Inorganic Chemistry

Article

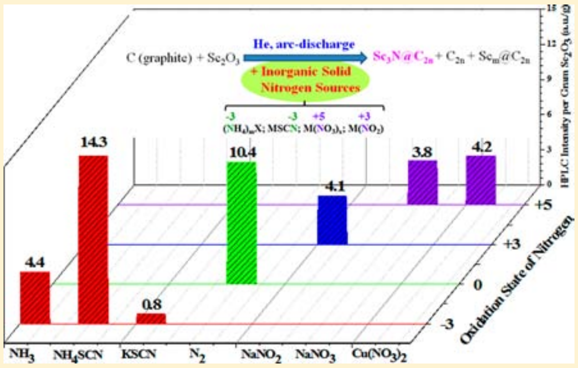
pubs.acs.org/IC

A Series of Inorganic Solid Nitrogen Sources for the Synthesis of Metal Nitride Clusterfullerenes: The Dependence of Production Yield on the Oxidation State of Nitrogen and Counter Ion

Fupin Liu, Jian Guan, Tao Wei, Song Wang, Mingzhi Jiao, and Shangfeng Yang*

Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials for Energy Conversion and Department of Materials Science and Engineering, University of Science and Technology of China (USTC), Hefei 230026, China

Supporting Information



ABSTRACT: A series of nitrogen-containing inorganic solid compounds with variable oxidation states of nitrogen and counter ions have been successfully applied as new inorganic solid nitrogen sources toward the synthesis of Sc-based metal nitride clusterfullerenes (Sc-NCFs), including ammonium salts [$(NH_4)_xH_{3\text{-}x}PO_4$ (x = 0−2), $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4X (X = F, Cl), NH_4SCN], thiocyanate (KSCN), nitrates ($Cu(NO_3)_2$, $NaNO_3$), and nitrite ($NaNO_2$). Among them, ammonium phosphates ($(NH_4)_xH_{3\text{-}x}PO_4$, x = 1−3) and ammonium thiocyanate (NH_4SCN) are revealed to behave as better nitrogen sources than others, and the highest yield of Sc-NCFs is achieved when NH_4SCN was used as a nitrogen source. The optimum molar ratio of Sc_2O_3:$(NH_4)_3PO_4\cdot 3H_2O$:C and Sc_2O_3:NH_4SCN:C has been determined to be 1:2:15 and 1:3:15, respectively. The thermal decomposition products of these 12 inorganic compounds have been discussed in order to understand their different performances toward the synthesis of Sc-NCFs, and accordingly the dependence of the production yield of Sc-NCFs on the oxidation state of nitrogen and counter ion is interpreted. The yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) per gram Sc_2O_3 by using the N_2-based group of nitrogen sources (thiocyanate, nitrates, and nitrite) is overall much lower than those by using gaseous N_2 and NH_4SCN, indicating the strong dependence of the yield of Sc-NCFs on the oxidation state of nitrogen, which is attributed to the "in-situ" redox reaction taking place for the N_2-based group of nitrogen sources during discharging. For NH_3-based group of nitrogen sources (ammonium salts) which exhibits a (−3) oxidation states of nitrogen, their performance as nitrogen sources is found to be sensitively dependent on the anion, and this is understood by considering their difference on the thermal stability and/or decomposition rate. Contrarily, for the N_2-based group of nitrogen sources, the formation of Sc-NCFs is independent to both the oxidation state of nitrogen (+3 or +5) and the cation.

■ INTRODUCTION

Since the discovery of $Sc_3N@C_{80}$ as the first member of metal nitride clusterfullerenes (NCFs) in 1999 via a modified Krätschmer−Huffman dc-arc discharging method,[1] the family of endohedral fullerenes has been significantly enlarged by clusterfullerenes, which are featured by the encapsulation of metal clusters within the interior of fullerene cage.[2−9] In particular, NCF is the most rapidly growing branch of clusterfullerenes because of its extraordinarily high yield and unique electronic, physical, and chemical properties, which promise potential applications in biomedicines and organic photovoltaics, etc.[2−8] Despite the considerable advance in the synthesis of novel types of NCFs in the past decade,[10−17] the development of synthetic routes for NCFs has been quite limited, which is crucial since the applications of NCFs put a high demand on their yield.

Up to now only few synthetic routes for NCFs have been developed with few nitrogen sources,[2−9] and all are based on the modifications of the standard Krätschmer−Huffman dc-arc discharging method. As the first success, the "trimetallic nitride template" (TNT) process with the introduction of a small portion of gaseous nitrogen (N_2) into the Krätschmer−Huffman generator led to the discovery of $Sc_3N@C_{80}$ by Dorn et al. in 1999.[1] In 2003 Dunsch et al. invented the "reactive gas atmosphere" method with gaseous ammonia (NH_3) used as nitrogen source, and realized the selective synthesis of NCFs for the first time enabling NCFs as the main products in the soot.[18] Although these two routes appear to be the most commonly used methods for NCF synthesis in laboratories, an additional heating pretreatment up to 1000 °C is generally required to "activate" the metal (or metal oxide) before introducing the gaseous N_2 or NH_3 into chamber, and an additional gas inlet may be required for the introduction the gaseous nitrogen sources.[19,20] Thus, it is highly desirable to simplify the synthesis procedure without decreasing the production yield and selectivity of NCFs.

Received: November 7, 2012
Published: March 12, 2013

dx.doi.org/10.1021/ic302436k | *Inorg. Chem.* 2013, 52, 3814−3822

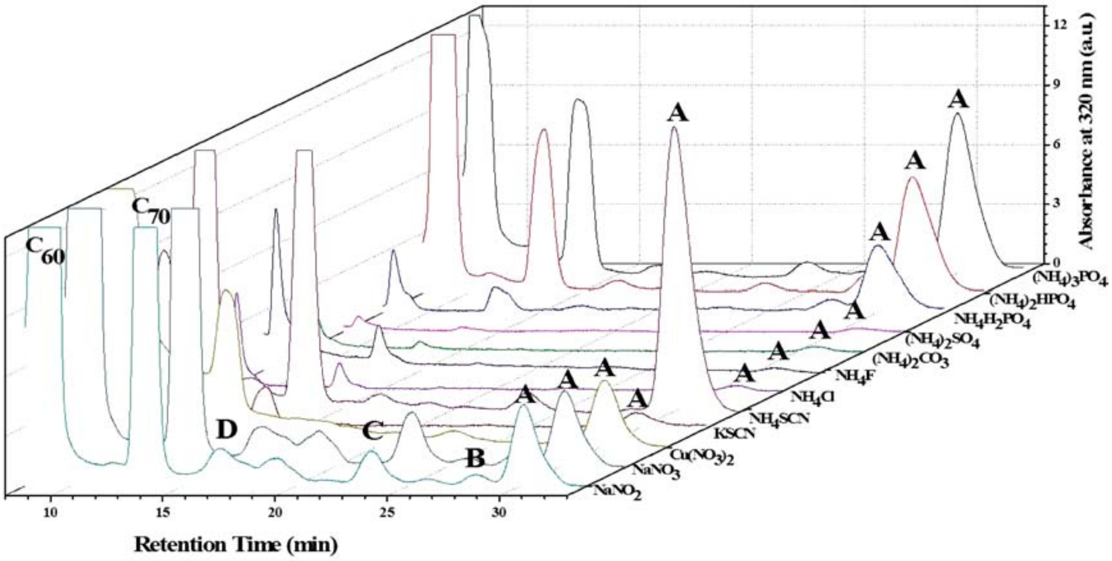


Figure 1. HPLC chromatograms of fullerene extracts obtained from discharging of mixture of Sc_2O_3 and 12 individual nitrogen-containing inorganic compounds (10 mm × 250 mm Buckyprep column; flow rate 5.0 mL/min; injection volume 5 mL; toluene as eluent (mobile phase); 40 °C). Fractions A–D mainly consist of $Sc_3N@C_{80}$ (I_h, D_{5h}): $Sc_3N@C_{78}$ + C_{86}, $Sc_3N@C_{70}$ + C_{84}, $Sc_3N@C_{68}$ + C_{76} + C_{78}, respectively.

The progress toward the facile synthesis of NCFs has recently been achieved by the "solid nitrogen" routes developed as the effective solution for simplification of the synthesis procedure.[21,22] So far only three inorganic or organic solid nitrogen-containing compounds were applied as the nitrogen sources of the "solid nitrogen" routes. In 2010 we established the "selective organic solid" (SOS) route with guanidinium salts such as guanidinium thiocyanate ($CH_5N_3{\cdot}HSCN$) used as the organic solid nitrogen sources, and achieved comparable yield and selectivity of NCFs to those by using gaseous NH_3 of the "reactive gas atmosphere" route.[21,23] More recently, we used urea ($CO(NH_2)_2$) as a cheaper organic solid nitrogen source for the synthesis of Sc-based NCFs, and found that the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) per gram Sc_2O_3 by using $CO(NH_2)_2$ is almost identical to that by using gaseous N_2 but much higher than that by using NH_3.[22] Hence, urea and guanidinium thiocyanate can be regarded as the alternative organic solid nitrogen sources substituting gaseous N_2 or NH_3, respectively. On the other hand, inorganic solid nitrogen source has been rarely reported. To our knowledge, until now only calcium cyanamide (CaNCN) was applied as inorganic solid nitrogen source for NCF synthesis by Dunsch et al. in 2004, resulting in the synthesis of $Sc_3N@C_{80}$ NCF with a variable selectivity ranging from 3% to 42%, and such a low reproducibility of yield is presumably caused by traces of water and/or hydrocarbons in the raw material.[9] Therefore, this "inorganic solid nitrogen" route using CaNCN could not be widely applied in the synthesis of NCFs. Given that inorganic compounds typically have a higher thermal stability and are more readily available than organic compounds, to modify the "inorganic solid nitrogen" route using other nitrogen-containing inorganic compounds as nitrogen sources for NCF synthesis is of practical importance but challenging still.

In this Article, we report the successful application of a series of nitrogen-containing inorganic solid compounds as new nitrogen sources for the synthesis of Sc-based NCFs, including 12 compounds belonging to four categories: ammonium salts, thiocyanates, nitrates, and nitrite. Among these 12 nitrogen-containing inorganic compounds, the oxidation state of nitrogen changes for different categories, and within the same category the counter ion varies. In this way the role of the oxidation state of nitrogen and counter ion on the yield of Sc-NCFs is addressed, shedding light on the correlation between the NCF yield and the decomposition products of these new inorganic nitrogen sources upon discharging.

■ RESULTS AND DISCUSSION

Different Nitrogen-Containing Inorganic Compounds as Nitrogen Sources for the Synthesis of Sc-NCFs. To vary the oxidation state of nitrogen, 12 nitrogen-containing inorganic compounds falling into four categories were chosen in this study for comparison. As the protonated form of ammonia popularly used in the "reactive gas atmosphere" method,[18] ammonium salts were preferably considered, and 8 representative compounds with the same oxidation state of nitrogen (−3) but different anions were investigated, including triammonium phosphate hydrate ($(NH_4)_3PO_4{\cdot}3H_2O$, hereafter the water moiety is omitted for clarity), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), ammonium sulfate ($(NH_4)_2SO_4$), ammonium carbonate ($(NH_4)_2CO_3$), ammonium fluoride (NH_4F), ammonium chloride (NH_4Cl), and ammonium thiocyanate (NH_4SCN). It is noteworthy that, for ammonium thiocyanate (NH_4SCN), both the cation (NH_4^+) and anion (SCN^-) contain nitrogen with the same oxidation state of nitrogen (−3). In order to investigate whether NH_4^+ and SCN^- behave the same as the nitrogen sources, another thiocyanate, potassium thiocyanate (KSCN), was selected and compared with NH_4SCN. On the other hand, among the known positive oxidation states of nitrogen (+2 ∼ +5), the highest oxidation state of nitrogen is +5 and is popularly found in the inorganic nitrates. Thus, two nitrates including copper nitrate hydrate ($Cu(NO_3)_2{\cdot}3H_2O$, hereafter the water moiety is omitted for clarity) and sodium nitrate ($NaNO_3$) were chosen and compared so as to study the effect of cation. Finally, an intermediate oxidation state of nitrogen (+3) is accessible in nitrite, and sodium nitrite ($NaNO_2$) was investigated and compared with $NaNO_3$ aiming to study further the effect of

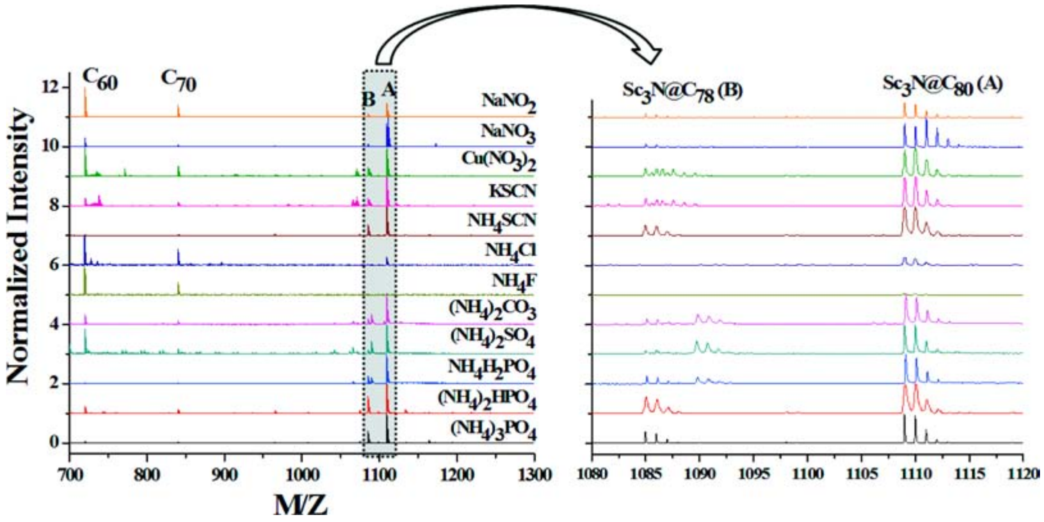


Figure 2. Positive-mode laser desorption time-of-flight (LD-TOF) mass spectroscopic (MS) spectra of fullerene extracts obtained from discharging of mixture of Sc_2O_3 and 12 individual nitrogen-containing inorganic compounds. The inset shows the enlarged mass region of 1080−1120. The intensity of the MS spectra were normalized by the most intense mass peak of the spectrum.

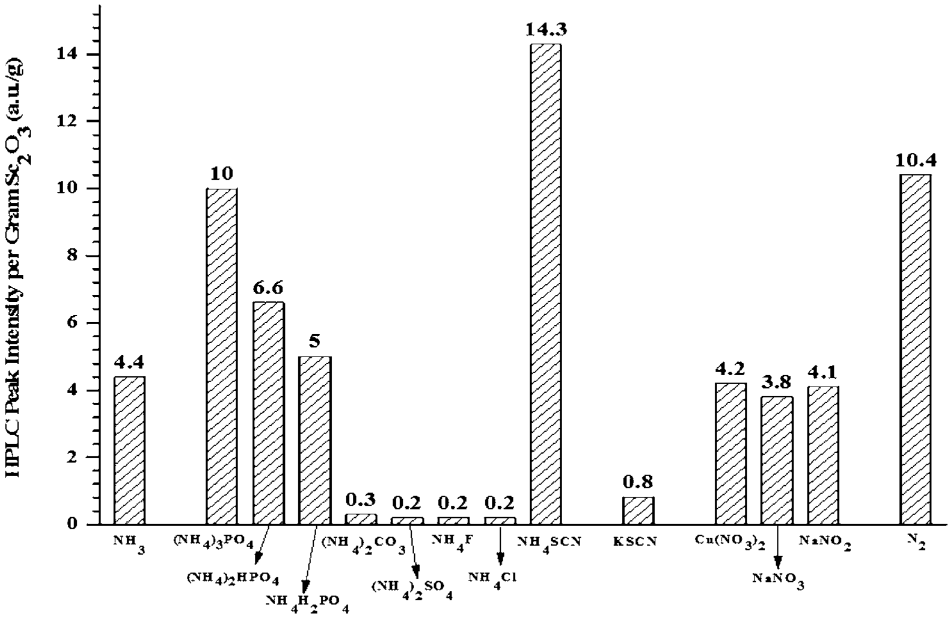


Figure 3. Comparison of the HPLC intensity of fraction A per gram Sc_2O_3 obtained from different nitrogen sources. See Supporting Information (part S1) for the details of calculations.

oxidation state of nitrogen on their performance as nitrogen sources.

Figure 1 presents the HPLC profiles of the fullerene extracts, which were obtained from dc-arc discharges of one rod filled with a mixture of Sc_2O_3 and 12 individual nitrogen-containing inorganic compounds under the condition optimized, respectively, as discussed below. Obviously all of the HPLC profiles of these extracts are quite similar to those obtained by using the reported gaseous nitrogen sources (N_2 or NH_3) or organic solid nitrogen sources ($CO(NH_2)_2$ or $CH_5N_3·HSCN$) in terms of the overall distribution of different fractions,[21,22] suggesting the formation of similar fullerene products in these extracts. This is experimentally confirmed by laser desorption time-of-flight (LD-TOF) mass spectroscopic (MS) analysis, indicating clearly the existence of a series of reported Sc-NCFs $Sc_3N@C_{2n}$ ($2n$ = 80, 78, 70, 68) in all of the extracts (see Figure 2). Therefore, combining both HPLC and MS analysis results, we conclude that all of the 12 nitrogen-containing inorganic compounds can behave as new inorganic nitrogen sources leading to the successful synthesis of Sc-NCFs.

On the basis of our earlier reports on Sc-NCFs synthesized via other nitrogen sources, including N_2, NH_3, $CH_5N_3·HSCN$, or $CO(NH_2)_2$, fractions A−D can be assigned to a series of Sc-NCFs, $Sc_3N@C_{2n}$ ($2n$ = 80, 78, 70, 68), respectively, which are coeluted with different empty fullerenes.[21,22] Among them, fraction A with the highest abundance is mainly composed of the mixture of two isomers (I_h and D_{5h}) of $Sc_3N@C_{80}$, and is selected for further analysis. Figure 3 compares the HPLC intensity of fraction A per gram Sc_2O_3 obtained via different nitrogen sources, which visualizes the variation of the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) on different nitrogen sources. These results reveal that the yield of Sc-NCFs depends strongly on

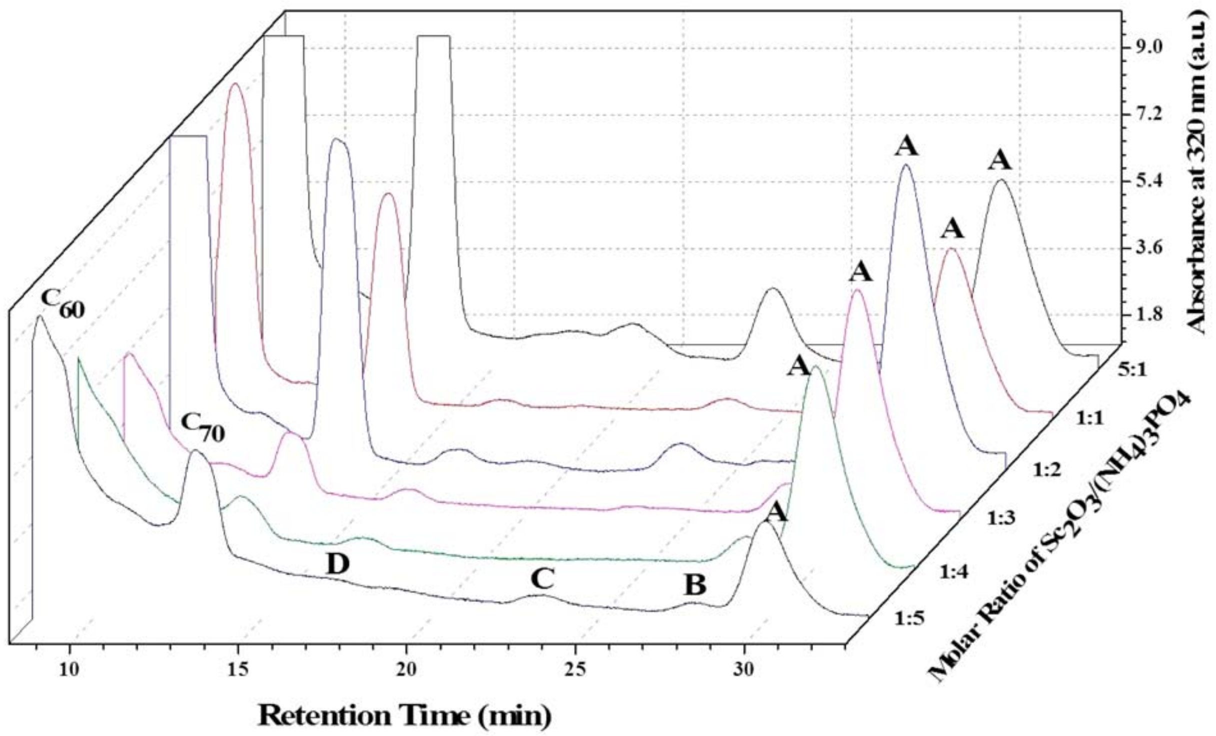


Figure 4. HPLC chromatograms of $Sc_2O_3/(NH_4)_3PO_4{\cdot}3H_2O$ extracts obtained by using $(NH_4)_3PO_4{\cdot}3H_2O$ as the nitrogen source with different molar ratio of $Sc_2O_3/(NH_4)_3PO_4{\cdot}3H_2O$ (10 mm × 250 mm Buckyprep column; flow rate 5.0 mL/min; injection volume 5 mL; toluene as eluent (mobile phase); 40 °C). Fraction A mainly consists of $Sc_3N@C_{80}$ (I_h + D_{5h}).

not only the nitrogen-containing group but also its counter ion as discussed in more detail below. According to the comparison of the HPLC intensity of fraction A, clearly ammonium phosphates ($(NH_4)_xH_{3-x}PO_4$, x = 1−3) and ammonium thiocyanate (NH_4SCN) work as better nitrogen sources than others, and the highest yield is achieved when NH_4SCN was used as a nitrogen source (see Figure 3).

Among these 12 new inorganic nitrogen sources, NH_4SCN is noteworthy because it affords the highest yield of $Sc_3N@C_{80}$ (I_h + D_{5h}). Moreover, although NH_4SCN works as an efficient nitrogen source for the synthesis of Sc-NCFs, surprisingly our previous attempts to use it as a nitrogen source for the synthesis of Dy-NCFs was not successful as evidenced from both HPLC and MS analysis.[21] Replacing Dy (dysprosium) metal atom with Sc (scandium) which has a much smaller ionic radius (0.75 Å for Sc^{3+}) than that of Dy^{3+} (0.91 Å),[16] we now successfully synthesized Sc-NCFs by using NH_4SCN as nitrogen source. A plausible reason might be the extremely low yield of Dy-NCFs below the detection limit of MS spectroscopy under the synthesis condition used in our previous work[21] (no preheating treatment, which seems however necessary for the yield enhancement of Sc-NCFs as discussed below), which is to be further verified experimetally later. Besides, $Cu(NO_3)_2{\cdot}2.5H_2O$ was previously used by Stevenson et al. as an additive for the synthesis of Sc-NCFs via the TNT process with gaseous N_2 as the nitrogen source, resulting in the selective synthesis of Sc-NCFs.[24] Two roles of $Cu(NO_3)_2{\cdot}2.5H_2O$ as additive were proposed on the basis of the thermally decomposed products: (1) the generated NO_x vapor may suppress the formation of empty fullerenes; (2) Cu moiety generated from a nonvolatile route functions as a catalyst additive which may offset the reactive plasma environment and enhance the yield of Sc-NCFs. Nevertheless, in that report the major nitrogen source was still gaseous N_2, and $Cu(NO_3)_2$ was believed to behave as an additive, while the effectiveness of $Cu(NO_3)_2$ as a nitrogen source independently was not studied.[24] Therefore, our present work demonstrates clearly that $Cu(NO_3)_2$ can work as an independent nitrogen source. Interestingly, in addition to the successful synthesis of Sc-NCFs using two nitrates ($Cu(NO_3)_2$ and $NaNO_3$) as nitrogen sources, metal oxide clusterfullerene such as $Sc_4O_2@C_{80}$, which was discovered by Stevenson et al. in 2008 by introducing flowing air into the arc discharge process,[25] was also detected in the MS spectra of their extract mixtures as a minor product with much lower yield than that of $Sc_3N@C_{80}$ NCF (see Supporting Information, Figure S1), suggesting that both nitrates could function as oxygen sources for the synthesis of metal oxide clusterfullerenes as well.

Optimization of the Synthesis Conditions of Sc-NCFs. Considering that NH_4SCN and $(NH_4)_3PO_4$ work as the best nitrogen sources for the synthesis of Sc-based NCFs in terms of the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) as discussed above, we optimized their synthesis conditions by varying the molar ratio of Sc:N with the molar ratio of Sc:C fixed at 1:7.5.[26] The HPLC profiles of a series of fullerene extracts obtained under different molar ratios of $(NH_4)_3PO_4$:Sc_2O_3 ranging from 5:1 to 1:4.5 (i.e., molar ratio of N:Sc ranging from 7.5:1 to 1:3) are compared in Figure 4, indicating the strong dependence of the HPLC peak intensity of $Sc_3N@C_{80}$ (I_h + D_{5h}) in fraction A as well as the empty fullerenes (mainly C_{60} and C_{70}) on the molar ratio of $(NH_4)_3PO_4$:Sc_2O_3. Such a dependence is illustrated in Figure 5 and can be used to evaluate the dependence of the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) which is proportional to the HPLC peak intensity of fraction A. Thus, the optimum molar ratio of $(NH_4)_3PO_4$:Sc_2O_3 is determined to be 2:1 (i.e., the atomic molar ratio of N:Sc = 3:1). Besides, the effect of the molar ratio of $(NH_4)_3PO_4$:Sc_2O_3 on the intensity ratio of

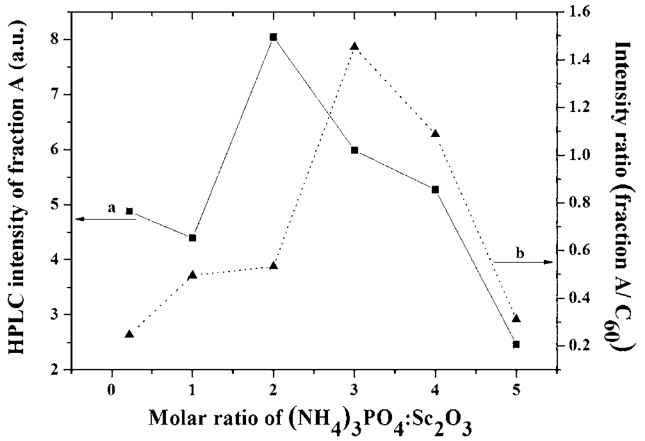


Figure 5. Effect of the molar ratio of $(NH_4)_3PO_4$:Sc_2O_3 on the HPLC peak intensities of A (a) and its relative yield to C_{60} (b).

fraction A ($Sc_3N@C_{80}$ (I_h + D_{5h})) to C_{60} is also plotted in Figure 5, which is directly correlated to the relative yield of ($Sc_3N@C_{80}$ (I_h + D_{5h})) to C_{60} as an indication of the selectivity of $Sc_3N@C_{80}$ (I_h + D_{5h}). Obviously the highest selectivity of $Sc_3N@C_{80}$ (I_h + D_{5h}) is achieved when the molar ratio of $(NH_4)_3PO_4$:Sc_2O_3 is set at 3:1, which is somewhat different to the optimum one (2:1) in terms of the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}). This discrepancy suggests that there is probably a trade-off between the yield and selectivity of Sc-NCFs when $(NH_4)_3PO_4$ is used as the nitrogen source, and this phenomena might be due to the influence of the $(PO_4)^{3-}$ anion as discussed below. Likewise, the optimum molar ratio of NH_4SCN:Sc_2O_3 is determined to be 3:1 (i.e., the atomic molar ratio of N:Sc = 3:1) (see Supporting Information, part S3).

As another strategy to optimize the synthesis conditions, we noticed that some of the inorganic nitrogen sources studied in the present work are hydrates (e.g., $(NH_4)_3PO_4 \cdot 3H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$) or hygroscopic, hence an "in-situ" preheating treatment was carried out in order to remove the hydrated/adsorbed water. Because of the relatively low decomposition temperatures of all of 12 inorganic nitrogen sources (see Table 1), such an "in-situ" preheating treatment should be made by contacting two electrodes for 30 min under a very low dc current (ca. 10 A for the graphite rods of Φ 8 mm ×150 mm used in our generator). Interestingly, applying such an "in-situ" preheating treatment, we found that the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) increased dramatically as demonstrated for several nitrogen sources including NH_4SCN, $(NH_4)_3PO_4$, and $(NH_4)_2HPO_4$ (see Supporting Information, Figures S4−S6). These results suggest that water may indeed affect the dc-arc discharging process sensitively and our preheating treatment even at such a low dc current leads to the successful removal of water contaminant in the raw mixture. Although this preheating treatment adds an additional step prior to dc-arc discharging, it can be made "in-situ" with a relatively short time; therefore, such an "in-situ" preheating treatment was applied for all of 12 inorganic nitrogen sources in this work.

Decomposition Process of the New Inorganic Nitrogen Sources During Discharging. In order to understand the different performances of these 12 nitrogen sources, their difference on the decomposition products should be considered. The thermal decomposition products of 12 inorganic compounds under conventional heating conditions are available in the literature,[27−39] and summarized in Scheme 1 (see also Table 1).

In general ammonia salts decompose with temperature below 300 °C and generate gaseous ammonia (NH_3), which plays a key role for the formation of Sc-NCFs. On the other hand, for other three types of nitrogen sources including thiocyanate, nitrates, and nitrite, obviously their decompositions lead to the generation of gaseous nitrogen (N_2) instead (see Table 1). Assuming that the thermal decomposition behavior of these inorganic compounds under rapid heating and extremely high temperature during discharging (~4000 K[40]) is similar to those under the conventional heating conditions, it is reasonable to attribute the difference on the decomposition products (NH_3 or N_2) between ammonia salts and other three types of nitrogen sources to their difference on the performance in terms of the yield of Sc-NCFs, and the detail is discussed below.

Dependence of the Yield of Sc-NCFs on the Oxidation State of Nitrogen and Counter Ion. Since the different performances of the 12 nitrogen sources in terms of the yield of Sc-NCFs are proposed to be correlated with their decomposition products (NH_3 or N_2) as the precursors for NCF formation, these 12 nitrogen sources can be divided into two groups based on their decomposition products: one is ammonium salts which decompose to NH_3 (NH_3-based group), and the decomposition products of another group (thiocyanate, nitrates, and nitrite) are all based on N_2 (N_2-based group). Figure 6 shows a close-up comparison of the HPLC profiles and yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) of these two

Table 1. Oxidation States and Decomposition Properties of Different Nitrogen Sources

entry	category	compd	oxidation state of nitrogen	decomp temp (°C)[a]	decomp products	refs
1	ammonium salt	$(NH_4)_3PO_4 \cdot 3H_2O$	−3	100	NH_3, P_2O_5, H_2O	27
2	ammonium salt	$(NH_4)_2HPO_4$	−3	100	NH_3, P_2O_5, H_2O	28
3	ammonium salt	$NH_4H_2PO_4$	−3	200	NH_3, P_2O_5, H_2O	28
4	ammonium salt	$(NH_4)_2SO_4$	−3	213	NH_3, H_2O, SO_2, N_2	28, 29
5	ammonium salt	$(NH_4)_2CO_3$	−3	20	NH_3, CO_2, H_2O	28
6	ammonium salt	NH_4F	−3	145	NH_3, HF	28
7	ammonium salt	NH_4Cl	−3	200	NH_3, HCl	28, 30
8	ammonium salt	NH_4SCN	−3	227	NH_3, CS_2, $C_3H_6N_6$ (melamine)	28, 31, 32
9	thiocyanate	KSCN	−3	450	K_2S, CS_2, $(CN)_2$, N_2	33
10	nitrate	$Cu(NO_3)_2 \cdot 3H_2O$	+5	109	CuO, Cu, O_2, H_2O, NO_x, N_2	34−36
11	nitrate	$NaNO_3$	+5	600	Na_2O, N_2, O_2	37−39
12	nitrite	$NaNO_2$	+3	620	Na_2O, N_2, O_2	37−39

[a] The temperature at which the decomposition reaction begins.

Scheme 1. Decomposition Reactions of 12 Inorganic Nitrogen Sources under Conventional Heating Conditions[a]

(I) $(NH_4)_xH_{3-x}PO_4$, x=1-3:

$$(NH_4)_3PO_4\cdot 3H_2O \xrightarrow{100\text{-}150\ ^{\circ}C} (NH_4)_2HPO_4 + NH_3 + 3H_2O \quad (1)$$

$$(NH_4)_2HPO_4 \xrightarrow{100\text{-}150\ ^{\circ}C} NH_4H_2PO_4 + NH_3 \quad (2)$$

$$2NH_4H_2PO_4 \xrightarrow{200\ ^{\circ}C} (NH_4)_2H_2P_2O_7 + H_2O \quad (3)$$

$$(NH_4)_2H_2P_2O_7 \xrightarrow{200\text{-}280\ ^{\circ}C} 2NH_4PO_3 + H_2O \quad (4)$$

$$2NH_4PO_3 \xrightarrow{600\text{-}800\ ^{\circ}C} P_2O_5 + 2NH_3 + H_2O \quad (5)$$

$$\text{Overall reaction: } 2(NH_4)_3PO_4\cdot 3H_2O \rightarrow P_2O_5 + 6NH_3 + 9H_2O \quad (6)$$

$$2(NH_4)_2HPO_4 \rightarrow P_2O_5 + 4NH_3 + 3H_2O \quad (7)$$

$$2NH_4H_2PO_4 \rightarrow P_2O_5 + 2NH_3 + 3H_2O \quad (8)$$

(II) $(NH_4)_2SO_4$, $(NH_4)_2CO_3$:

$$(NH_4)_2SO_4 \xrightarrow{213\text{-}308\ ^{\circ}C} NH_4HSO_4 + NH_3 \quad (9)$$

$$2NH_4HSO_4 \xrightarrow{308\text{-}330\ ^{\circ}C} (NH_4)_2S_2O_7 + H_2O \quad (10)$$

$$3(NH_4)_2S_2O_7 \xrightarrow{330\text{-}419\ ^{\circ}C} 2NH_3 + 2N_2 + 6SO_2 + 9H_2O \quad (11)$$

$$\text{Overall reaction: } 3(NH_4)_2SO_4 \longrightarrow 4NH_3 + N_2 + 3SO_2 + 6H_2O \quad (12)$$

$$(NH_4)_2CO_3 \xrightarrow{20\text{-}100\ ^{\circ}C} 2NH_3 + CO_2 + H_2O \quad (13)$$

(III) NH_4X, X=F, Cl:

$$2NH_4F \xrightarrow{145\ ^{\circ}C} NH_4F\cdot HF + NH_3 \quad (14)$$

$$NH_4F\cdot HF \xrightarrow{225\ ^{\circ}C} 2HF + NH_3 \quad (15)$$

$$\text{Overall reaction: } NH_4F \rightarrow NH_3 + HF \quad (16)$$

$$NH_4Cl \xrightarrow{200\text{-}345\ ^{\circ}C} NH_3 + HCl \quad (17)$$

(IV) NH_4SCN, KSCN:

$$6NH_4SCN \xrightarrow{227\ ^{\circ}C} 6NH_3 + 3CS_2 + C_3H_6N_6\ (\text{melamine})^{a} \quad (18)$$

$$4KSCN \xrightarrow{450\ ^{\circ}C} 2K_2S + CS_2 + C_3N_4 \quad (19)$$

$$2C_3N_4 \longrightarrow 3(CN)_2 + N_2 \quad (20)$$

$$\text{Overall reaction: } 8KSCN \longrightarrow 4K_2S + 2CS_2 + 3(CN)_2 + N_2 \quad (21)$$

(V) $Cu(NO_3)_2$. 3H2O :

$$Cu(NO_3)_2\cdot 3H_2O \xrightarrow{109\text{-}194\ ^{\circ}C} CuOH\cdot NO_3 + HNO_3 + 2H_2O \quad (22)$$

$$2CuOH\cdot NO_3 \xrightarrow{170\text{-}220\ ^{\circ}C} CuOCuONO_3 + NO_2 + H_2O \quad (23)$$

$$CuOCuONO_3 \xrightarrow{280\text{-}320\ ^{\circ}C} 2CuO + NO_2 + 1/2O_2 \quad (24)$$

$$2HNO_3 \longrightarrow H_2O + 2NO_2 \quad (25)$$

$$2NO_2 \xrightarrow{CuO} 2NO + O_2 \quad (26)$$

$$NO_x + NO_x \xrightleftharpoons{\sim 1600\ ^{\circ}C} N_2 + xO_2 \quad (27)$$

$$\text{Overall reaction: } 2Cu(NO_3)_2\cdot 3H_2O \rightarrow 2CuO + 2N_2 + 5O_2 + 6H_2O \quad (28)$$

(VI) $NaNO_x$, x=2, 3:

$$2NaNO_3 \xrightarrow{600\ ^{\circ}C} 2NaNO_2 + O_2 \quad (29)$$

$$4NaNO_2 \xrightarrow{620\ ^{\circ}C} 2Na_2O + 2N_2 + 3O_2 \quad (30)$$

$$\text{Overall reaction: } 4NaNO_3 \rightarrow 2Na_2O + 2N_2 + 5O_2 \quad (31)$$

[a] These are presumed to be the possible decomposition processes during discharging as well. In eq 18, the generated melamine condenses into "melem" with the further release of NH_3.[22,32]

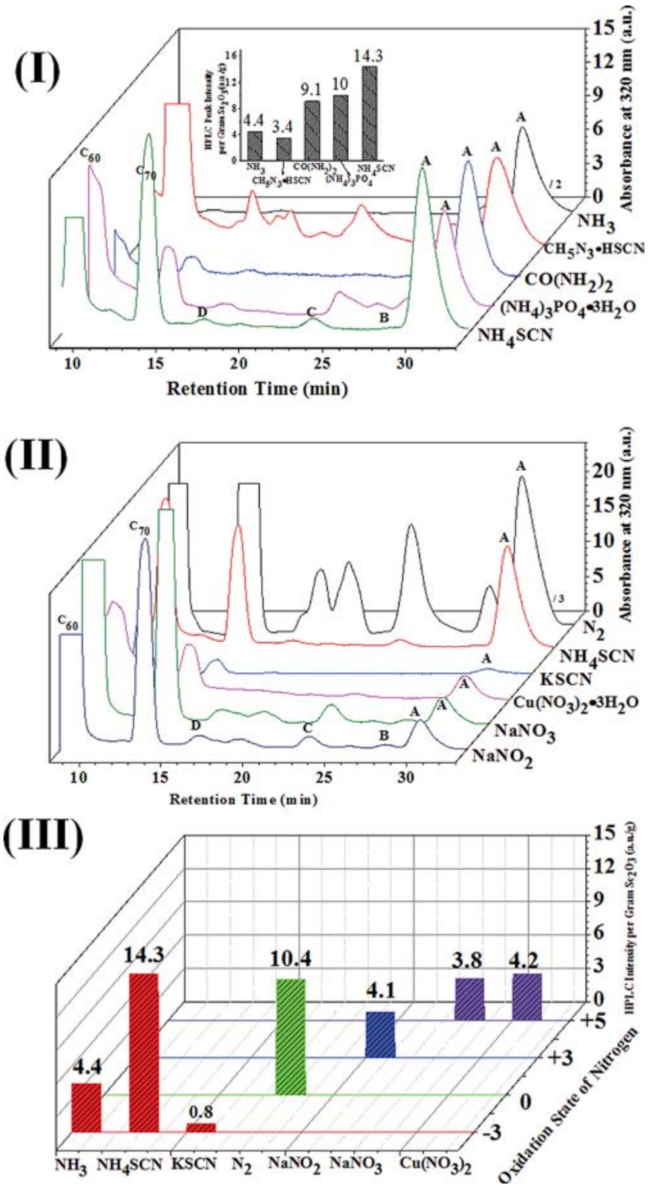


Figure 6. (I) HPLC chromatograms of $Sc_2O_3/(NH_4)_3PO_4\cdot 3H_2O$ and Sc_2O_3/NH_4SCN) extracts obtained by using $(NH_4)_3PO_4\cdot 3H_2O$ and NH_4SCN as the nitrogen sources (copied from Figure 1). For comparison, the chromatograms of $Sc_2O_3/CO(NH_2)_2$, Sc_2O_3/NH_3, and $Sc_2O_3/CH_5N_3\cdot HSCN$ (two rods) extracts reported previously (refs 21 and 22) were also included. Note that the $Sc_2O_3/CO(NH_2)_2$ extract was obtained from the discharging of one rod of $Sc_2O_3/CO(NH_2)_2$ (1:3 molar ratio) mixture with an "in-situ" preheating treatment. Inset: Comparison of the HPLC intensity of fraction A per gram Sc_2O_3 obtained from different nitrogen sources. (II) HPLC chromatograms of Sc_2O_3/NH_4SCN, $Sc_2O_3/KSCN$, $Sc_2O_3/Cu(NO_3)_2$, $Sc_2O_3/NaNO_3$, and $Sc_2O_3/NaNO_2$ extracts obtained by using NH_4SCN, KSCN, $Cu(NO_3)_2$, $NaNO_3$, and $NaNO_2$ as the nitrogen sources, respectively (copied from Figure 1). The chromatogram of Sc_2O_3/N_2 (three rods) extract is also plotted for comparison. (III) Comparison of the HPLC intensity of fraction A per gram Sc_2O_3 obtained from different nitrogen sources.

groups. For the ammonia salts, only NH_4SCN and $(NH_4)_3PO_4$ as the best nitrogen sources are taken for clarity, which are compared with the reported nitrogen sources based on NH_3, including gaseous NH_3, guanidinium thiocyanate ($CH_5N_3\cdot HSCN$), and urea ($CO(NH_2)_2$) (Figure 6I). Obviously the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) per gram Sc_2O_3 by using NH_4SCN and $(NH_4)_3PO_4$ surpasses those by using other NH_3-based nitrogen sources, indicating the advantage of these two new inorganic nitrogen sources (see inset of Figure 6I and Supporting Information, Table S1). Likewise, the HPLC profiles and yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) of the N_2-based group of nitrogen sources, i.e., thiocyanate, nitrates, and nitrite, are compared to those of gaseous N_2 (Figure 6II). NH_4SCN

represents the best nitrogen source in terms of the yield of Sc-NCFs in the NH_3-based group and is thus also included for comparison. Interestingly, it is found that the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) per gram Sc_2O_3 by using this N_2-based group of nitrogen sources is overall much lower than those by using gaseous N_2 and NH_4SCN (see Figure 6III and Supporting Information, Table S1). These results indicate the strong dependence of the yield of Sc-NCFs on the nitrogen-containing group in which the oxidation state of nitrogen is different (see Table 1).

For ammonium salts as the NH_3-based group of nitrogen source, the oxidation states of nitrogen (−3) keep constant in the decomposed product: NH_3. However, within the N_2-based group of nitrogen sources, thiocyanate, nitrite, and nitrates adopt −3, +3, and +5 oxidation states of nitrogen, respectively, which change upon the formation of the decomposed product: N_2. Hence, an "in-situ" redox reaction takes place along with the decomposition reaction of these N_2-based group of nitrogen sources during the discharging, which is however not required for the ammonium salts. Such an "in-situ" redox reaction may be regarded as a side reaction and partially dissipate the energy generated from dc-arc discharging, consequently affecting the fullerene growth and lowering the yield of Sc-NCFs. Hence, the dependence of the yield of Sc-NCFs on the oxidation state of nitrogen may be attributed to the "in-situ" redox reaction of the nitrogen sources.

The yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) by using different nitrogen sources within the same NH_3- or N_2-based group is then compared and analyzed in detail so as to study the effect of counter ion. For ammonium salts, when the anion changes from the oxyacidic groups ($(H_{3-x}PO_4)^{x-}$, SO_4^{2-}, CO_3^{2-}) to halogen, the yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) decreases dramatically (see Figure 3), suggesting that the performance of ammonium salts as nitrogen sources is sensitively dependent on the anion despite the gaseous NH_3 generating "in situ" directly leads to the formation of Sc-NCFs. A possible reason for this phenomena is that such compounds like $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, NH_4F, and NH_4Cl are more easily decomposed at the beginning of discharging because of their much lower thermal stabilities as indicated by their lower decomposition temperatures and/or larger decomposition rate, resulting in the inevitable loss of reactants. Indeed, we found that the decompositions of $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, NH_4F, and NH_4Cl were so violent that some mixture jetted from the filled graphite rod at the beginning of discharging and became far away from the arc center. Besides, the existence of the nonmetal atom other than oxygen atom (P, S, F, Cl, etc.) might affect the formation of Sc-NCFs as well. Contrarily, the decomposition temperature of NH_4SCN is even higher than $(NH_4)_xH_{3-x}PO_4$), so the loss of reactant at the beginning of discharging could be suppressed; thus, the higher yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) is achieved.

In the N_2-based group of nitrogen sources including thiocyanate, nitrates, and nitrite, nitrogen atom is a component of anion, and we vary the cation so as to study its effect on the yield of Sc-NCFs. When the cation of NH_4SCN is substituted by K^+, the yield of Sc-NCFs decreases dramatically (see Figure 6II and Supporting Information Table S1). This suggests that for NH_4SCN the ammonium cation (NH_4^+) contributes overwhelmingly to the formation of Sc-NCFs instead of the thiocyanate anion (SCN^-).

For the three nitrates (nitrite) which also belong to the N_2-based group of nitrogen sources, including $Cu(NO_3)_2$, $NaNO_3$, $NaNO_2$, the yield of Sc-NCFs is found to be quite comparable (see Figure 6III and Supporting Information, Table S1), suggesting that in this case the formation of Sc-NCFs is independent to both the oxidation state of nitrogen (+3 or +5) and the cation. This phenomenon is obviously different from cases of NH_3-based group of nitrogen source. A plausible interpretation is that the "in situ" generated gaseous N_2 in the decomposed products plays a dominant role in the formation of Sc-NCFs, whereas other "in situ" generated species, which are variable with the change of cation, affect little of this formation process. On the other hand, in terms of the relative yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) to C_{60}, interestingly $Cu(NO_3)_2$ exhibits a much higher selectivity of Sc-NCFs than those obtained by $NaNO_3$ and $NaNO_2$, suggesting Cu^{2+} is more beneficial to the formation of Sc-NCFs compared to Na^+. According to a previous study by Stevenson et al. reporting the use of $Cu(NO_3)_2 \cdot 2.5H_2O$ as additive for the synthesis of Sc-NCFs via the TNT process with gaseous N_2 as the nitrogen source, the generated NO_x vapor as the decomposed product of $Cu(NO_3)_2$ may suppress the formation of empty fullerenes, and concurrently the Cu moiety generated from a nonvolatile route may enhance the yield of Sc-NCFs by offsetting the reactive plasma environment. As a result the selective synthesis of Sc-NCFs was accomplished.[24] In our case, a similar mechanism may be applicable to interpret the observed higher selectivity achieved by $Cu(NO_3)_2$ than those by $NaNO_3$ and $NaNO_2$.

■ CONCLUSIONS

In summary, 12 nitrogen-containing inorganic solid compounds with variable oxidation states of nitrogen and counter ions, including ammonium salts ($(NH_4)_xH_{3-x}PO_4$ (x = 0−2), $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4X (X = F, Cl), NH_4SCN), thiocyanate (KSCN), nitrates ($Cu(NO_3)_2$, $NaNO_3$), and nitrite ($NaNO_2$), have been successfully applied as new inorganic solid nitrogen sources toward the synthesis of Sc-NCFs. Among them, triammonium phosphate hydrate ($(NH_4)_3PO_4 \cdot 3H_2O$) and ammonium thiocyanate (NH_4SCN) are revealed to behave as better nitrogen sources than others, and the highest yield of Sc-NCFs is achieved when NH_4SCN was used as a nitrogen source. The optimum molar ratio of Sc_2O_3:$(NH_4)_3PO_4 \cdot 3H_2O$:C and Sc_2O_3:NH_4SCN:C has been determined to be 1:2:15 and 1:3:15, respectively. An "in-situ" preheating treatment by contacting two electrodes under a very low dc current has been also developed as another strategy to optimize the synthesis conditions in order to remove the hydrated/adsorbed water of these inorganic compounds.

The thermal decomposition products of these 12 inorganic compounds have been discussed in order to understand their different performances toward the synthesis of Sc-NCFs, and accordingly the dependence of the production yield of Sc-NCFs on the oxidation state of nitrogen and counter ion is interpreted. These 12 nitrogen sources can be divided into two groups: one is ammonium salts which decompose to NH_3 (NH_3-based group), and the decomposition products of another group (thiocyanate, nitrates, and nitrite) are all based on N_2 (N_2-based group). The yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) per gram Sc_2O_3 by using the N_2-based group of nitrogen sources is overall much lower than those by using gaseous N_2 and NH_4SCN, indicating the strong dependence of the yield of Sc-NCFs on the oxidation state of nitrogen, which is attributed to the "in-situ" redox reaction taking place for the N_2-based group of nitrogen sources during discharging. For NH_3-based group of nitrogen sources which exhibits a (−3) oxidation states of nitrogen, their performance as nitrogen sources is found to be sensitively dependent on the anion, and this is understood by considering their difference on the thermal stability and/or decomposition rate. Contrarily, for the N_2-based group of nitrogen sources, the formation of Sc-NCFs is independent to both the oxidation state of nitrogen (+3 or +5) and the cation. The new synthesis method by using a series of inorganic solid nitrogen sources is expected to be developed as a general route to the high yield synthesis of NCFs, and the versatility of the nitrogen sources revealed in this study provides a new insight into the chemical reactions involving NCF formation during arc-discharging.

■ EXPERIMENTAL DETAILS

All of the 12 nitrogen-containing inorganic compounds studied in this work are purchased from Sinopharm Chemical Reagent Co., Ltd., including ammonium phosphates ($(NH_4)_xH_{3-x}PO_4$), x = 1−3), ammonium sulfate ($(NH_4)_2SO_4$), ammonium carbonate ($(NH_4)_2CO_3$), ammonium fluoride (NH_4F), ammonium chloride (NH_4Cl), ammonium thiocyanate (NH_4SCN), potassium thiocyanate (KSCN), copper nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$), sodium nitrate ($NaNO_3$), and sodium nitrite ($NaNO_2$). For several compounds only hydrated ones are commercially available and used without further purification. The different nitrogen-containing inorganic compound was mixed with Sc_2O_3 (99.99%) and graphite powder with a certain molar ratio and filled into the drilled graphite rod (Φ 8 mm ×150 mm), which was subjected for dc-arc discharging. One rod per run was used in the study, and an undrilled graphite rod (Φ 40 mm ×33 mm) was applied as cathode. Prior to discharging, a preheating treatment of the filled rod was carried out by contacting the filled rod and the cathode graphite rod under a very low dc current of 10 A for 30 min. Direct current-arc discharging was carried out under 400 mbar He and input current of 120 A. Several other reference discharging experiments were also carried out and reported previously, by using N_2, NH_3, guanidinium thiocyanate, or urea as different nitrogen source, respectively.[11,21,22]

The as-produced soot was Soxhlet-extracted by CS_2 for 24 h, and the resulting brown-yellow solution was distilled to remove CS_2 and then immediately redissolved in 100 mL of toluene. The fullerene extract was passed through a 0.2 μm Telflon filter (Sartorius AG, Germany) for HPLC analysis using a semipreparative 10 mm × 250 mm Buckyprep column (Nacalai Tesque, Japan) and toluene as the eluent. A UV detector set to 320 nm was used for fullerene detection. The composition of fullerene extract mixture was checked by LD-TOF MS analysis running in both positive and negative ion modes (Autoflex speedTM TOF/TOF, Bruker Daltonics Inc., Germany).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Comparison of yield of $Sc_3N@C_{80}$ (I_h + D_{5h}) per gram Sc_2O_3 by using different nitrogen sources, enlarged MS spectra of fullerene extracts obtained by using $Cu(NO_3)_2 \cdot 3H_2O$ or $NaNO_3$ as nitrogen sources, optimization of molar ratio of Sc:N by using NH_4SCN as nitrogen source, and effect of the "in-situ" preheating treatment on the synthesis of Sc-NCFs, etc. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sfyang@ustc.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the financial support from the National Natural Science Foundation of China (90921013, 21132007), "100 Talents Programme of CAS" from Chinese Academy of Sciences, and National Basic Research Program of China (2010CB923300, 2011CB921400).

■ REFERENCES

(1) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maitra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55−57.

(2) Yang, S. F.; Liu, F. P.; Chen, C. B.; Jiao, M. Z.; Wei, T. *Chem. Commun.* **2011**, *47*, 11822−11839.

(3) Yang, S. F.; Liu, F. P.; Chen, C. B.; Zhang, W. F. *Prog. Chem.* **2010**, *22*, 1869−1881.

(4) Chaur, M. N.; Melin, F.; Ortiz, A. L.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7514−38.

(5) Dunsch, L.; Yang, S. F. *Small* **2007**, *3*, 1298−1320.

(6) Dunsch, L.; Yang, S. F. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3067−3081.

(7) Lu, X.; Feng, L.; Akasaka, T.; Nagase, S. *Chem. Soc. Rev.* **2012**, *41*, 7723−7760.

(8) Rodriguez-Fortea, A.; Balch, A. L.; Poblet, J. M. *Chem. Soc. Rev.* **2011**, *40*, 3551−3563.

(9) Dunsch, L.; Krause, M.; Noack, J.; Georgi, P. *J. Phys. Chem. Solids* **2004**, *65*, 309−315.

(10) Chen, C. B.; Liu, F. P.; Li, S. J.; Wang, N.; Popov, A. A.; Jiao, M. Z.; Wei, T.; Li, Q. X.; Dunsch, L.; Yang, S. F. *Inorg. Chem.* **2012**, *51*, 3039−3045.

(11) Yang, S. F.; Chen, C. B.; Popov, A. A.; Zhang, W. F.; Liu, F. P.; Dunsch, L. *Chem. Commun.* **2009**, 6391−6393.

(12) Yang, S. F.; Popov, A. A.; Dunsch, L. *Chem. Commun.* **2008**, 2885−2887.

(13) Yang, S. F.; Popov, A. A.; Dunsch, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 8196−8200.

(14) Yang, S. F.; Popov, A.; Kalbac, M.; Dumsch, L. *Chem.—Eur. J.* **2008**, *14*, 2084−2092.

(15) Yang, S. F.; Popov, A. A.; Dunsch, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 1256−1259.

(16) Yang, S. F.; Troyanov, S. I.; Popov, A. A.; Krause, M.; Dunsch, L. *J. Am. Chem. Soc.* **2006**, *128*, 16733−16739.

(17) Yang, S. F.; Dunsch, L. *J. Phys. Chem. B* **2005**, *109*, 12320−12328.

(18) Dunsch, L.; Georgi, P.; Ziegs, F.; Zöller, H. German Patent DE 10301722 A1, 2003.

(19) Bandow, S.; Shinohara, H.; Saito, Y.; Ohkohchi, M.; Ando, Y. *J. Phys. Chem.* **1993**, *97*, 6101−6103.

(20) Liu, B. B.; Xu, W. G.; Liu, Z. Y.; Yang, H. B.; Li, M. H.; Liu, S. Y.; Zou, G. T. *Solid State Commun.* **1996**, *97*, 407−410.

(21) Yang, S. F.; Zhang, L.; Zhang, W. F.; Dunsch, L. *Chem.—Eur. J.* **2010**, *16*, 12398−12405.

(22) Jiao, M. Z.; Zhang, W. F.; Xu, Y.; Wei, T.; Chen, C. B.; Liu, F. P.; Yang, S. F. *Chem.—Eur. J.* **2012**, *18*, 2666−73.

(23) Dunsch, L.; Yang, S. F.; Zhang, L.; Svitova, A.; Oswald, S.; Popov, A. A. *J. Am. Chem. Soc.* **2010**, *132*, 5413−5421.

(24) Stevenson, S.; Thompson, M. C.; Coumbe, H. L.; Mackey, M. A.; Coumbe, C. E.; Phillips, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 16257−16262.

(25) Stevenson, S.; Mackey, M. A.; Stuart, M. A.; Phillips, J. P.; Easterling, M. L.; Chancellor, C. J.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 11844−11845.

(26) For other compounds studied in the present work, the molar ratio of Sc:N:C is fixed at 1:3:7.5 which is selected according to the optimized conditions for NH_4SCN or $(NH_4)_3PO_4$ (see Table S1).

(27) Andrew, K. G.; Michael, E. B. Decomposition of Ammonium Salts. In *Studies in Physical and Theoretical Chemistry*; Andrew, K. G., Michael, E. B., Eds.; Elsevier: New York, 1999; Vol. *86*, Chapter 15, pp 415−440.

(28) Erdey, L.; Gál, S.; Liptay, G. *Talanta* **1964**, *11*, 913−940.

(29) Fan, Y.; Cao, F. *J. Chem. Eng. Chin. Univ.* **2011**, *25*, 341−346.

(30) Schultz, R. D.; Dekker, A. O. *J. Phys. Chem.* **1956**, *60*, 1095−1100.

(31) Ohta, M.; Hirai, S.; Kato, H.; Sokolov, V. V.; Bakovets, V. V. *Mater. Trans.* **2009**, *50*, 1885−1889.

(32) Costa, L.; Camino, G. *J. Therm. Anal. Calorim.* **1988**, *34*, 423−429.

(33) Semencha, A.; Pozdnyakov, O.; Pozdnyakov, A.; Blinov, L. *Glass Phys. Chem.* **2008**, *34*, 103−109.

(34) Ding, Z.; Martens, W.; Frost, R. L. *J. Mater. Sci. Lett.* **2002**, *21*, 1415−1417.

(35) Živković, Ž.; Živković, D.; Grujičić, D. *J. Therm. Anal. Calorim.* **1998**, *53*, 617−623.

(36) Tomeczek, J.; Gradoń, B. *Combust. Sci. Technol.* **1997**, *125*, 159−180.

(37) Bond, B. D.; Jacobs, P. W. M. *J. Chem. Soc. A* **1966**, 1265−1268.

(38) Freeman, E. S. *J. Phys. Chem.* **1956**, *60*, 1487−1493.

(39) Bartos, H. R.; Margrave, J. L. *J. Phys. Chem.* **1956**, *60*, 256−256.

(40) Tan, Y. Z; Chen, R. T.; Liao, Z. J.; Li, J.; Zhu, F.; Lu, X.; Xie, S. Y.; Li, J.; Huang, R. B; Zheng, L. S. *Nat. Commun.* **2011**, *2*, 420.