Supplementary Information for:

Collagen based magnetic nanocomposites for oil removal applications

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Table S1 XRD results of pristine collagen and collagen-SPION nanobiocomposite fibers

Collagen/ SPION (Wt.%)	Intermolecular lateral packing (nm) (1)	Amorphous region (nm) (2)	Helical rise per residue (nm) (3)	N telopeptide (nm) (4)	C telopeptide (nm) (5)	Collagen/ amorphous (gelatin) ratio
100/0	1.107	0.396	0.279	0.221	0.201	2.5
100/50	1.025	0.436	0.280	0.237	0.214	1.4

Raman spectroscopic analysis of collagen-SPION nanobiocomposites. Raman spectra of the pristine collagen fibers and collagen-SPION nanobiocomposite are shown in Figure S1. It is seen that both pristine and SPION treated collagen exhibit almost similar Raman bands. The bands at 917 and 852 cm^{-1} correspond to Pro while that at 878 cm^{-1} assigned for Hyp, which are observed due to strong Raman scattering of saturated side chain rings. The presence of Hyp is noted only in collagen occurring due to the post translational modification of Pro offering additional stability to collagen. This clearly shows the presence of Gly-X-Hyp and Gly-Pro-Y sequence in both pristine and iron oxide nanoparticle treated collagen. The C-C stretching band of the peptide backbone is observed at 937 cm^{-1} while the band at 1450 cm^{-1} corresponds to CH_2 deformation. A strong band at 1673 cm^{-1} is generally assigned to amide I band of carbonyl stretching vibration from peptide backbone. The bands at 1270 and 1240 cm^{-1} correspond to amide III band originating from the N-H in plane deformation and C-N stretching mode, respectively. Amide II bands are too weak (1555-1575 cm^{-1}) and are not generally visible in the Raman spectra. The results clearly indicate that the interaction of SPION does not alter or destroy the triple helical structure of collagen.

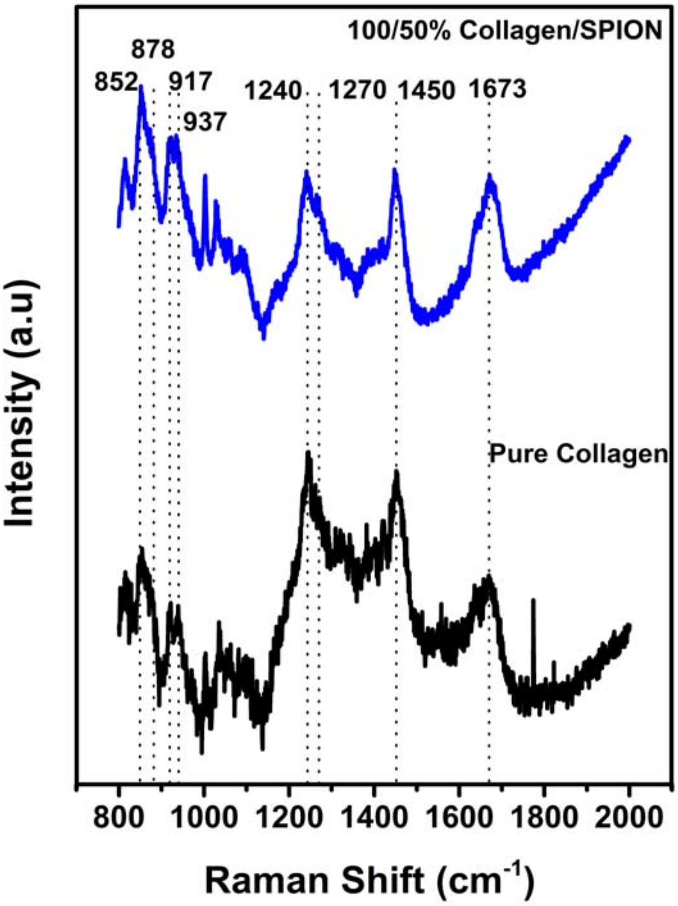
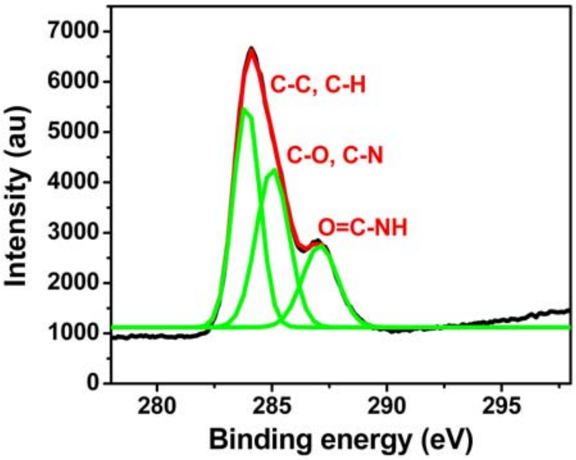


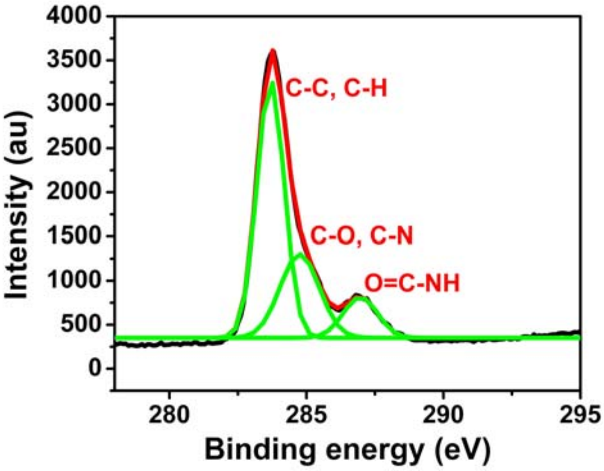
Figure S1 Raman spectrum of the pristine collagen and collagen-SPION nanobiocomposite.

XPS analysis of collagen-SPION nanobiocomposites. XPS spectra of the pristine collagen fibers and collagen-SPION nanobiocomposite are shown in Figure S2. It is seen that the C(1s) core level spectra results in three binding energies corresponding to components such as C-C/C-H bonds, C-O/C-N bonds and O=C-NH peptide bonds, respectively when deconvoluted. Two components were observed namely O=C and O-C bonds when O(1s) core level spectra was deconvoluted, while N(1s) core level spectra show a single component corresponding to O=C-N-H group. Thus, all the C(1s), O(1s) and N(1s) core level spectra demonstrate the presence of polypeptides in the pristine collagen fibers. It is not surprising to note that the collagen-SPION nanobiocomposite fibers exhibit almost similar C(1s), O(1s) and N(1s) spectra indicating that the primary structure and chemical functionalities of the collagen fibers are not altered upon reaction with SPION. It is interesting to note that the collagen-SPION nanobiocomposite fibers show characteristic peaks of Fe^{3+} based compound at 709.4 and 723.6 eV, which correspond to $2p_{3/2}$ (L_3) and $2p_{1/2}$ (L_2) edges, respectively[1]. This indicates the presence of SPION nanoparticles in the collagen-SPION nanobiocomposite fibers.

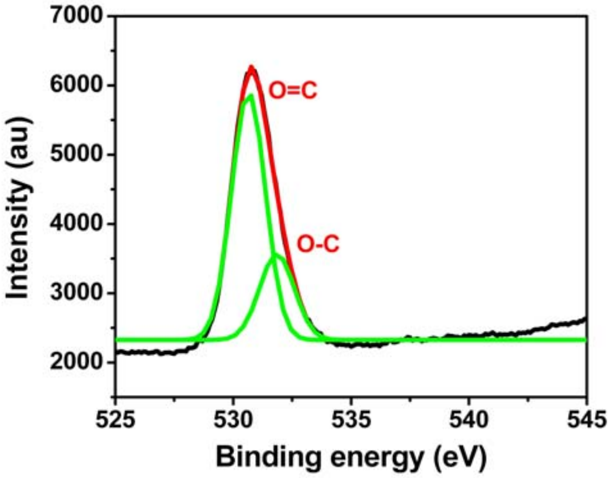
a


C-C, C-H
C-O, C-N
O=C-NH
Intensity (au)
0
1000
2000
3000
4000
5000
6000
7000
280
285
290
295
Binding energy (eV)

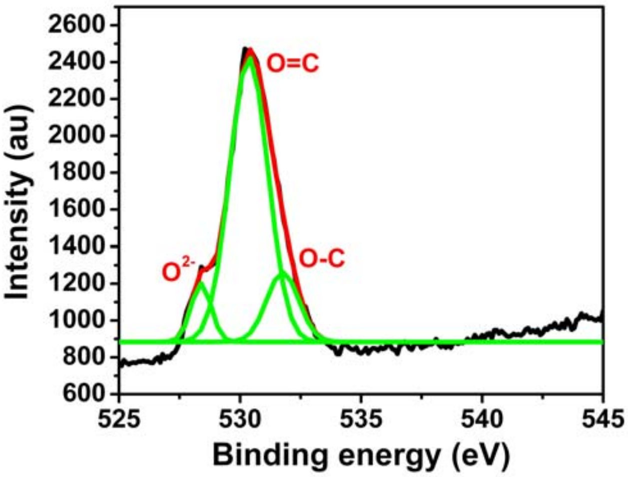
b


C-C, C-H
C-O, C-N
O=C-NH
Intensity (au)
0
500
1000
1500
2000
2500
3000
3500
4000
280
285
290
295
Binding energy (eV)

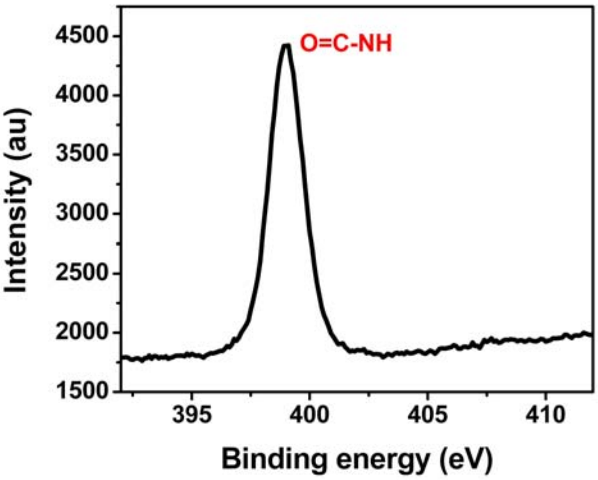
c


O=C
O-C
Intensity (au)
2000
3000
4000
5000
6000
7000
525
530
535
540
545
Binding energy (eV)

d


O=C
O-C
O^{2-}
Intensity (au)
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
525
530
535
540
545
Binding energy (eV)

e


O=C-NH
Intensity (au)
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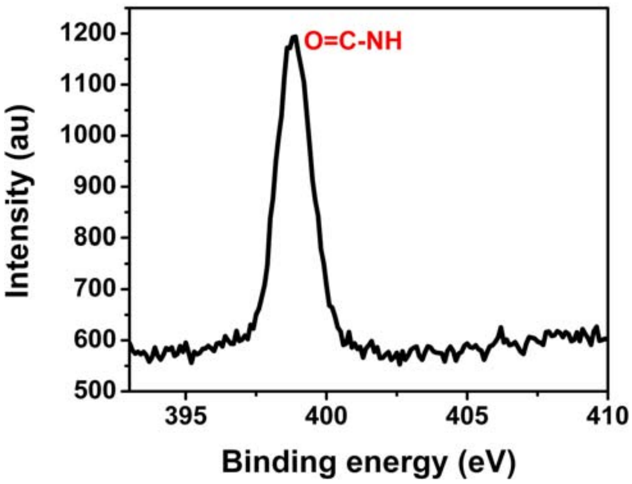
2000
2500
3000
3500
4000
4500
395
400
405
410
Binding energy (eV)

f


O=C-NH
Intensity (au)
500
600
700
800
900
1000
1100
1200
395
400
405
410
Binding energy (eV)

g

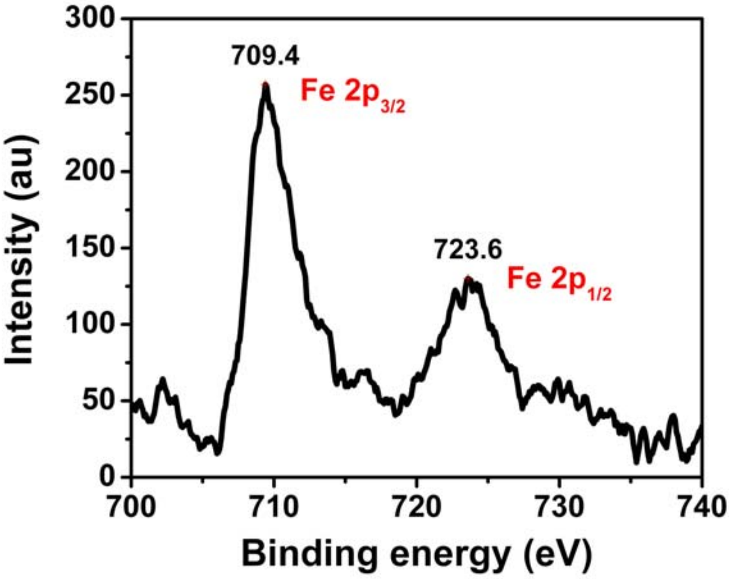


Figure S2 XPS core level spectra of the pristine collagen (a, c and e) and collagen-SPION nanobiocomposite (b, d, f and g) fibers.

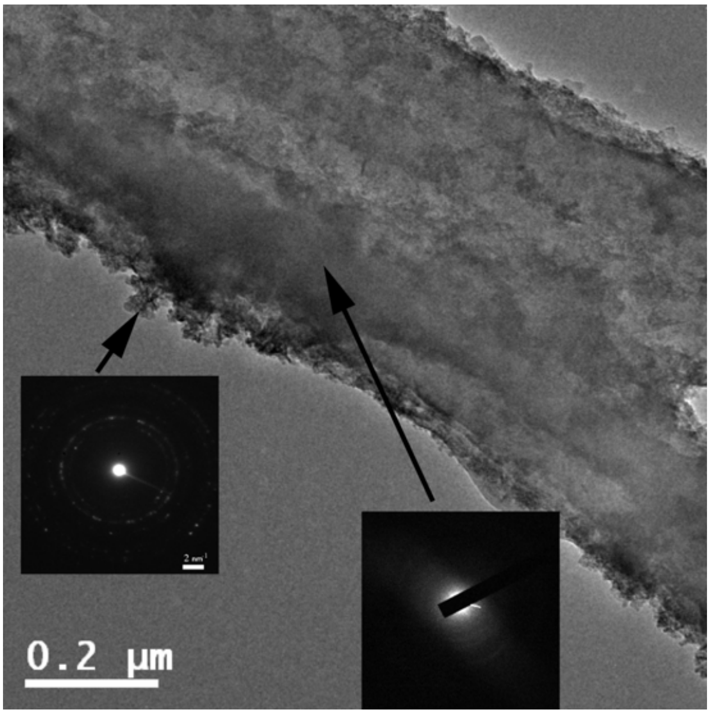
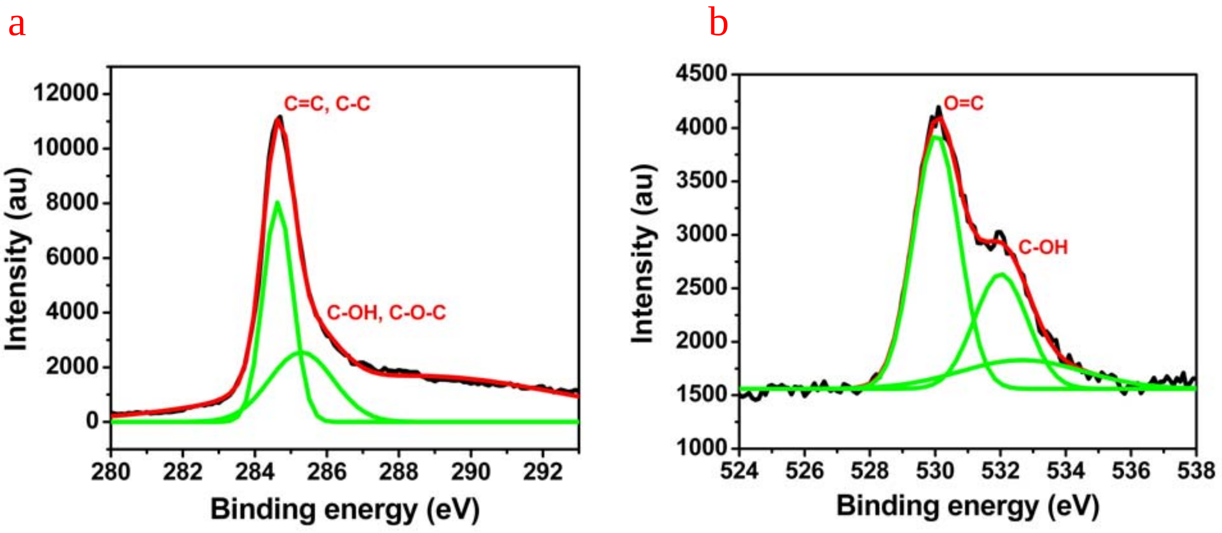


Figure S3 TEM image of collagen-SPION nanobiocomposite showing the SAED patterns of SPION and collagen fiber. SPION exhibits nanocrystalline diffused spots whereas collagen fiber shows amorphous pattern.

XPS analysis of the derived graphitic carbon. XPS spectra of the graphitic carbon derived from oil absorbed collagen-SPION nanobiocomposite are shown in Fig. S4. The C(1s) core level spectra exhibits binding energies corresponding to C=C/C-C bonds of aromatic rings in sp^2 graphitic carbon as well as C-OH/C-O-C functional groups, when deconvoluted. A possible contribution from sp^2 carbon atoms bonded to N in the aromatic ring is also noticed for the higher binding energy component of C(1s) spectra. Deconvolution of O(1s) core level spectra reveals the presence of O=C and C-OH functional groups. Whereas N(1s) core level spectra show a single component corresponding to highly coordinated N atoms substituting inner C atoms (quaternary N) on the graphene layers and bonded to three C atoms[2]. Thus, the graphitic carbon obtained from oil absorbed collagen-SPION nanobiocomposite is doped with oxygen and nitrogen functionalities. It is not surprising to note only one of the characteristic peaks of iron compound at 709.4 eV corresponding to $2p_{3/2}$ (L_3) edge since Fe_3O_4 nanocrystals are buried inside the carbon matrix. These results are in agreement with the TEM and XRD observations.



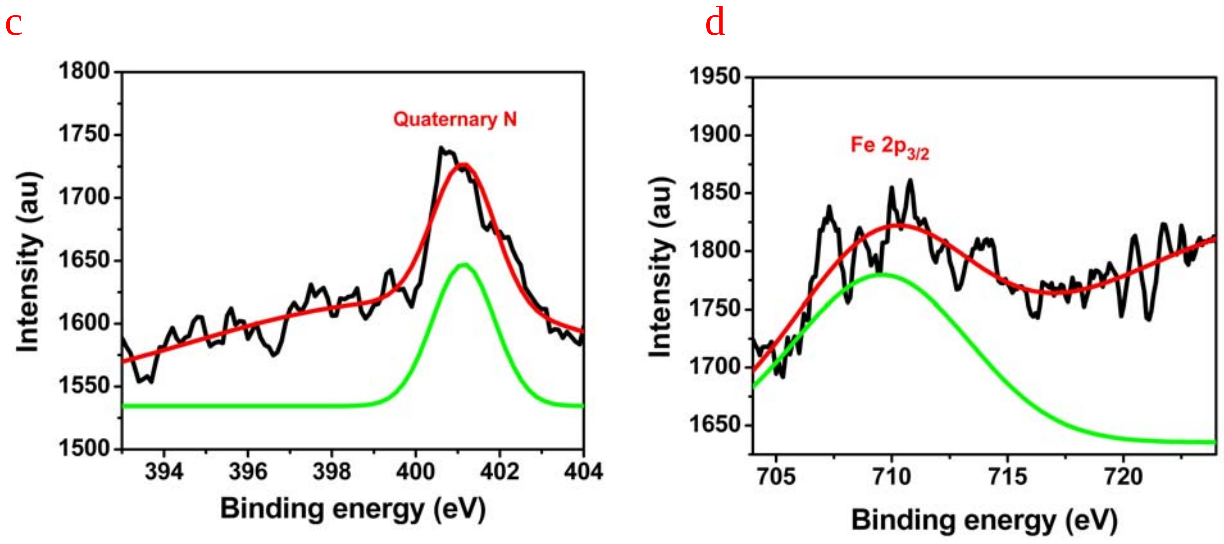


Figure S4 XPS spectra of graphitic carbon derived from oil absorbed nanobiocomposite. (a) C(1s) core level spectra; (b) O(1s) core level spectra; (c) N(1s) core level spectra; (d) Fe(2p) core level spectra.

References

1. Mills, P. & Sullivan J. L. A study of the core level electrons in iron and its three oxides by means of X-ray photoelectron spectroscopy. *J. Phys. D: Appl. Phys.* **16,** 723-732 (1983).

2. Casanovas, J., Ricart, J. M., Rubio, J., Illas, F. & Mateos, J. M. J. Origin of the large N 1s binding energy in X-ray photoelectron spectra of calcined carbonaceous materials. *J. Am. Chem. Soc.* **118,** 8071-8076 (1996).

List of Supplementary Movies

Movie S1: Video showing the ability of magnetic collagen-SPION nanocomposite for selective oil absorption and tracking under magnetic field.