Iron carbide clusters with near-sub-nanometer size have been synthesized by employing a tetr phenylmethane-cored phenylazomethine dendrimer generation 4 (TPM-DPAG4) as a molecular template. Magnetic measurements reveal that these iron carbide clusters exhibit a magnetization–field hysteresis loop at 300 K. The data indicate that these iron carbide clusters are ferromagnets at room temperature.

The properties of many substances are thus sensitively affected by particle size, particularly in the near-sub-nanometer range. In this context, the smallest iron carbide nanoparticles reported to date are as small as ca. 2 nm,\textsuperscript{7,16} aside from the gas phase experiments\textsuperscript{26,27} and the theoretical studies.\textsuperscript{28–32} In these cases, the iron carbide nanoparticles exhibit superparamagnetism, \textit{i.e.}, they do not act as magnets at ambient temperature. However, sub-nanosized iron carbide particles have remained elusive to date. In the present study, we have synthesized near-sub-nanometer iron carbide particles/clusters, and these iron carbide clusters are ferromagnets, even at room temperature, thereby countering superparamagnetism. Bulk iron carbide is an old material; however, the iron carbide clusters synthesized in this work are the smallest room temperature magnets reported to date.

Fig. 1 shows the strategy employed for the synthesis of near-sub-nanometer-sized iron carbide clusters. The macromolecular tetr phenylmethane-cored dendritic phenylazomethine dendrimer generation 4 (TPM-DPAG4) was used as a molecular template. This DPA-type dendrimer coordinates to metal ions in solution via its imine sites, and complexation proceeds stepwise from the center of the dendrimer to its periphery due to its basicity gradient.\textsuperscript{33–37} Stepwise complexation was confirmed in the present study by UV-Vis titrations. Upon the addition of FeCl\textsubscript{3} to a solution of TPM-DPAG4, spectral changes and shifts in the isosbestic point were observed (Fig. S1†); these changes reached saturation after the combined addition of 60 eq. of FeCl\textsubscript{3}. Different isosbestic points were observed in the ranges of 0–4, 6–12, 16–28, and 32–60 eq., respectively, which is consistent with the number of imines at each type of site and reflects the stepwise complexation from the central to the peripheral sites. The \textit{in situ}-prepared dendrimer complexes, \textit{i.e.}, TPM-DPAG4 with 4, 12, 28, or 60 eq. of FeCl\textsubscript{3} incorporated were

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then adsorbed onto a graphitic carbon support (graphitized mesoporous carbon: GMC). Carbothermal hydrogen reduction (CHR), which is a synthetic method used to obtain metal carbides, was subsequently applied. After CHR at 773 K for 30 min, the samples (Fe12/C, Fe28/C, and Fe60/C) were examined using transmission electron microscopy (TEM), and the results are shown in Fig. 2 and S2.† There are several reports for TEM observations of iron carbide nanoparticles larger than 2 nm diameter without atomic-resolution. Very fine particles dispersed over the carbon support were observed as blurry black dots in the TEM images. The mean particle diameter and standard deviation of the size distribution were estimated to be 0.9 ± 0.2 nm (Fe12/C), 1.0 ± 0.3 nm (Fe28/C), and 1.3 ± 0.3 nm (Fe60/C), respectively. The average particle size consistently increased with the FeCl3 content in the TPM-DPAG4 template. These samples represent the first examples of near-sub-nanometer-sized iron carbide particles. However, we could not observe any individual particles in the Fe60/C sample, because the particle size was too small. In this case, the particle size was estimated to be ca. 0.6 nm using the tetra-nuclear cluster model of the [Fe4C(CO)12]2– carbocarbonyl complex reported by Boehme et al. (Fig. S3a†) as well as the theoretical studies.† It should be noted that atomic-resolution images that would project the clusters could not be obtained, because these samples exhibit ferromagnetism, even at room temperature.

Powder X-ray diffraction (PXRD) analysis cannot be applied to the characterization of such sub-nanosized particles on solid supports, as they do not adopt any long-range-ordering crystal structure. On the other hand, X-ray absorption fine structure (XAFS) is a powerful tool to clarify the local structure around the metal atoms. We found that the X-ray absorption near edge structure (XANES) spectra of Fe60/C, Fe28/C, and Fe4/C after CHR are very similar to those of metallic iron (Fe foil) and FeC, whereas they are substantially different from those of iron oxides such as Fe3O4 and α-Fe2O3 as well as from that of the FeCl3 starting material (Fig. S4†). Therefore, it can be concluded that these samples are not oxides. XANES spectrum of FeC and metallic iron can clearly be distinguished in their first derivatives form (Fig. 3). Metallic iron and FeC have a pre-edge peak in common at ca. 7111 eV (3s → 4d transitions). Metallic iron exhibits two maxima in the range of 7115–7130 eV (3s → 4p transitions), while FeC exhibits one maximum and several shoulders in this region. The spectra of Fe60/C, Fe28/C, and Fe4/C after CHR had a pre-edge peak at ca. 7111 eV, together with a maximum peak in the 7115–7130 eV region, which indicates the iron carbide nature. Therefore, it can be concluded that Fe60/C, Fe28/C, and Fe4/C are iron carbides rather than metals. The white-line peak was slightly shifted to the higher energy side with downsizing (Fig. 3b), i.e., 7129.4 eV (FeC), 7130.2 eV (Fe60/C), 7130.1 eV (Fe28/C), 7131.2 eV (Fe12/C), and 7131.4 eV (Fe4/C). The experimental error was estimated to be ±0.3 eV based on the applied energy resolution. This shift tendency supported that the cluster samples (Fe60/C, Fe28/C, Fe12/C, and Fe4/C) are very fine particles with high specific surface. In addition, the assignment as iron carbides is decisively supported by their Curie temperatures (TC), which were measured to be 483–488 K (Fig. 4). These TC values are comparable to that of Fe3C (483 K, Fig. S5 and S6†), which suggests that the ferromagnetic interactions originate from iron carbides. The Curie temperature of Fe3C is far from those of metallic iron (1043 K) and iron oxides e.g. Fe3O4 (850 K) and α-Fe2O3 (820–986 K). It should also be noted that Fe3C forms a complicated crystal structure that involves nine types of Fe–Fe bonds (2.455–2.714 Å; Fig. S3b†). The presence of the corresponding Fe–Fe bonds in Fe60/C was suggested by extended X-ray absorption fine structure (EXAFS) measurements conducted in transmission mode (Fig. S7†). The Curie temperature for Fe3C mainly represents the average of the direct exchange interactions between the Fe–Fe bonds, similar to that in amorphous ferromagnets such as the Fe–C–P system, and thus, TC would be considered not to show a significant size dependence.

Fig. 5 shows magnetization-field (M–H) loops for the iron carbide clusters, and the magnetic data are summarized in Table S1†. The M per the sample weight data are shown in Fig. S8–S12.† The four cluster samples show hysteresises in their M–H loops at 1.9 K (Fig. 5a), which indicates that they are ferromagnets with an associated coercivity (Hc). The Hc value
increased with a decrease in the cluster size, \( i.e., 603 \text{ Oe (Fe}_{60}/C), 939 \text{ Oe (Fe}_{28}/C), 1856 \text{ Oe (Fe}_{12}/C), \) and \( 2697 \text{ Oe (Fe}_{4}/C) \). In contrast, bulk iron carbide cementite (Fe\(_3\)C) with an average crystal size of 39 nm has a smaller hysteresis with \( H_c \) values of 166 and 21 Oe at 1.9 and 300 K, respectively (Fig. S8\( ^\dagger \)). The magnetic behavior of bulk Fe\(_3\)C indicates ferromagnetism with a multi-magnetic-domain structure.\(^5\) On the contrary, iron carbide nanoparticles have been reported to exhibit more pronounced hysteresis at room temperature than bulk Fe\(_3\)C, with \( H_c \) values of 700 Oe (15 nm) and 544 Oe (14.1 ± 0.8 nm) by Grimes \textit{et al.}\(^5\) and Hou \textit{et al.}\(^6\), respectively, which suggests a single-magnetic-domain structure. Therefore, the smaller iron carbide clusters in this study are considered to have a single-magnetic-domain structure. The increase in coercivity with the decrease in single-magnetic-domain particle size has been reported by Lartigue \textit{et al.} for iron carbide nanoparticles with sizes of 15.1 nm (\( H_c = 331 \text{ Oe} \)), 7.4 nm (\( H_c = 405 \text{ Oe} \)), 5.5 nm (\( H_c = 625 \text{ Oe} \)), and 2.8 nm (\( H_c = 1099 \text{ Oe} \)) at 2.5 K.\(^7\) On the other hand, the iron carbide clusters exhibit hysteresis loops at 300 K (Fig. 5b), \( i.e., H_c = 140 \text{ Oe (Fe}_{60}/C), 163 \text{ Oe (Fe}_{28}/C), 367 \text{ Oe (Fe}_{12}/C), \) and 666 Oe (Fe\(_4)/C), which indicates that they are ferromagnets, even at room temperature. Clusters or near-sub-nanosize particles generally exhibit superparamagnetism with a complete loss of coercivity at room temperature.\(^3\)

\[
\tau_N \propto \exp(E_a/k_B T) \quad (1)
\]

\[
E_a = K_{\text{eff}} V \quad (2)
\]

Eqn (1) is the Néel–Arrhenius equation,\(^4\) where \( \tau_N, E_a, k_B, T, K_{\text{eff}}, \) and \( V \) are the Néel relaxation time, magnetic anisotropy energy, Boltzmann constant, temperature, effective magnetic anisotropy constant, and volume of a single-magnetic-domain particle, respectively. The term for the angle between the magnetic moment and the easy magnetic axis was not introduced (eqn (2)), because these were powder samples. Therefore, superparamagnetism emerges with a decrease in size \( V \) because \( E_a \) increases comparable to the thermal energy \( \{k_B T\} \). Lartigue \textit{et al.} have reported superparamagnetism for iron carbide nanoparticles with sizes less than 5.5 nm.\(^7\) Fig. S13\( ^\dagger \) shows field-cooling (FC) and zero-field-cooling (ZFC) magnetization curves used to determine the blocking temperature \( (T_B) \) at which the magnets completely lose their coercivity. Fe\(_3\)C shows a \( T_B \) of 467 K which is near the Curie point (483 K). On the other hand, the \( T_B \) of Fe\(_{60}/C \) is clearly lower (ca. 385 K) than the Curie point, which was attributed to the influence of superparamagnetism in light of the results of Lartigue \textit{et al.} In contrast, Fe\(_{28}/C \) has higher \( T_B \) values close to the Curie point at 473 K. This behavior is contrary to superparamagnetism and cannot be explained without increased effective magnetic anisotropy \( (K_{\text{eff}}) \). The interactions between the iron carbide clusters and the graphitic carbon surface may be a mechanism to afford large \( K_{\text{eff}} \), because the ratio of the interacting Fe atoms increases by decreasing size. The oxidation of Fe\(_4)/C \) in air at 553 K for 30 min significantly decreased the magnetization and coercivity (Fig. S14\( ^\dagger \)). Carbides can be the magnets at sub-nano scale, while oxides would not. Due to the measurement sensitivity limit and noise, the \( T_B \) values were at least above room temperature. It should also be noted here that the magnetic moment per Fe atom of these cluster samples (1.0–2.3 \( \mu_B \text{ atom}_\text{Fe}^{-1} \)) was almost identical to that of Fe\(_3\)C (1.5 \( \mu_B \text{ atom}_\text{Fe}^{-1} \)), regardless of the Fe content (wt%) over an order of magnitude (Table S1\( ^\dagger \)). The variation in the magnetic moment may involve not only experimental errors, but also atomicity. Becker \textit{et al.} reported that Fe clusters exhibit an atomicity-dependent variation in their magnetic moment in the gas phase, especially below 100
atoms. Additionally, the density functional theory studies have reported that the iron carbide clusters show the magnetic moment of ca. 1–3.5 \( \mu_B \) atom\( ^{Fe}_1 \), which is consistent with those in this study. Therefore, with consideration of the magnetic moment and the Curie temperature, it was concluded that the magnetic behavior of the iron carbide cluster samples is derived from the carbides themselves, and not from impurities. The reproducibility of the \( M–H \) hysteresis loop at 300 K for Fe\(_x\)/C was certainly confirmed including another batch sample (sample B: Fig. S15†). It was also confirmed that a blank sample (GMC) showed diamagnetism measured at both 1.9 and 300 K (raw \( M \) data shown in Fig. S16–S23†).

Nanoparticle magnets have a single magnetic-domain structure and exhibit hysteresis at room temperature; however, they lose this hysteresis upon downsizing by superparamagnetism. There have been no reports of sub-nanoparticle magnets (diameter: \( \sim \)1 nm or less) that exhibit coercivity above room temperature: neither for e.g. Fe–Pt bimetallic nanoparticles\(^\text{19} \) nor iron oxide nanoparticles.\(^\text{21} \) The iron carbide clusters in this study are unique magnets that are different from both nanoparticle magnets. They do not have a long-range-ordering crystal structure such as nanoparticles and bulk substances on account of their sub-nanometer size. The iron carbide clusters in this study were carefully characterized by XAFS (Fig. 3) as well as by the Curie temperature (Fig. 4). The magnetic measurements (Fig. 5) revealed that the iron carbide clusters represent room-temperature magnets. Therefore, the iron carbide clusters discussed in this study can represent room-temperature magnets. This work has synthesized the first examples of sub-nanosized iron carbides on a graphitic carbon support. These iron carbide clusters act as magnets at room temperature. This study would open up the new research field of sub-nano magnets.

Conflicts of interest

There are no conflicts to declare.

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