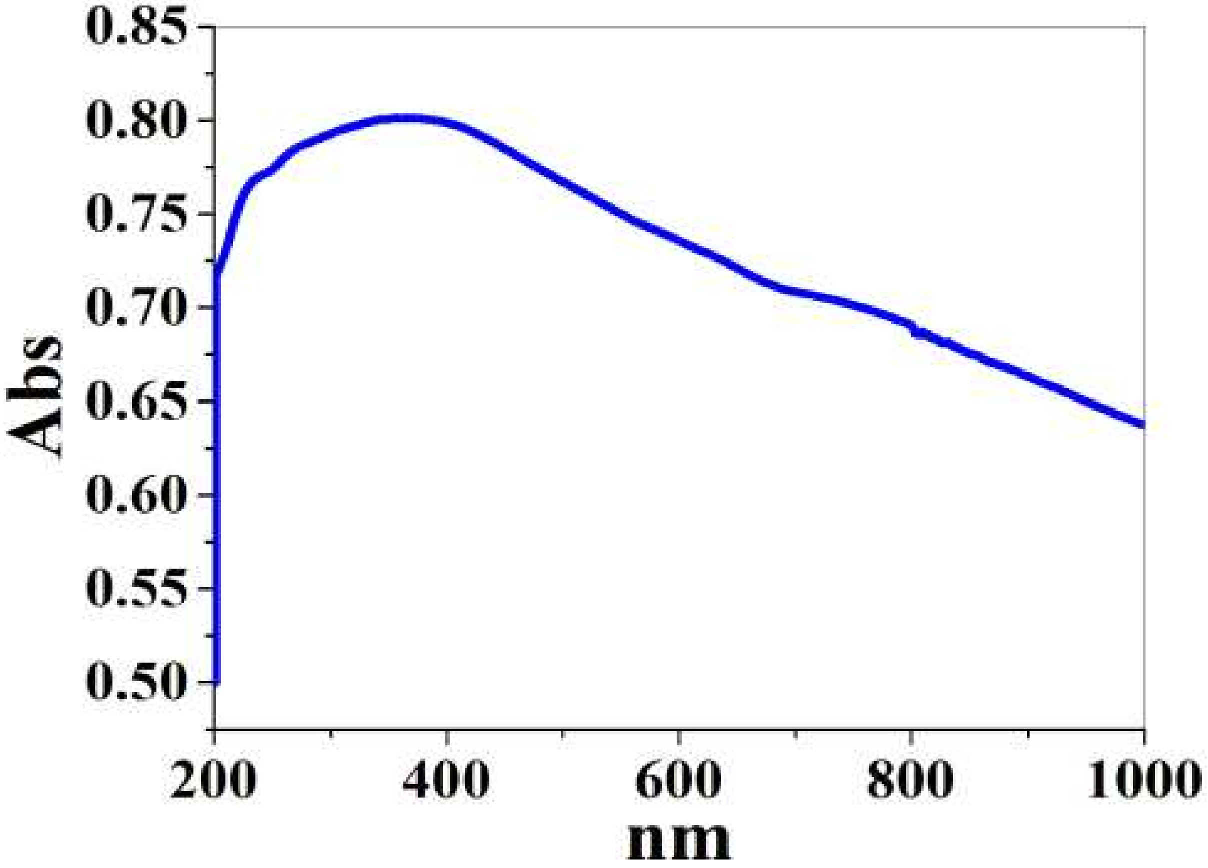
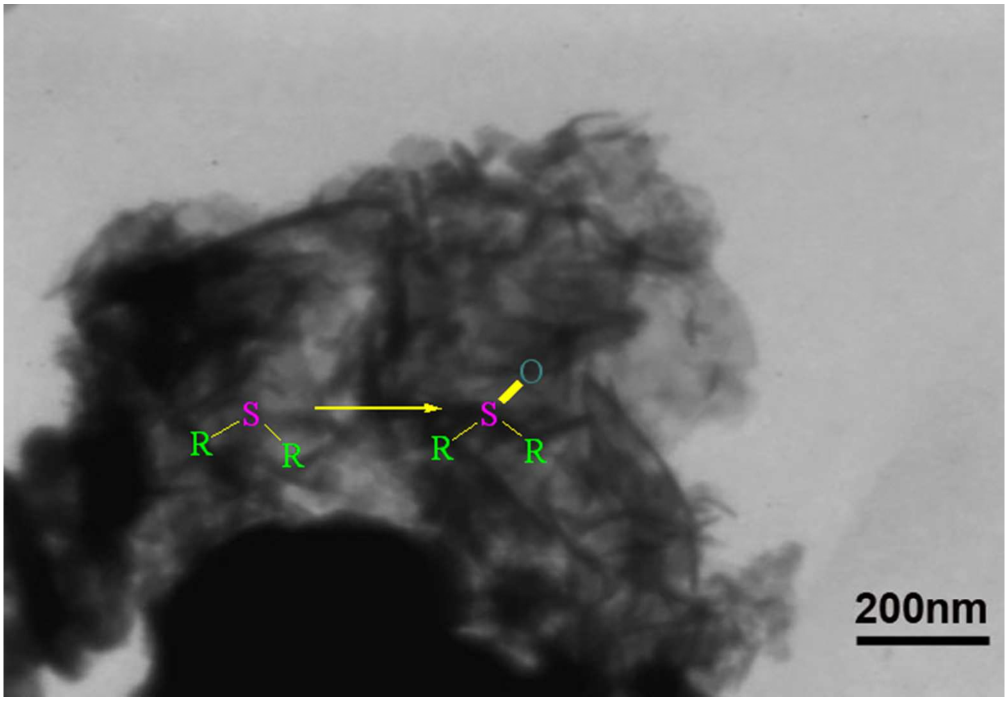


Fig. S5 Solid UV-Vis spectrum of Mn-Ca oxide

We for the first time report that nanolayered Mn-Ca oxide in the presence of H_2O_2 is an efficient catalyst toward sulfide oxidation to sulfoxide.



179x124mm (96 x 96 DPI)