**Supporting information on**

**Modulating non-linear optical absorption through controlled graphitization of carbon nanostructures containing Fe3C-graphite core-shell nanoparticles**

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**Figure S1**. SEM images of (i) F-RT and (ii) F-600 samples. The average outer diameter of the nanotubes for F-RT sample is ~ 150 nm, where as ~ 30 nm for F-600 sample.

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**Figure S2.** Raman spectra of the synthesized samples.

**Table S1**. Rietveld refined parameters obtained from the XRD patterns of the synthesized samples.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Phase** | **Space group** | **Weight fraction %** | **Cell parameters(Å)** | **Cell volume (Å)3** | **FWHM (Hw) (2θ)** | **Crystallite size (nm)** |
| **F-RT** | Graphite (1)  Graphite (2)  α-Fe  Fe3C  Fe3O4 | *P63/mmc(Hexagonal)*  *P63/mmc*  *Im3̅m* (bcc)  *Pnma*(orthorhombic)  *Fd3̅m(cubic)* | 35.1  54.9  1.9  7.1  0.9 | a=b=2.5621  c=6.7474  a=b=2.4600  c=6.8263  a=b=c=2.8689  a=5.0963  b=6.7452  c=4.5323  a=b=c=8.3661 | 38.36  35.78  23.61  155.78  585.56 | 0.509542 (26.39)  1.643934  (26.09)  0.305298  (44.63)  0.223836  (44.97)  0.354996  (35.56) | 17.3  5.4  36.6  50.2  27.5 |
| **F-300** | Graphite (1)  Graphite (2)  α-Fe  Fe3C  Fe3O4 | *P63/mmc*  *P63/mmc*  *Im3̅m* (bcc)  *Pnma*(orthorhombic)  *Fd3̅m* | 30.2  58.8  1.1  9.2  0.7 | a=b=2.5562  c=6.7510  a=b=2.4593  c=6.8222  a=b=c=2.8655  a=5.0950  b=6.7436  c=4.5282  a=b=c=8.3572 | 38.20  35.73  23.53  155.58  583.76 | 0.509542 (26.40)  1.824568  (26.10)  0.350466  (44.69)  0.260547  (44.99)  0.605012  (35.60) | 17.4  4.8  31.9  43.1  16.1 |
| **F-400** | Graphite (1)  Graphite (2)  α-Fe  Fe3C  Fe3O4 | *P63/mmc*  *P63/mmc*  *Im3̅m* (bcc)  *Pnma*(orthorhombic)  *Fd3̅m* | 31.9  58.1  0.3  9.3  0.4 | a=b=2.5605  c=6.7443  a=b=2.4587  c=6.8265  a=b=c=2.8560  a=5.0920  b=6.7412  c=4.5287  a=b=c=8.3621 | 38.29  35.74  23.29  155.45  584.73 | 0.629725  (26.40)  2.067224  (26.09)  0.203648  (44.84)  0.231220  (44.99)  0.344333  (35.58) | 14.1  4.3  55.0  48.6  28.4 |
| **F-500** | Graphite (1)  Graphite (2)  α-Fe  Fe3C  Fe3O4 | *P63/mmc*  *P63/mmc*  *Im3̅m* (bcc)  *Pnma*(orthorhombic)  *Fd3̅m* | 31.4  60.0  0.9  6.7  1.0 | a=b=2.5616  c=6.7622  a=b=2.4664  c=6.8500  a=b=c=2.8659  a=5.0932  b=6.7428  c=4.5305  a=b=c=8.3779 | 38.43  36.09  23.54  155.59  588.05 | 0.749121 (26.34)  2.040365  (25.99)  0.317205  (44.68)  0.225958  (44.97)  0.545425  (35.51) | 11.8  4.3  35.2  49.7  17.9 |
| **F-600** | Graphite (1)  Graphite (2)  α-Fe  Fe3C  Fe3O4 | *P63/mmc*  *P63/mmc*  *Im3̅m* (bcc)  *Pnma*(orthorhombic)  *Fd3̅m* | 35.7  55.6  0.4  7.6  0.7 | a=b=2.5556  c=6.7626  a=b=2.4438  c=6.9071  a=b=c=2.8559  a=5.0963  b=6.7452  c=4.5323  a=b=c=8.3671 | 38.25  35.72  23.29  155.35  585.77 | 1.027389 (26.33)  2.546268  (25.77)  0.185600  (44.84)  0.191009  (45.01)  0.412731  (35.56) | 8.6  3.5  60.4  58.8  23.6 |

**Table S2.** Mössbauerspectral parameters obtained fromthe fits. The isomer shift (IS) values are w.r.t 57Co source. The most probable hyperfine fields P(*Bhf*) for the A and B sites of Fe3O4 phase are given in brackets. The values in < > indicate the values for the most probable peak maximum in the distribution profile. It should be noted that, since the amount of Fe3O4 and Fe(C) is very low to obtain an accurate fit in the distribution profile, large discrepancies in isomer shifts and quadrupole splitting (QS) can occur.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Sub-spectra** | **Phase** | ***IS* (mm/s)**  **±0.001** | ***QS* (mm/s)**  **±0.05** | ***Bhf* (T)**  **±0.1** | **Area%**  **±2** |
| **F-RT** | Dx  S1  S2  D | Fe3O4  α-Fe(C)  Fe3C (1)  Fe3C (2)  Paramagnetic (Fe-C) | <-0.09>  0.1  0.1 | <-0.18>  0.10  -0.04  0.48 | (50,42)  32  20.9  20.1 | 37  25  31  7 |
| **F-300** | Dx  S1  S2  D | Fe3O4  α-Fe(C)  Fe3C (1)  Fe3C (2)  Paramagnetic (Fe-C) | <-0.17>  0.1  0.1 | <-0.13>  0.03  -0.01  0.85 | (50,43)  32  20.9  20.1 | 24  31  38  7 |
| **F-400** | Dx  S1  S2  D | Fe3O4  α-Fe(C)  Fe3C (1)  Fe3C (2)  Paramagnetic (Fe-C) | <-0.17>  0.1  0.1 | <-0.38>  0.05  -0.03  0.78 | (50,43)  32  20.9  20.1 | 20  40  33  7 |
| **F-500** | Dx  S1  S2  D | Fe3O4  α-Fe(C)  Fe3C (1)  Fe3C (2)  Paramagnetic (Fe-C) | <-0.09>  0.1  0.1 | <-0.07>  0.04  -0.02  1.00 | (48,41)  32  20.9  20.1 | 23  36  30  7 |
| **F-600** | Dx  S1  S2  D | Fe3O4  α-Fe(C)  Fe3C (1)  Fe3C (2)  Paramagnetic (Fe-C) | <0.23>  0.1  0.1 | <0.16>  0.03  0.01  0.72 | (47,39)  31  20.9  20.1 | 22  38  30  10 |

**Table S3**. Intensity ratios calculated from the Raman spectral fits. IG is the intensity of the graphitic peak (G), ID is the sum of intensities of all the defect peaks (D1, D2, D3 and D4) and ID3 is the intensity of the amorphous carbon peak (D3).

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **IG/ID** | **IG/ID3** | **IG/ID2** |
| F-RT | 0.14 | 2.01 | 1.47 |
| F-300 | 0.16 | 1.08 | 3.08 |
| F-400 | 0.19 | 1.04 | 3.35 |
| F-500 | 0.17 | 2.19 | 2.29 |
| F-600 | 0.18 | 2.47 | 2.94 |



**Figure S3**. TGA plots of the synthesized samples.

**Table S4**. Compositional analysis from the TGA plots.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Carbon content %** | | **Residual weight %** |
| **Surface moieties** | **Microcrystalline graphite** |
| F-RT | 1 | 78 | 21 |
| F-300 | 2 | 78 | 20 |
| F-400 | 2 | 80 | 18 |
| F-500 | 3 | 80 | 17 |
| F-600 | 4 | 79 | 17 |

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**Fig S4.** Structure of ferrocene and Fe(acac)3.



**Figure S5.** Z-scan plot for (a) ethylene glycol and (b) amorphous carbon.