Electronic Supplementary Material (ESI) for RSC Advances.

Low temperature synthesis of carbon fibres and metal-filling carbon nanoparticles in near-critical benzene with irradiation of the second, third and fourth harmonics generated from a neodymium doped yttrium/aluminium/garnet laser

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1. Fibres formed after irradiation of a laser beam of 533, 355 and 266 nm wavelengths into near-critical benzene

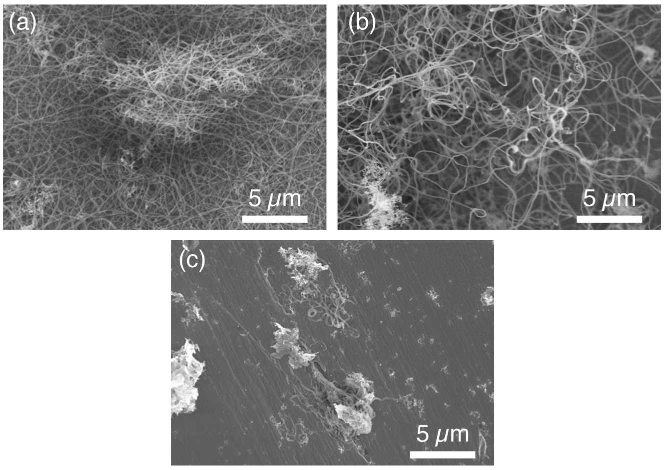

Fig. S1 SEM images of carbon fibres created by irradiation of the second (532 nm), third (355 nm) and fourth (266 nm) harmonics.

2. Iron/chromium-filling carbon nanoparticles

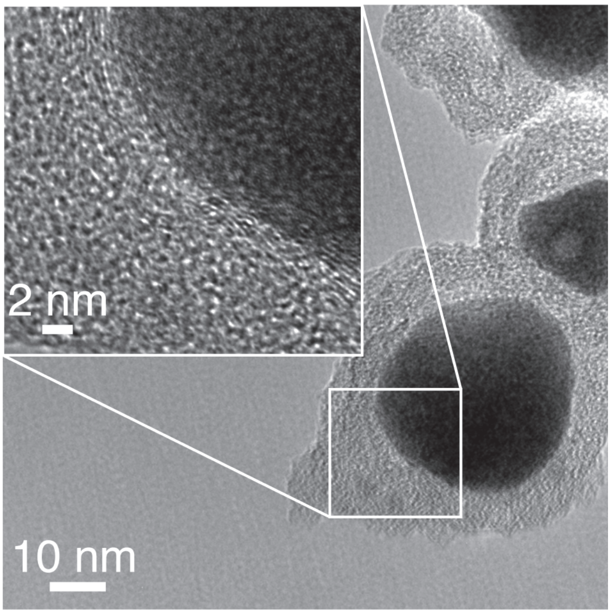

Fig. S2 TEM images of iron/chromium-filling carbon nanoparticles created by irradiation of photons of 532 nm wavelength. Carbon shells are mostly amorphous.

3. Diameter distributions of carbon fibres

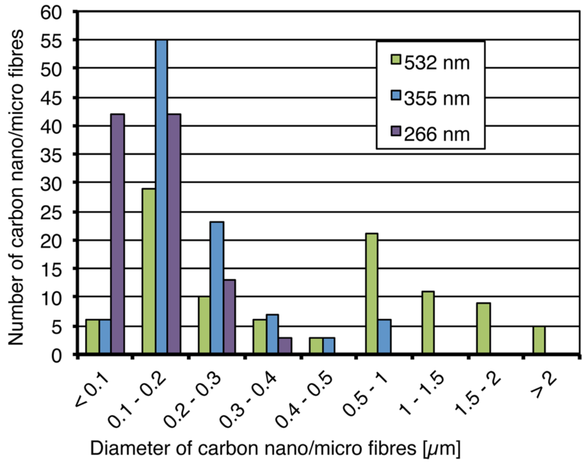

Fig. S3 Diameter distributions of carbon fibres created by irradiation of the second (532 nm), third (355 nm) and fourth (266 nm) harmonics laser.

4. Metal nanoparticles formed on the surface of alloy rods by laser ablation

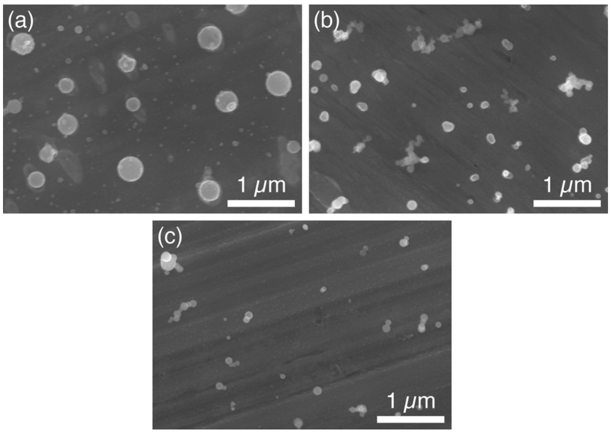

Fig. S4 SEM images of metal nanoparticles formed on the surface of alloy rods in air at 290 °C and 1 atm. (a) Metal nanoparticles formed by the second harmonic laser (532 nm). (b) Metal nanoparticles formed by the third harmonic laser (355 nm). (c) Metal nanoparticles formed by the fourth harmonic laser (266 nm).

5. Weight of carbon structures created after irradiation of a laser beam of 532, 355 and 266 nm wavelengths into near-critical benzene

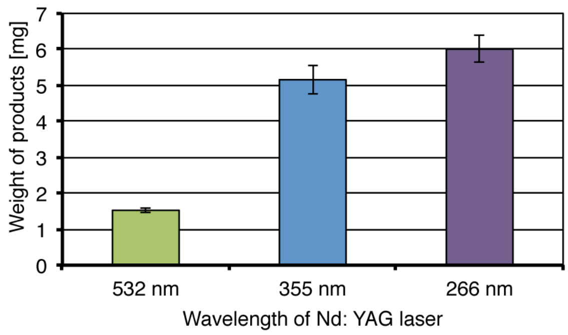

Fig. S5 Effect of the wavelength of a laser beam on the weight of carbon structures such as amorphous carbon and carbon fibres and coils created in near-critical benzene.

6. Fibres formed after irradiation of a laser beam of 266 nm wavelength into near-critical benzene

A cylindrical alloy catalyst was placed at the bottom of the container in super-critical carbon dioxide at 41 °C, which was irradiated with 10,000 pulses of the fourth harmonic (266 nm) laser. Note that the critical temperature and pressure of carbon dioxide are 31.0 °C and 7.38 MPa.[1] It is known that there is no UV absorption by carbon dioxide.[2] The laser was focused on the surface of the alloy catalyst to create metal alloy nanoparticles in super-critical carbon dioxide (see Fig. S5(a) and (b)). It is supposed that there was no oxidation of metal nanoparticles in carbon dioxide

We then placed the alloy rod, on which metal nanoparticles had been formed by laser ablation, in near-critical benzene. We irradiated 50000 pulses of the fourth harmonic (266 nm) laser into near-critical benzene. We found that benzene was dissociated and carbon fibres and coils and metal-filling carbon nanoparticles were created as efficiently as in the case of the second harmonic (532 nm) laser (see Fig. S5(c) and (d)).

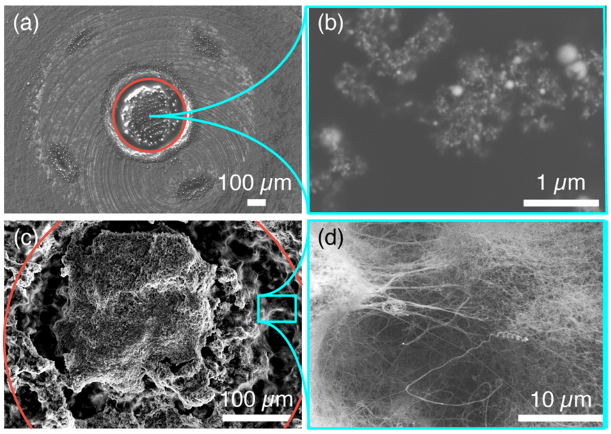

Fig. S6 SEM images of the structures formed on the surface of alloy rods. (a), (b) SEM images of nanoparticles produced by irradiation of a focused laser of the fourth harmonic (266 nm) into super-critical carbon dioxide. The red circle represents the area ablated by laser irradiation. (c), (d) SEM images of carbon fibres created by irradiation of the fourth harmonic laser into near-critical benzene using the catalytic nanoparticles.

1. K.A. Kobe and R.E. Lynn Jr., *Chem. Rev.*, 1953, **52**, 117-236.
2. T. Fukuda, T. Maekawa, T. Hasumura, N. Rantonen, K. Ishii, Y. Nakajima, T. Hanajiri, Y. Yoshida, R. Whitby and S. Mikhalovsky, *New J. Phys.*, 2007, **9**, 321-331.

7. TGA curve of $Cu(tbaoac)_2$

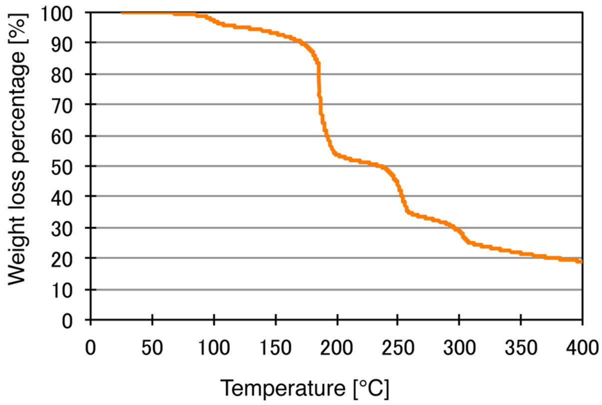

Fig. S7 TGA curve of $Cu(tbaoac)_2$. The temperature was increased from 25 to 400 °C under a nitrogen flow (100 mL min^{-1}). The rate of temperature increase was set at 10 °C min^{-1}. The weight of $Cu(tbaoac)_2$ started to decrease at around 100 °C and decreased rapidly up to 190 °C. Finally, the weight-loss of the original $Cu(tbaoac)_2$ was approximately 81 % at 400 °C.

8. Copper nanoparticles formed by pyrolytic decomposition of Cu(tbaoac)$_2$

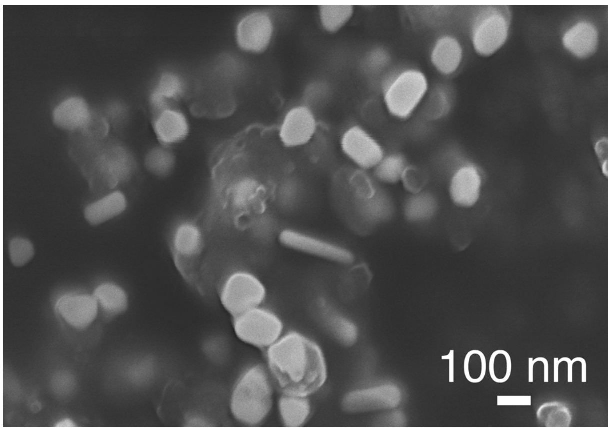

Fig. S8 SEM image of copper nanoparticles formed after pyrolytic decomposition of Cu(tbaoac)$_2$ on the window of the container. The particles were collected on a carbon tape and observed by an SEM.