

Purification of Single-Wall Carbon Nanotubes by Selective Microwave Heating of Catalyst Particles

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A new scalable method for purification of single-wall carbon nanotubes (SWNTs) by using microwave heating in air is developed. The microwaves couple to the residual metal catalyst, raising significantly the local temperature leading to both the oxidation and rupturing of the carbon passivation layer over the metal catalyst particles. With this protective carbon coating weakened or removed, a mild acid treatment is then sufficient to remove most of the metal in the sample, leaving the nanotubes in tact. Using microwave processing and 4 M HCl acid reflux for 6 h we were able to remove residual metal (Ni, Y) in arc-discharge SWNTs to a level lower than 0.2 wt % (~ 0.04 at. %). Results from transmission and scanning electron microscopy, Raman spectroscopy, and thermogravimetric studies were discussed.

Introduction

Single-wall carbon nanotubes (SWNTs) were first reported by Iijima and co-workers at NEC, and Bethune and co-workers at IBM in 1993.^{1,2} Most of the synthesis methods today produce tubes in the diameter range 1–2 nm, and they are arranged in bundles of ten to hundreds of tubes. SWNTs are often a minority constituent (<50 wt %) in the reaction product. Also present, for example, is amorphous carbon, which can coat the bundle walls, residual metal catalyst, and multi-shell sp^2 carbon, which covers the metal catalyst residue. Proposed applications of SWNTs, i.e., nanoelectronic devices, field emitters, gas sensors, high-strength composites, and hydrogen storage require reasonably pure SWNT material.³

It is a challenging problem to purify the reaction product without damaging the tubes. Many procedures have been developed for purification of SWNTs, i.e., hydrothermal,⁴ gaseous or catalytic oxidation,^{5,6} nitric acid reflux,^{7–9} peroxide reflux,¹⁰ cross-flow filtration,¹¹ and chromatography.¹² Purification based on an initial selective oxidation to remove amorphous carbon (and not induce serious SWNTs loss), followed by a reflux in concentrated HNO_3 acid, has also been found to be effective in removing metal from the reaction products.^{13–16} However, refluxing in nitric acid can induce wall damage in the tubes,¹³ and removing the carbon-coated residual catalyst without this wall damage remains a serious problem.

In the present work, we show that local heating of the carbon-over coated metal catalyst particles in air using microwave radiation is a very beneficial first step in a general purification scheme for SWNT. We shall show here that the local microwave heating in air induces combustion of the carbon shell to form CO/CO₂, and also may drive the expansion of the metal core

of the catalyst particle, opening cracks in the carbon overcoating. This microwave processing step then allows an acid treatment (4 M HCl) at low temperature to remove most of the residual metal catalyst. Microwave materials processing has been successfully applied to a wide variety of materials, including rubber, oxide/non-oxide ceramics, carbide semimetals, and powdered metals.¹⁸ In particular, microwave sintering of metal powders with different shapes and sizes have been reported, maintaining sintering temperatures in the range 20–2000 °C.¹⁷ To our knowledge, this work is the first study of the application of microwaves to the purification of SWNTs.

Experimental Section

SWNT materials for our study were produced by Carbox, Inc. (U.S.A.) using the arc-discharge technique and a Ni–Y catalyst added to the electrodes.¹⁸ As it is well-known, arc-derived carbon nanotube material is generally accepted as the most challenging soot to remove metal catalyst residue. We find that the residual catalyst in the Carbox SWNT reaction product material is 4–6 at. % (20–40 wt %) as determined by temperature-programmed oxidation (TPO) using an IGA-3 Hiden thermogravimetric analyzer (TGA). In this analysis, all the carbon is assumed converted to CO/CO₂, and the metal is converted to an oxide. Within the TGA, the carbon SWNT material to be analyzed for metal was maintained in a flow of dry air at 100 sccm while the temperature was ramped linearly in time (5 °C/min) from 25 to 1000 °C. The temperature (T) [or time-(t)] dependence of the evolution of the sample mass m is measured. With increasing T , carbon is converted to CO/CO₂ and $m(T)$ decreases. Characteristic combustion temperatures of various carbon phases in the soot, e.g., amorphous carbon, SWNT, can be identified by the peak positions in the derivative data (DTPO), i.e., dm/dT vs T data. The positions of these peaks can be affected by the amount of residual catalyst in the sample. Increasing metal catalysts residue tends to shift the DTPO peaks to lower temperature, i.e., the growth catalyst also acts as an oxidation catalyst and lowers the combustion temperature.^{5,13,19}

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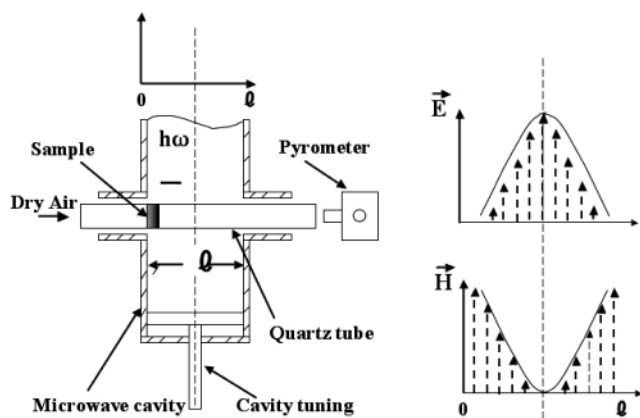


Figure 1. A schematic diagram of the microwave system. The microwave magnetic field distribution within TE₁₀₃ single mode microwave cavity where the sample is located is shown.

The microwave heating of the SWNT soot was conducted at different temperatures in flowing dry air (100 sccm) using a tuned TE₁₀₃ single mode cavity driven by a 1.5 kW, 2.45 GHz power supply. The sample (100 mg) was placed in a quartz tube that passed through the cavity, as shown schematically in (Figure 1). The maximum microwave power used here was only 150 W. The induced effective temperature in the sample was measured by an infrared optical pyrometer (Mikron M90BT, Mikron, Inc.) with an accuracy ± 5 °C.

Microwave heating as an initial step for metal removal will be compared to “selective oxidation”. Selective oxidation is a term in the literature that refers to a “selective oxidation of undesirable minority phases (e.g., amorphous carbon, multishell carbon, carbon onions). In fact, this terminology is a little misleading, because inevitably, some SWNTs are also converted to CO/CO₂ during “selective” oxidation. Perhaps the term “preferential” oxidation is more appropriate. Conditions such as temperature, time, flow of dry air, etc., are chosen to create a combustion which preferentially removes amorphous carbon, and, to a lesser extent, other carbons, and further attempts to minimize the loss of SWNTs from the sample. We have found that for arc-derived tubes, the following conditions are optimal for “selective oxidation”: $T = 405$ °C, dry air flow sccm = 100, time = 30 min. The point we wish to stress is that SWNTs are lost because this carbon phase also reacts with dry air at the same temperature as the multishell carbon encasing the metal particles. However, with the microwave processing in air we create much higher temperature in the carbon on the metal particles than in metal-free regions of the sample, e.g., SWNTs rich regions. The microwave process should thus be expected to cause less SWNTs loss than “selective oxidation”.

Transmission electron microscopy (JEOL JEM 1200EX and Hitachi 2000F) and scanning electron microscopy (Philips XL 20) were used for the characterization of the samples. Also, Raman scattering spectra were collected on a BOMEM DA 3+ FTIR spectrometer equipped with Nd:YAG Laser for excitation (1.06 μ m).

Results and Discussion

Morphology Characterization. Transmission electron microscopy (TEM) of the as-prepared, arc-derived SWNTs revealed a high density of 1–4 micron long bundles of nanotubes and with mean bundle diameter ~ 15 nm (Figure 2a). The SWNTs exhibited diameters in the range $1 < d < 2$ nm, as determined by Raman spectroscopy.^{21,22} Also, an amorphous carbon coating on the outside of the bundle, and catalyst particles

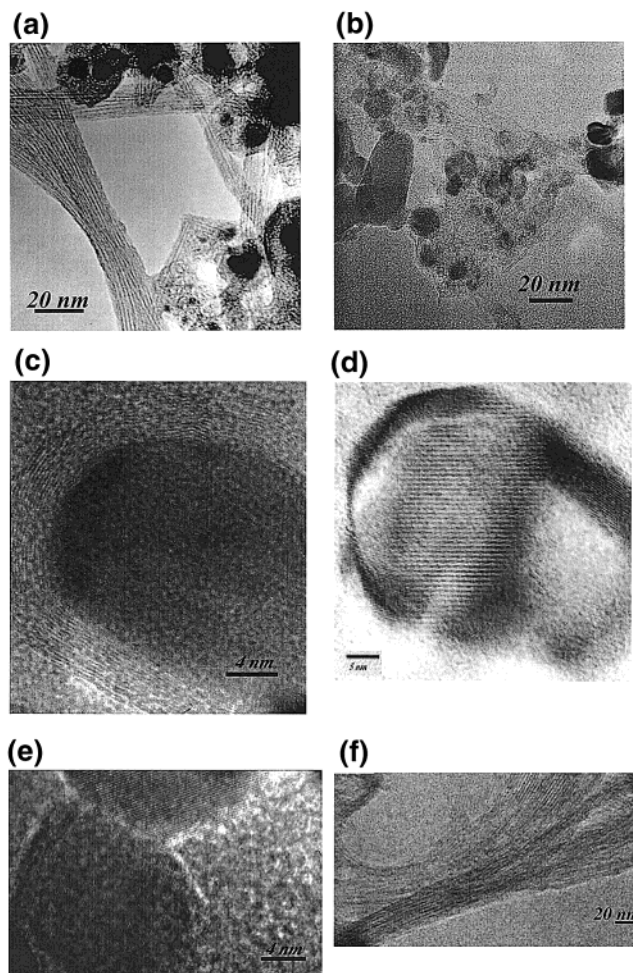


Figure 2. TEM and HRTEM micrographs of (a) as-prepared SWNT material; (b) SWNTs material after microwave heating at 500 °C for 20 min; (c) metal catalyst covering with multishell carbon in the as-prepared sample; (d) metal catalyst surface after microwave treatment at 500 °C for 20 min; (e) example of sintering of metal catalyst particles due to the local temperature driving by microwave heating; (f) SWNT material after mild 4 M HCl acid refluxing for 6 h following the microwave heating.

encapsulated within multilayer graphitic shells were observed in the TEM images. The goal of purification of the SWNT material is the removal of all of these impurity phases (i.e., amorphous carbon, multishell carbon, and metal). A successful process, of course, should not cause significant damage to the nanotubes, or be responsible for much nanotube weight loss. Thus, a local heating process targeting the metal particles and its carbon overcoating is desirable. As the microwaves couple primarily to the metal particles, they provide such a localized heating.

Figure 2b shows the TEM image of SWNTs after a short microwave treatment at 500 °C for 20 min in flowing dry air. After microwave heating, the carbon coating is observed to be almost completely removed from the surface of most of the metal catalyst particles, as observed by HRTEM images of many metal particles before (Figure 2c) and after (Figure 2d) microwave treatment. Before microwave treatment, the HRTEM image of a typical catalyst particle is observed to be covered with ~ 10 graphitic carbon layers exhibiting a plane spacing of 0.34 nm (002 plane) (Figure 2c). The chemical inertness of this covering is the reason that arc-derived SWNTs are so difficult to purify. After the microwave treatment at 500 °C for 20 min (Figure 2d), most of the catalyst particles are found to be free

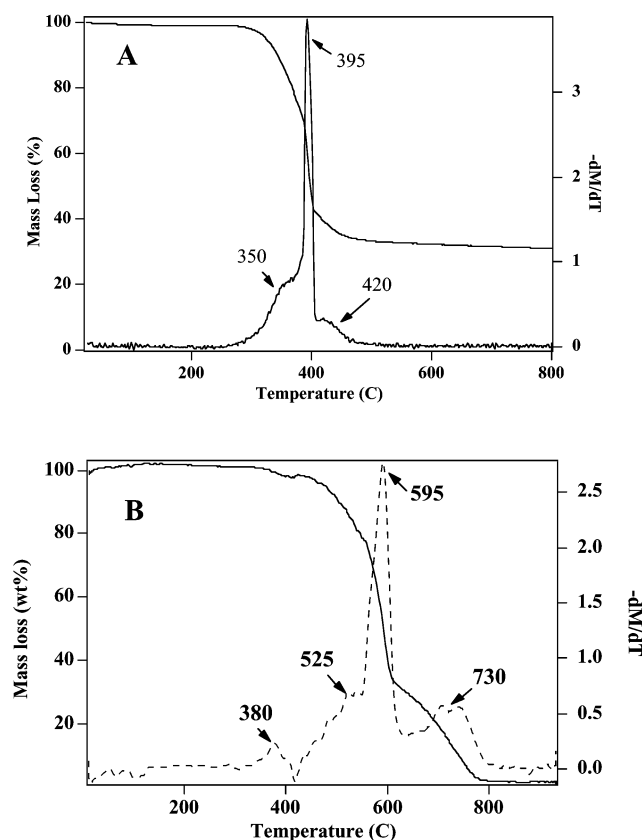


Figure 3. TPO (solid curve) and DTPO (dash curve) profiles of SWNT materials; (a) as-prepared; (b) after microwave treatment at 500 °C for 20 min followed by 4 M HCl refluxing for 6 h.

of this graphitic covering, the lattice fringes of the metal nanoparticle can also clearly be observed. The regular spacing of the observed lattice plane was 0.24 nm, which corresponds to the separation of (111) planes of cubic NiO. Most of the images of the nanoparticles after microwave heating in air exhibited these general features. From these TEM images, we conclude that during microwave heating in air, the carbon coating on the metal particles was primarily converted to CO/CO₂. The metal (Ni) was converted to a metal oxide. As shown in the HRTEM image of Figure 2e, the local temperature at the particle surface must also drive some sintering of these metal particles. This is the reason the metal particle size appears much larger in the low-resolution image of Figure 2b relative to that shown in Figure 2a. Finally, we show an HRTEM image of SWNT ropes after microwave processing and after 4 M HCl acid refluxing for 6 h (Figure 2f). As can be seen, the ropes remain in tact and most of the metal particles have been removed by the HCl treatment. No apparent structural damage to the SWNT was detected by Raman scattering, as discussed below.

Thermogravimetric Analysis. In Figure 3a we show the TPO and DTPO curves for the as-prepared arc-discharge SWNT soot. A three-peak structure in the DTPO data is observed: amorphous carbon (~350 °C), SWNTs (~400 °C) and multishell carbons (~450 °C). These peaks are downshifted to these lower temperatures due to residual growth catalyst that also acts as an oxidation catalyst. Our assignments of the peaks in the DTPO data to specific carbon phases are consistent with the literature,^{5,13,19} and are supported by a TEM image analysis not discussed here.¹³ As one can see in Figure 3a, the oxidation temperature range of different carbon structures overlap the oxidation range for SWNTs. Therefore, one cannot expect global oxidation to selectively remove the amorphous carbon and

multishell carbon phases. This DTPO data clearly shows that an experimental approach that can locally change the temperature of the multishell carbon covering the metal particles is very desirable. The metal content (~35 metal wt %) in the soot was obtained from the mass at 800 °C, i.e., the far right edge of the TPO curve (Figure 3a). Microwave processing of the as-prepared material followed by the 4M HCl treatment changed the TPO/DTPO characteristics dramatically, as shown in Figure 3b. First, all the peaks in DTPO data upshift to higher temperature, consistent with the removal of the metal residue (oxidation catalyst) by 6M HCl refluxing. For example, the largest peak identified with the combustion of SWNTs, upshifts by ~200 °C. Second, the low temperature shoulder in the DTPO data that is identified with amorphous carbon is reduced in strength. Third, the separation between the large SWNT peak and the higher temperature peak identical with multishell carbon has increased from a temperature difference of ~40 °C to ~150 °C. From the TPO data, or m(T) data (solid curve Figure 3b), we estimate that after microwave treatment and 6M HCl reflux ~0.04 at. % metal or a factor of a ~ 200 reduction in metal. These TGA results are in good agreement with energy dispersion X-ray microprobe results (EDX).

Instead of a 4M HCl reflux, we found that simply heating the microwave-processed material in 4M HCl at ~60 °C for 6 h is fairly effective at removing metal. This is much easier (and lower cost) than refluxing. The DTPO data after this HCl treatment is very similar to that shown in Figure 3b. However, more metal residue remained (~4 wt %) than after refluxing. It is also of interest to mention here that if we carry out a reflux in 3M HNO₃, after HNO₃ refluxing, we did find no improvement (decrease) in the metal content over HCl reflux. However, we observe considerable damage in the tube walls by Raman scattering. This will be discussed next. In Table 1 we compare results of the metal content for the as-prepared sample and samples purified by selective oxidation/HNO₃ reflux and microwave heating followed by HCl treatment. As one can be seen from the table, the microwave treatment is very effective, allowing a mild HCl treatment to remove most of the catalyst residue from the sample.

We have estimated the yield of our purification procedure. According to literature, the yield of the carbon nanotubes for different purification approaches is vary from 1 wt % [16] up to 25–30 wt % [20]. After microwave treatment, the weight of the soot was reduced about 25–30 wt % of the as-prepared samples, as a result of oxidation of amorphous and multishell carbons. During acid treatment, sample lost about 50 wt % of the microwave treated samples mainly due to the removal of metal residue. Thus, the total yield for our two-step purification procedure is about 35 wt %. As one can see from TPO/DTPO curves even after two step purification, the samples still content multishell carbons (peak T~730 °C). It is obvious that the yield calculated by this way strongly depends on the amount of the metal residue in the as-prepared sample (~35 wt % for the samples were studied in this work).

Resonant Raman Scattering Spectra. Raman scattering spectra of arc-derived SWNT soots, taken at room temperature using IR ($\lambda = 1064$ nm) excitation was used to investigate possible SWNT damage from the purification process. Four spectra are shown in Figure 4: as-prepared (Figure 4a), after microwave processing (Figure 4b), as-prepared material subjected to microwave/HCl reflux purification treatment (Figure 4c), and microwave/HNO₃ reflux treatment (Figure 4d). Three Raman bands are observed: ~190 cm⁻¹ (R), 1280 cm⁻¹ (D), and 1593 cm⁻¹ (T), where the letters (R, D, T) in parentheses,

TABLE 1: Results for Metal Contents Analysis for Samples Purified by Different Ways

sample	postsynthesis treatments	metal content (wt %)	comments(HRTEM)
(arc-discharge method, Ni:Y catalysts)	as-prepared	~35	SWNTs and metal residue covered by amorphous and multishell carbon
	reflux HNO ₃ acid at 130 °C for 25 h	~4	significant wall damages and shorten tubes, losses of SWNTs
	reflux HNO ₃ acid at 130 °C for 50 h	<0.2	significant wall damages and shorten tubes, losses of SWNTs
	selective oxidation in air, 30 min, at 400 °C, then refluxing in HNO ₃ for 6 h	<1	no amorphous carbon, wall damages, and losses of SWNTs
	microwave heating in air at 500 °C for 10 min, then refluxing in HCl for 6 h	~1.5	some amorphous carbon on the walls, metal residue covered by multishell carbon
	microwave heating in air at 500 °C for 20 min, then refluxing in HCl for 6 h	<0.2	slight wall damages due to the metals attached on the tube's walls

respectively, refer to radial breathing modes, disorder band, and tangential bond. The D band can be activated by disorder in the tube wall.^{22,23} The D band's position is strongly dependent on the laser excitation frequency; it is a "dispersive" mode.²⁴ Unfortunately, it is present in many disordered sp² carbons,^{23–25} and we therefore do not consider this mode a good way to assess damage to the SWNTs caused by the materials processing. However, the R and T band's fwhm (full width at half-maximum) should provide a good measure of wall damage in the SWNT caused by the purification process. The fwhm of these bands should increase with increasing numbers of wall defects, as they affect the SWNT's phonon lifetime. Some significant changes in the SWNT Raman bands were observed after microwave/HCl reflux treatment. First, small broadening of the contributions to the R and T bands were observed after microwave processing (Figure 4b). This may be associated with oxidation of the tube walls which should be reversible by vacuum annealing at ~1000 °C. In (Figure 4c) we see a small change relative to (Figure 4b) spectra indicating that HCl reflux is not seriously damaging the SWNTs. In both (Figure 4b) and (Figure 4c), we see an interesting change in the R band structure relatively that is in the as-prepared arc material (Figure 4a). Notably, the lowest frequency (largest tube diameter) contribution is suppressed. We are not sure that this is significant; further samples would have to be evaluated for us to be convinced that the processing selectively attacks the large diameter tubes. In the case of the microwave/HNO₃ reflux treatment, significant line broadening (Figure 4d) in the T band is observed, and is attributed to wall defects introduced during the more aggressive HNO₃ acid reflux. The D band also is observed to grow in intensity, which suggests it might be identified with wall defects.

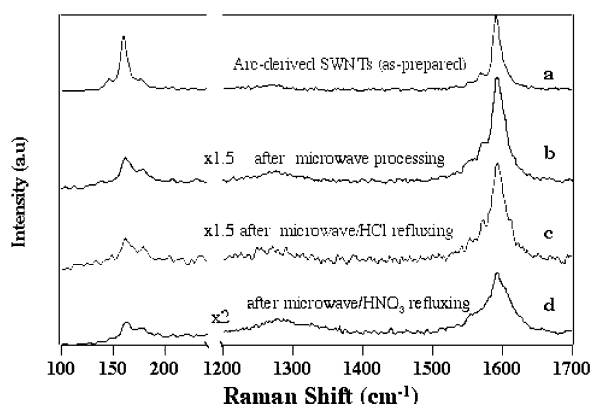


Figure 4. Raman spectra of (a) as-prepared SWNT material; (b) after microwave processing at 500 °C for 20 min; (c) after refluxing in 4 M HCl for 6 h preliminary heated by microwave at 500 °C for 20 min; (d) after refluxing in 3 M HNO₃ for 6 h preliminary heated by microwave at 500 °C for 20 min.

Summary and Conclusions

TEM, TGA/TPO, and Raman scattering support the idea that microwave treatment, establish as a high local temperature at the metal catalyst particles. The temperature is high enough to either burst the different carbon structures covering the catalyst particles (thermal expansion), or to drive preferential oxidation of the carbon coating over the catalyst particles. In either case, the carbon coating protecting the metal impurity is weakened, or removed allowing a mild acid (e.g., HCl) to be used to dissolve and remove the residual catalysts. We also tried several different microwave powers and heating times. In the case of high power (>200 W), the heating rate was too fast (~500 °C/min) and significantly exceeded the desired temperature (~500 °C). In this case, too high a loss of SWNTs was observed. When we applied a lower microwave power (<100 W), the sample did not reach the desirable temperature (or it took too long to achieve this temperature). So, in our preliminary studies microwave power of 150 W was found to be optimal under our experimental condition (e.g., dry air flow rate). For 150 W microwave power, we have studied the effect of different heating times; ~10, 40, and 60 min followed by 4 M HCl reflux. In case of 10 min microwave treatment the sample still contained ~1.5 wt % metal residue. Longer time microwave treatments (40; 60min) caused too high a loss of SWNTs and also led to additional wall damage.

Another important variable parameter for our experiment is the frequency of the microwaves. As described in the Experimental Section, we used 2.45 GHz for electromagnetic waves in our studies. This is the only frequency we tried because of equipment limitations. However, in ref 30 it has been shown that the imaginary microwave permeability μ'' (□) of the pure Ni powders (0.2–2 μm) depends weakly on particle size in the 0.1–18 GHz range and has a resonance at 1.6 GHz. Since particles are much smaller (~5–15 nm) it seems unlikely that the variation of the frequency will have a significant effect on the local microwave heating of the catalyst particles.

We would like also to mention that it possible to carry out microwave heating by placing the sample in other regions of the cavity. For our preliminary experiments, samples were placed in the cavity where the component of the magnetic field is the maximum (Figure 1). This was done to ensure that selective heating of the ferromagnetic (Ni) catalyst particles would occur (via the induced eddy currents). This sample position was also chosen to minimize inductive heating of the metallic carbon nanotubes in the sample. Summarizing, the optimal conditions for microwave processing of SWNTs are: flowing dry air (100 sccm), microwave heating at 2.45 GHz and 150 W to read, temperature 500 °C for 20 min. Microwave

heating was followed by 4 M HCl refluxing for 6 h and less than 0.2 wt % of catalyst metals was found to remain in the samples.

We should also point out that several reports have been published in which heating the as-prepared SWNT in dry air in the temperature range 300–500 °C was carried out as a first step to both remove the amorphous carbon and weaken the multishell carbon covering the metallic particles. This oxidation step cannot be achieved without some loss of SWNTs, as our DTPO data show. We have not considered here any additional benefit from an additional selective oxidation step.

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