

ELECTRONIC SUPPLEMENTARY INFORMATION

Responsive Copolymer-Graphene Oxide Hybrid Microspheres with Enhanced Drug Release Properties

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S1 Raman spectroscopy of GO and GO-wrapped PNIPAM-co-PS

Raman analysis was performed to verify the crystalline quality of the graphene oxide (GO) nanosheets and to get direct evidence of successful self-assembly of GO on the PNIPAM-co-PS spheres. As shown in Fig. S1, the two characteristic Raman peaks for GO, D at 1320cm^{-1} and the G at 1580cm^{-1} were observed. A similar Raman spectrum was obtained for copolymers hollow spheres wrapped with GO.

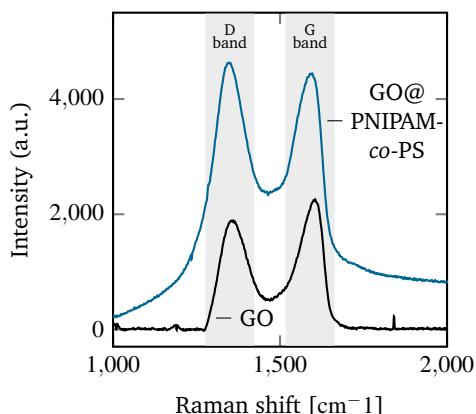


Figure S1 Raman spectra of graphene oxide nanosheets and GO@PNIPAM-co-PS.

S2 XRD pattern of GO and graphite

Figure S2 shows the XRD patterns of graphene oxide and natural graphite that were obtained by means of STADI P diffractometer (STOE, Darmstadt, Germany) with parafocussed trans-

mission geometry at 40kV and 30mA, using Cu Ka radiation ($\lambda = 154.06\text{pm}$). The pattern of GO has a peak centered at $2\theta = 10.1^\circ$, corresponding to the (002) inter-planar spacing of 1.01 nm. The post intense peak of graphite at $2\theta = 26.5^\circ$, which corresponds to d-spacing 0.34nm ,¹ is absent in the GO sample.

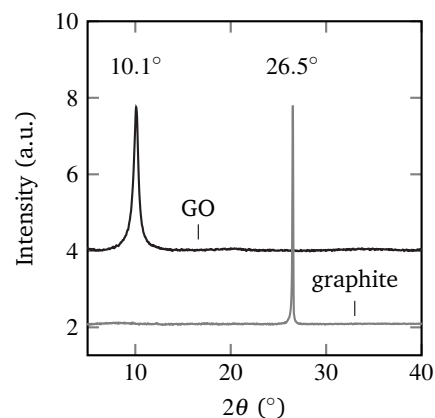


Figure S2 XRD spectra of graphene oxide and graphite.

S3 UV-VIS of GO-VAN

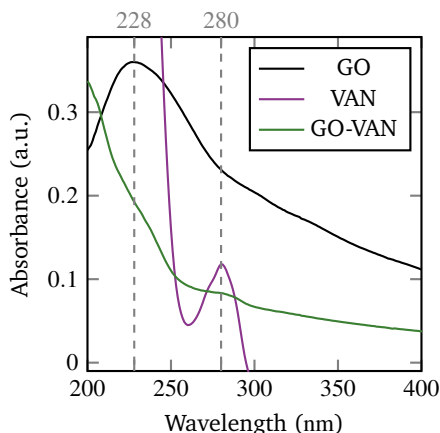


Figure S3 UV-VIS absorption spectra of graphene oxide, vancomycin and GO-VAN solution.

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UV-VIS absorption spectra were utilized to investigate the interaction of GO with vancomycin (VAN). As shown in Fig. S3, GO shows a peak at 228 nm due to $\pi - \pi^*$ transition of C-C bonds,² whereas VAN has a characteristic peak at 280 nm. As seen, no indication of a spectral shift was observed after VAN was added to the GO solution. For the mixture of GO and VAN the absorption spectrum is simply a superposition of the GO and the VAN absorption spectra.

S4 Graphene oxide and GO-VAN surface characterization with AFM

Atomic force microscopy (AFM) height and phase images were used to observe changes in the surface structure of GO upon interaction with VAN. For sample preparation, a highly diluted water solution of GO was spin coated on a freshly cleaved mica surface. Next, a low concentration of VAN solution was dropped onto the GO coated substrate, kept for 60 s, and then rinsed with water to remove free VAN molecules. Figure S4 shows representative height and phase images of both, bare GO and GO with VAN molecules. The observed topographical changes in the height images indicate the adsorption of VAN onto the surface of GO. The adsorption is driven by electrostatic attraction between the cationic VAN molecules and the negatively charged surface of GO. The measured surface mean roughness increased from

References

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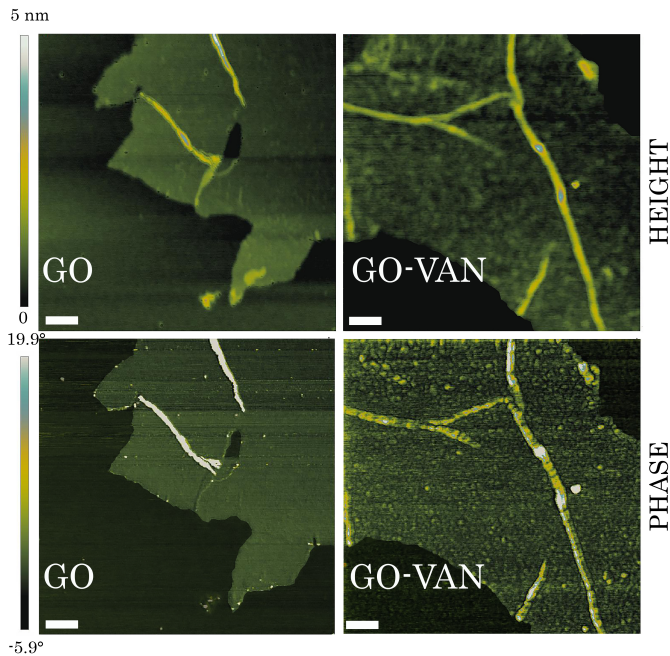


Figure S4 AFM height (top) and phase (bottom) images of graphene oxide (left) and GO-vancomycin (right). The scale bar is 110 nm for each.

$51.7 \pm 0.9 \text{ pm}$ to $124.5 \pm 11.2 \text{ pm}$ for GO and GO-VAN, respectively (for quantitative analysis of the images, we have consistently used areas of $150 \times 150 \text{ nm}^2$ size). Moreover, the striking differences in the obtained phase images (Fig. S4 right) indicate changes in surface chemical and physical properties,³ which very likely originate from VAN molecules.