Synthesis of carbyne nano-particles by dehydrochlorination of 1,1,1-trichloroethane

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Chemical dehydrochlorination of 1,1,1-trichloroethane with anhydrous KOH in the presence of a poly(ethylene glycol) oligomer as phase transfer catalyst leads to the formation of carbyne particles with diameters in the range of 30–50 nm.

Synthesis of carbynes or cumulenic carbons has attracted the attention of many researchers,[1] as we still know much less about this material than about the other carbon polymorphs such as graphite, fullerenes and diamond.[2] Several synthetic routes to carbynes have been developed,[3–5] however, none of them concerned dehydrochlorination of low molecular weight carbon halides. Presented here is a novel chemical approach for synthesizing a carbyne analogue from 1,1,1-trichloroethane.

Carbyne can be prepared by reaction of 1,1,1-trichloroethane with a large amount of anhydrous KOH powder (the molar ratio of the base and the halide should be greater than 5 : 1) in the presence of a poly(ethylene glycol) with molar mass greater than 200 g mol^{-1} as phase transfer catalyst. The reaction can be represented by eqn. (1).

$$n\ CH_3CCl_3 + 3n\ KOH \xrightarrow[20\text{–}30\ ^\circ C,\ 4\ h]{HO(CH_2CH_2O)_mH\ (m\ >\ 3)} \underset{42\%}{-(C\equiv C)_n-} + 3n\ KCl + 3n\ H_2O \quad (1)$$

KOH in excess acts as a water absorbent and removing of water forces the reaction to the right hand. Otherwise, as a large amount of water exist in the system, the reaction produces only 1-chloroacetylene or 1,1-dichloroethylene and no carbon is obtained.

The black powdery carbon obtained by this technique had a particle size of 30–50 nm as shown by its transmission electron micrograph (Fig. 1). Powder X-ray diffraction analysis showed a broad peak at 2θ = 21°, showing the product to be amorphous.

The FT-IR spectrum of the product (Fig. 2) shows no C–Cl bands in the region 520–700 cm^{-1}, indicating extensive dehydrochlorination of the halide. New absorption bands appear in 1600 and 2130 cm^{-1}. They are typical of valence vibrations of carbon–carbon double and triple bonds, respectively.[6,7] The band in the region of 1700 cm^{-1} may be attributed to cumulative double bonds.[8] The very strong band at 1100 cm^{-1} is assigned to the stretching vibration of the C–C bond.[6] Absorption bands typical of valence vibrations of CH_2 were found in the region of 2800–2990 cm^{-1}. No band was observed above 3000 cm^{-1}, which demonstrated that no substitution side reaction was present during the carbonization process.

In the FT-Raman spectrum (Fig. 2) there appears a broad band centered at *ca.* 1900 cm^{-1}, which is attributed to conjugated carbon–carbon triple bonds. A much weaker band centered at *ca.* 1600 cm^{-1} is of 'inner layer' graphite bound by two adjacent graphite planes and the band centered at *ca.* 1400 cm^{-1} is the A_{1g} mode of $D_{6h}{}^4$ symmetry for small graphitic crystallites.[9] The intensity ratio of the 1900 cm^{-1} ($I_{C\equiv C}$) band and 1600 cm^{-1} band (I_{g-C}) is calculated to be 4.0 ± 0.5. There exists no other solid carbon material showing such intense Raman signals for triple-bonded carbon (the $I_{C\equiv C}/I_{g-C}$ of carbynes made *via* other systems was found to be lower than 2.2).[2] The conjugation length of carbyne estimated by the equation developed by Kuzmany *et al.* is *ca.* 15. This value is higher than those of the carbynes reported previously (6–10).[2,4]

While the existence of carbyne has been repeatedly doubted, all the criticisms are not convincing enough to reject the concept of linear carbon allotropes.[10] On the other hand, the FT-IR and FT-Raman spectra results described above provide strong evidence of carbon particles made from 1,1,1-trichloroethane having a polyyne structure with high concentrations of relatively long conjugated triple-bonded carbon sequences.

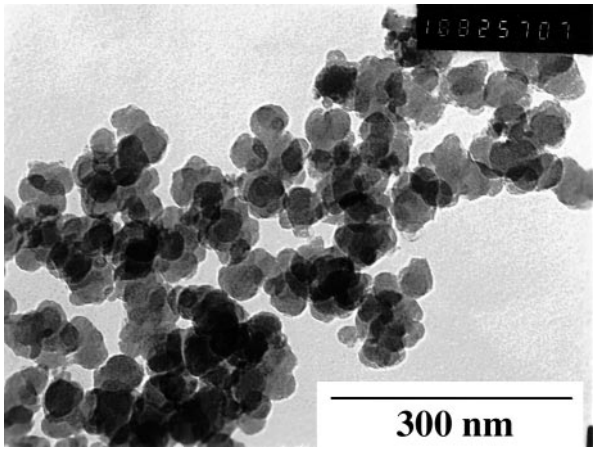

Fig. 1 Transmission electron micrograph of the carbon made from 1,1,1-trichloroethane.

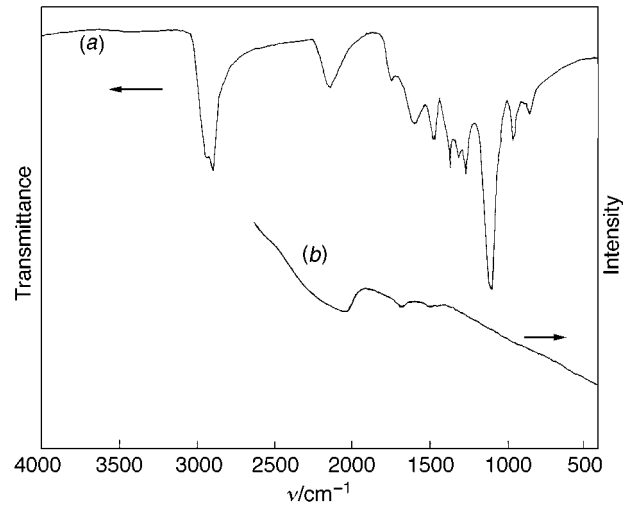

Fig. 2 (*a*) FT-IR and (*b*) FT-Raman spectra of the carbon made from 1,1,1-trichloroethane.

In conclusion, 1,1,1-trichloroethane can be carbonized by anhydrous KOH powder into amorphous carbyne nano-particles. This is the first example of dehydrochlorination of low molecule weight carbon halides into carbynes.

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Notes and References

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