Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

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Supporting Information

Graphene Oxide decorated diatom silica particles as a new nano-hybrid: towards smart natural drug microcarriers

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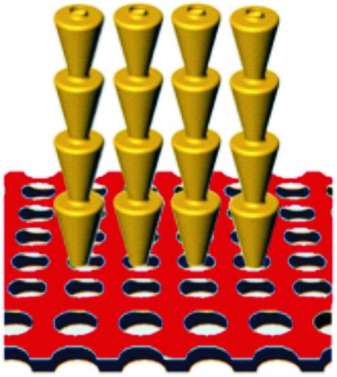

NanoTech Research

1) Diatom silica frustules after surface functnalization with APTES

SEM image of diatomaceous earth (DE) or diatom silica structure (frustule) obtained after APTES functionalization, showing no difference in its structure and morphology.

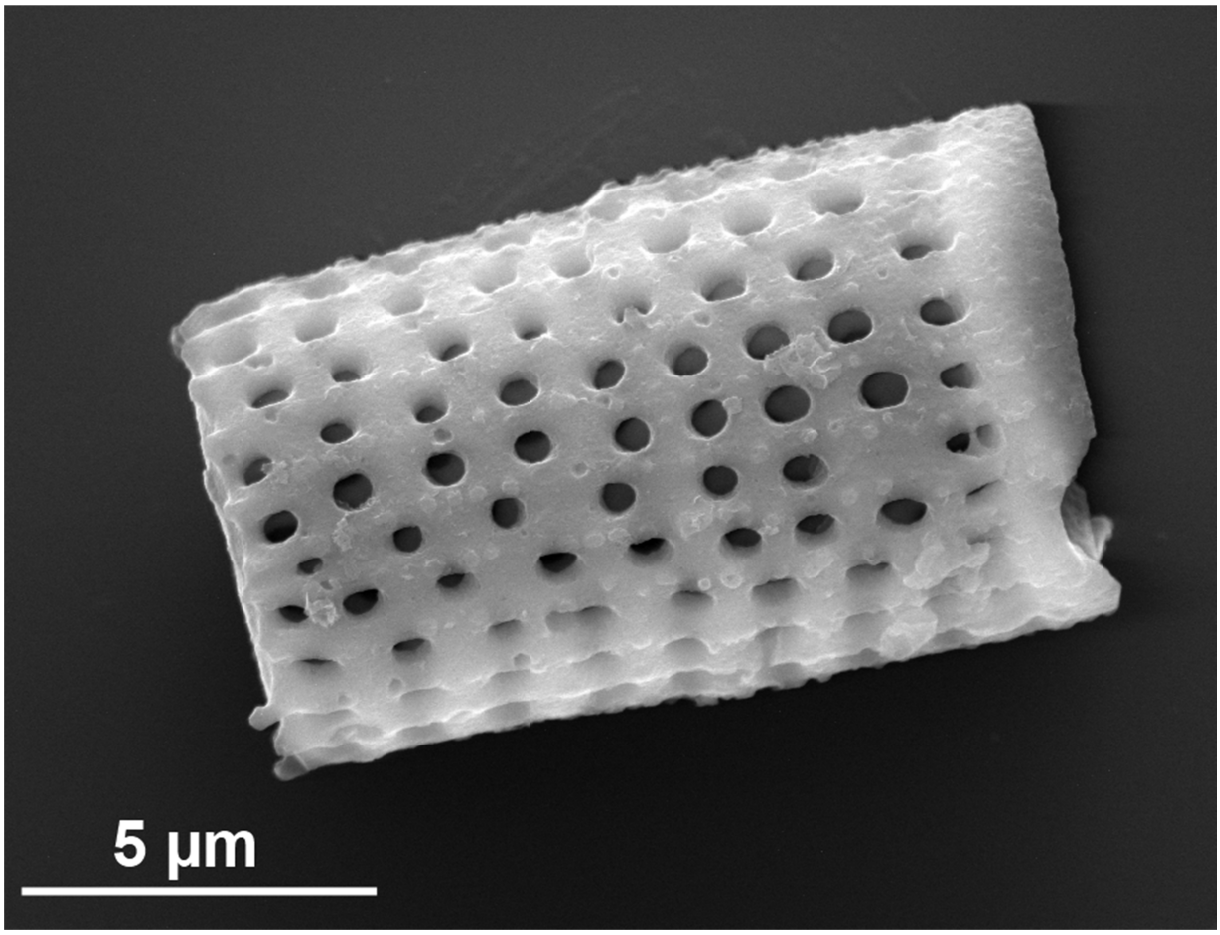

Fig. S1 SEM image of diatom silica structure after APTES functionalization.

2) FT-IR analysis of bare DE and APTES-DE.

Fig. S2 displays FT-IR spectra of bare DE (a) and APTES-DE (b). Characteristic peak of the diatom silica framework at wave numbers 1090 can be observed clearly in Fig. S2a, corresponding to asymmetric stretching modes of Si-O-Si bonds. Overlapping band between 3100 and 3700 cm^{-1} is indicative of O-H stretching vibrations of physisorbed water molecules; a shoulder peak at 3619 cm^{-1} due to Si-OH vibration was also obtained. Shifts or changes to these peaks indicate surface modfication. Appearance of additional bands (Fig. S2b) at 2929 cm^{-1} and 2869 $cm^{-1,}$ corresponding to $-CH_2$, and -C-H groups of propyl chain confirm the formation of APTES SAM on DE surface. These peaks did not appear in the FT-IR spectrum for bare DE. The scissor vibration due to presence of $-NH_2$ groups at ~1585cm^{-1} and the deformation mode of the $-NH_3^+$ group at ~1478cm^{-1} were also observed in the spectra. A composite band between 3100 cm^{-1} and 3700 cm^{-1} resulting from the overlapping of O-H and N-H stretching vibrations was also obtained[1].

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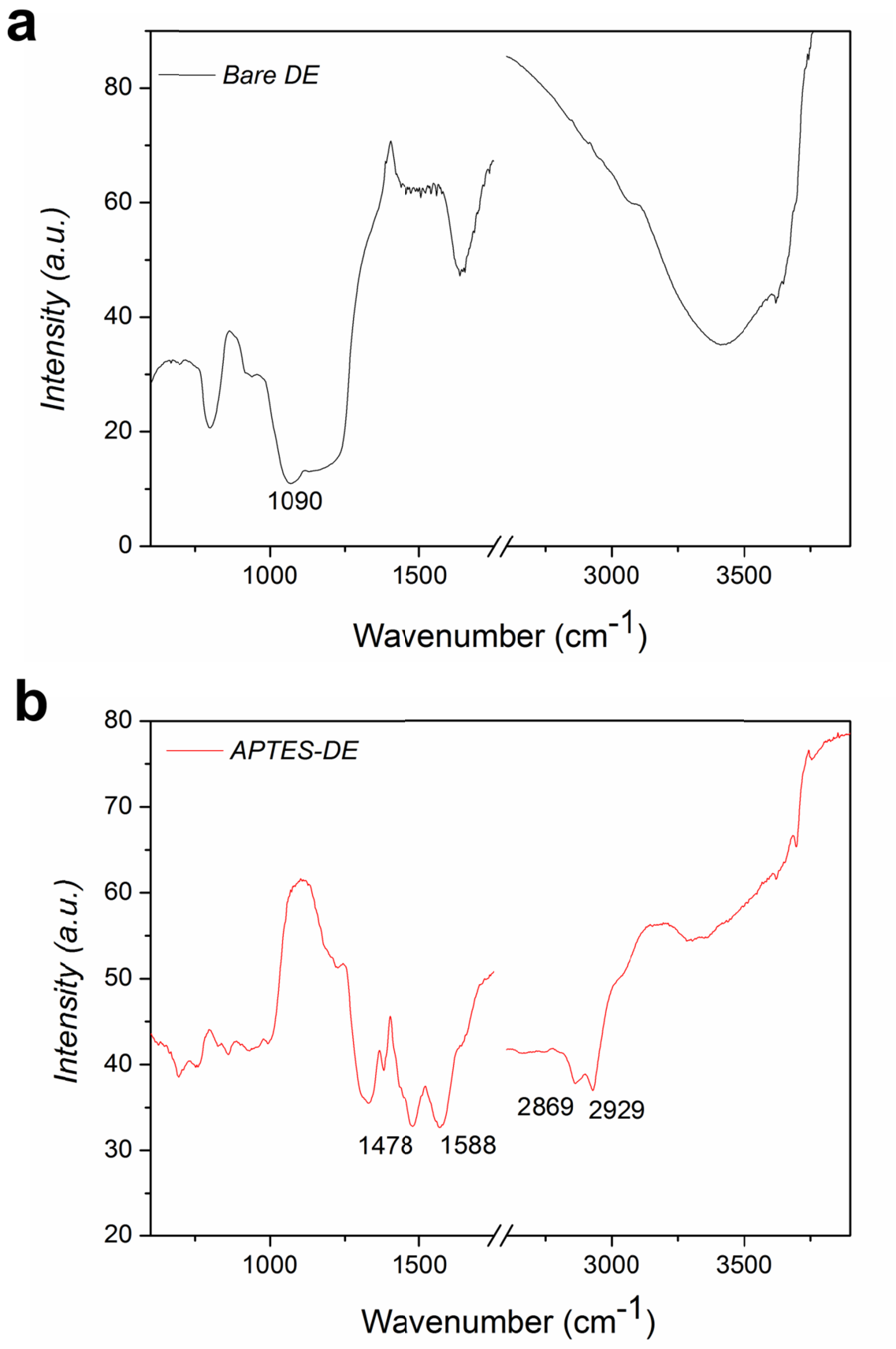

Fig. S2 FT-IR spectrum for a) bare DE and b) APTES-DE.

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3) SEM and TEM images of GO-DE hybrid

The SEM images of prepared GO-DE nano-hybrid showing GO attached to DE using covalent (Fig. S3a-c) and electrostatic attachment methods (Fig S3b-d). It was observed that almost all DE frustules analyzed (by SEM, TEM, and Raman) had GO adhered to DE surface. However, both the preparation methods resulted in non- homogeneous and random coverage of GO on DE, where some frustules very well wrapped in large GO patches, while other had only a partially wrapped or wrapped by smaller patches. Fig. S3c and Fig. S3d show the SEM images of partially covered and fully encapsulated DE frustule from GO-DEc nano-hybrid prepared by covalent attachment process.

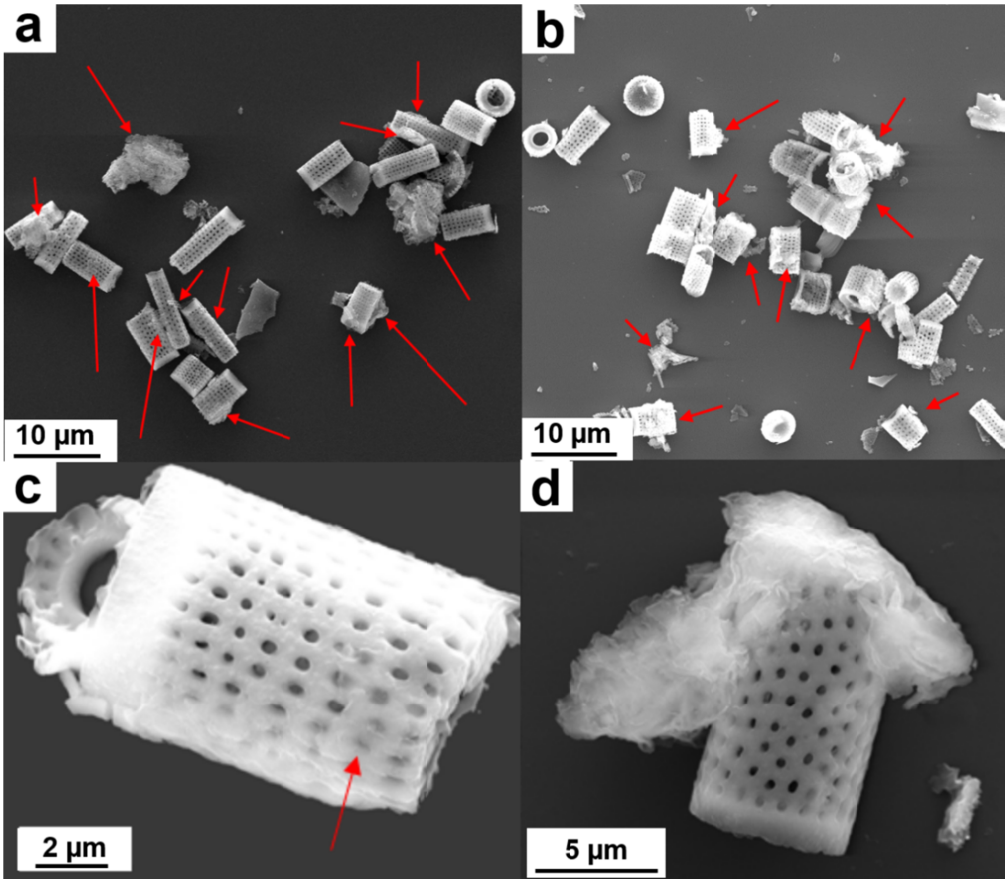

Fig. S3 SEM images of GO-D nano-hybrid material showing a) random coverage pattern of GO (marked in red arrows) on DE frustules of GO-DEc nano-hybrid b) random coverage pattern of GO (marked in red arrows) on DE frustules of GO-DEe nano-hybrid, c) small area of DE frustule covered by GO, and d) a full DE frustule covered by a big bundle GO on top.

TEM image of GO-DEc nano-hybrid confirms the attachment at nanoscale level, showing the partial coverage of DE frustules by GO.

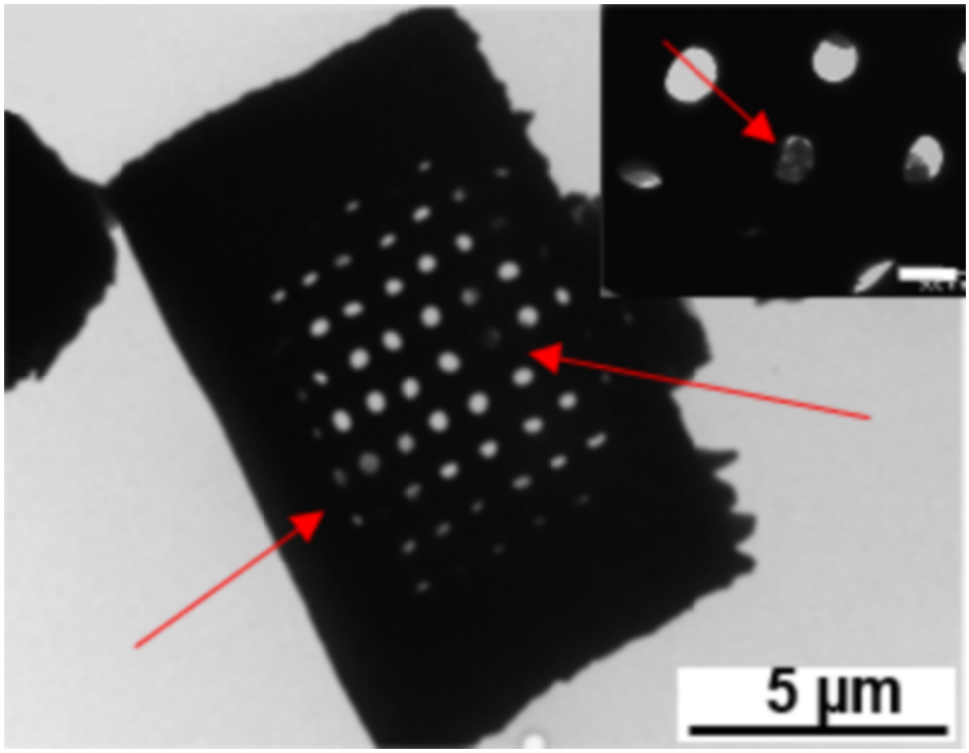

Fig. S4 TEM image GO-DEc nano-hybrid showing GO sheets shadowing of the pores of DE with a higher magnification in inset (scale bar 500 nm).

4) Raman analysis of diatom silica particles.

Raman spectroscopy analysis of DE is presented in Fig. S5, showing only one characteristic peak of silica around 900 cm^{-1}. Raman samples were prepared by drop casting DE dispersion in ethanol on a freshly cleaned silicon wafer. We did not observe any other peak in 750 to 2000 cm^{-1} range, which confirms the absence of any impurities and contaminations[2].

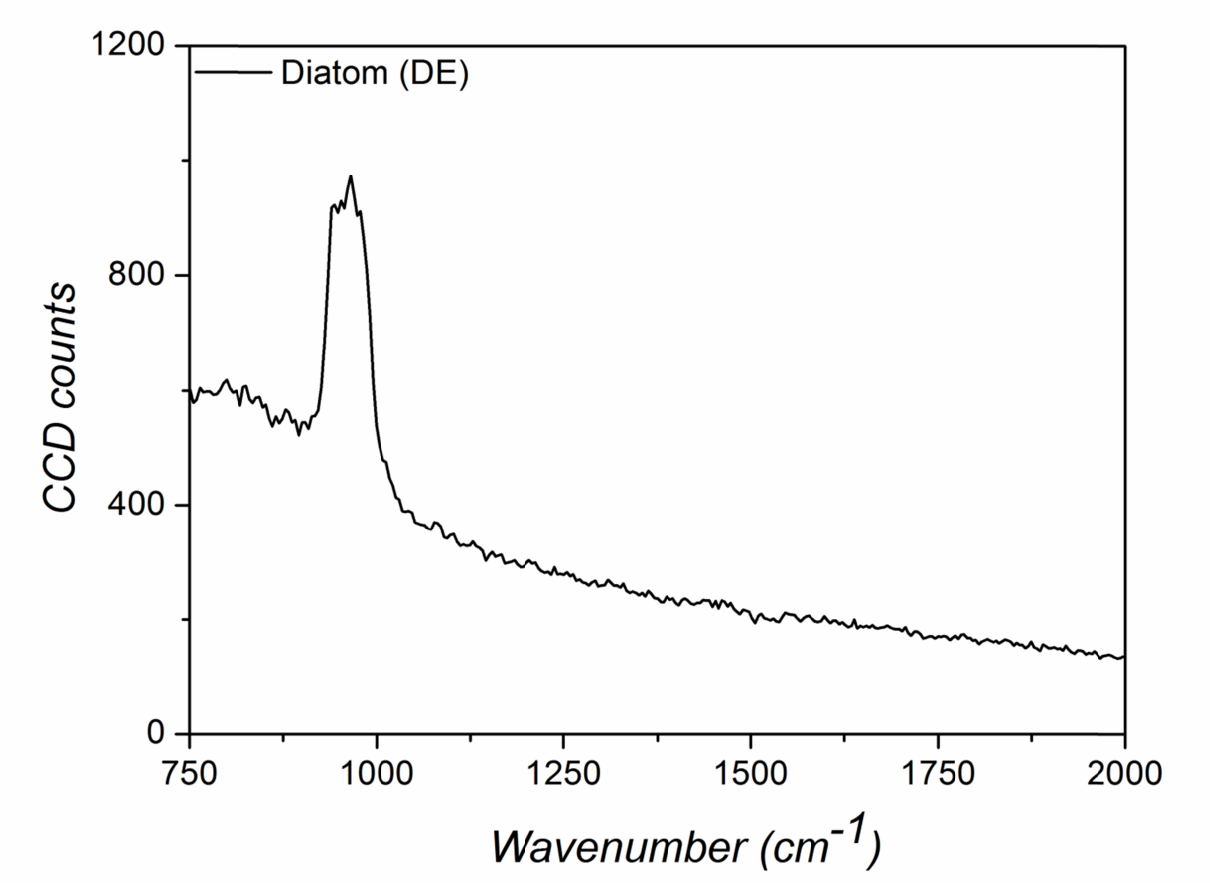

Fig. S5 Raman spectroscopy plot of DE sample.

5) Photoluminescence from GO-DE nano-hybrids.

Photoluminescence (PL) was observed while acquiring optical images using the Witec Raman microscope using a white light source with 100x magnification lens. The optical images indicated a PL response confined only to areas covered with GO. This can be observed for both GO-DEe and GO-DEc nano-hybrids in Fig. S6a and b, respectively. Furthermore, PL measurements of GO-DE nano-hybrids (i.e. GO-DEc and GO-DEe), as shown in Fig. S6c, were carried out by dispersing them in water. The excitation wavelength was 520 nm with excitation and emission slit size being 5 nm. PL emission was observed to be stronger for GO-DEe in comparison to GO-DEc which could be due to presence of more number of active functional groups on the former.

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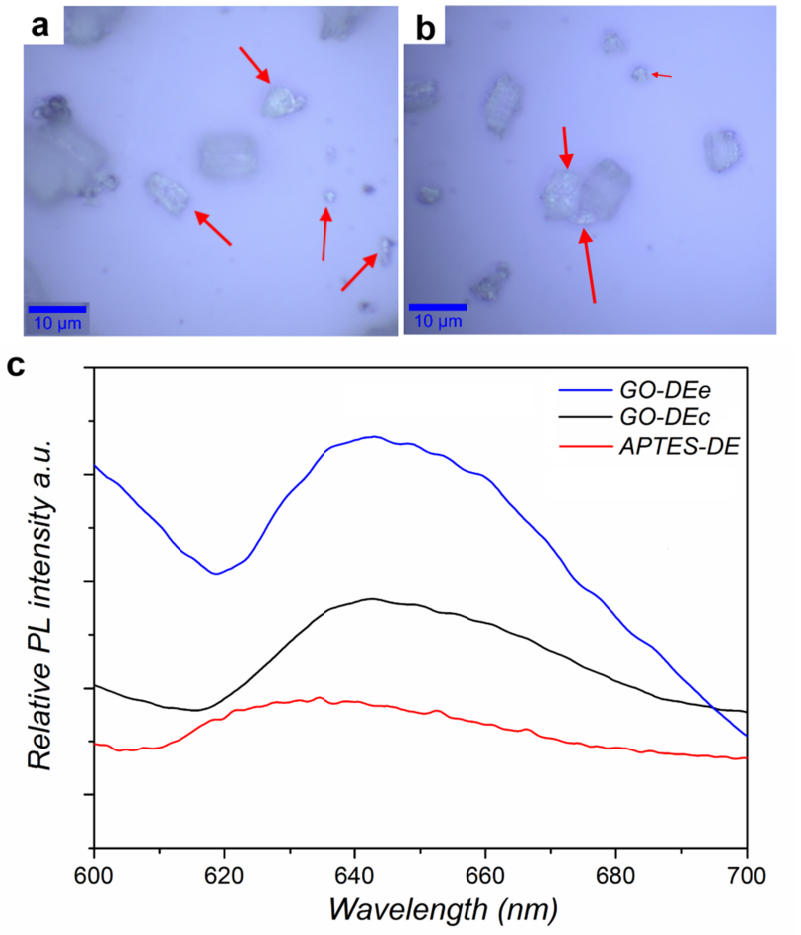

Fig. S6 Confined PL (marked with red arrows) observed during Raman spectroscopy. a) GO-DEe nano-hybrid, b) GO-DEc nano-hybrid, c) PL emission spectra for the prepared nano-hybrids.

6) *In-vitro* Drug release from GO-DEc nano-hybrid and control sample.

Table S7 summarises the *in-vitro* drug release data from the nano-hybrid and control samples. Notice that, more than 68 %, 87 %, and 97 % drug was released from APTES-DE control in 2 h, 24 h and 6 days, respectively. On the other hand, only 50 %, 70 %,and 96 % of loaded drug was eluted from GO-DEc nano-hybrid at pH 7.4 for the same time intervals. 100 % drug was eluted in 8 days from APTES-DE and in 12 days from GO-DEc nano-hybrid at pH 7.4. The drug release lasted for 37 days from GO-DEc nano-hybrid at pH 3.5 with only 20 %, 31 %, 50 %, 62 %, 75 %, and 91 % of drug release in 2 h, 24 h, 6 days, 12 days, 20 days, and 30 days, respectively.

Table S7 A summary of drug release with time for all the studied samples.

Sample name	***Cumulative release (%)***						
	2 h	*24 h*	*6 days*	*12 days*	*20 days*	*30 days*	*37 days*
APTES-DE	68.22	87.66	97.14	100	100	100	100
GO-DEc pH 7.4	50.58	70.82	96.13	100	100	100	100
GO-DEc pH 3.5	20.09	31.06	50.53	62.94	75.58	91.11	100

7) Stability of GO-DE nano-hybrid.

Stability of GO-DEc nano-hybrid prepared by covalent binding was confirmed by presence of GO sheets on DE even after 37 days of drug release. Fig. S8 provides the SEM image of GO-DEc sample used for drug release under acidic conditions

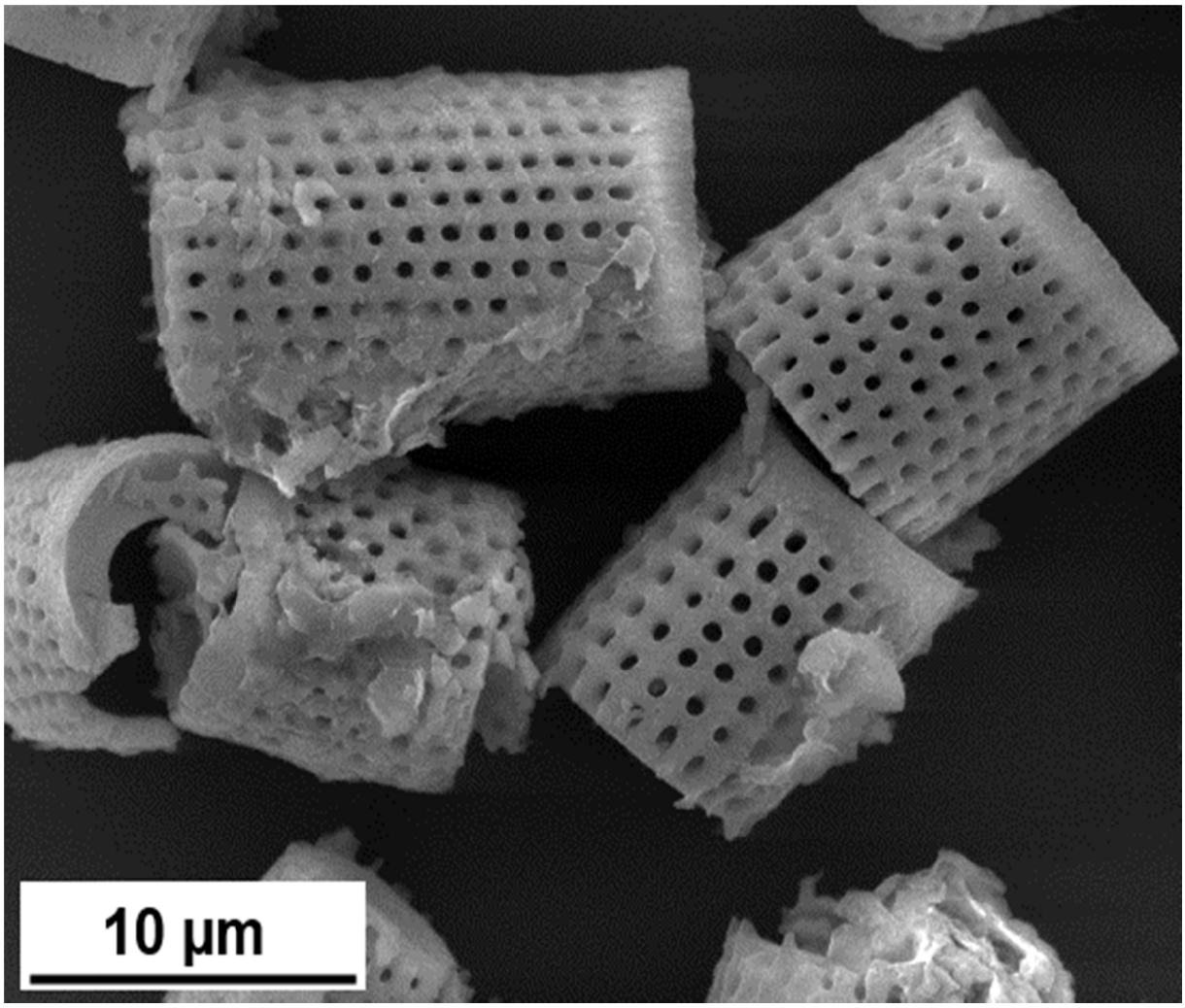

Fig. S8 SEM image of GO-DEc nano-hybrid after drug release at pH 3.5 for 37 days

8) Kinetic model fits for *in-vitro* drug release from GO-DE

In-vitro drug release data (i.e. burst + sustained release) from GO-DEc nano-hybrid at all pH values and APTES-DE control was fitted to two of the most commonly used release kinetic models, Zero-order model and Korsmeyer-Peppas model. The burst release data fits well to both the kinetic models, while sustained release only has good correlation with Korsmeyer-Peppas model. The Fitting plots for Zero-order model and Korsmeyer-Peppas model are provided n Fig. S9 (a, b) and Fig. S9 (c, d) respectively[3].

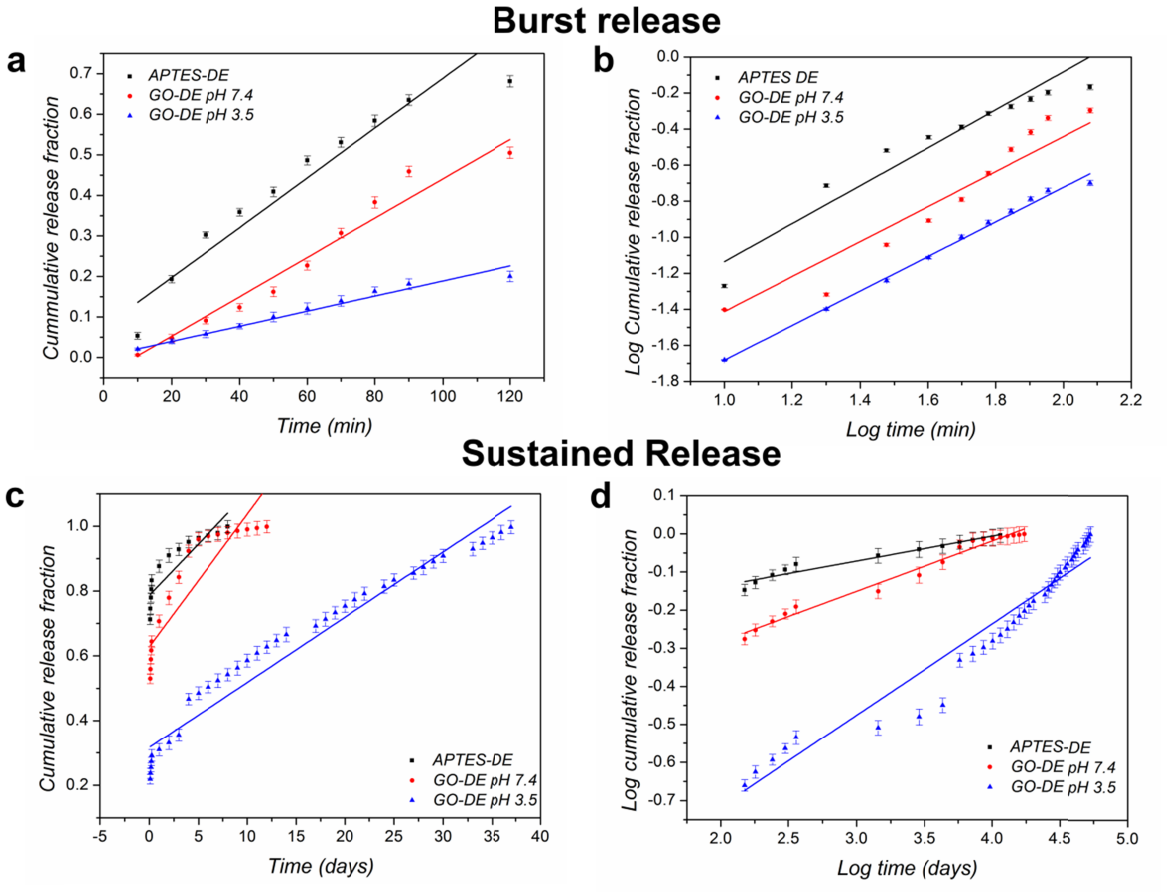

Fig. S 9 Kinetics model fitting plots for in-vitro release from GO-Decnano-hybrid and APTES-DE control, a) Zero-order model fit for brst release, b) Korsmeyer-Peppas model fit for burst release, c) Zero-order model fit for sustained release, and d) Korsmeyer-Peppas model fit for sustained release

References

1. M. Bariana, M. S. Aw, M. Kurkuri and D. Losic, *International journal of pharmaceutics*, 2012.
2. C. Gómez-Navarro, R. T. Weitz, A. M. Bittner, M. Scolari, A. Mews, M. Burghard and K. Kern, *Nano letters*, 2007, **7**, 3499-3503.
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