Hybrid organic-inorganic supramolecular hydrogel reinforced with CePO$_4$ nanowires[†]

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We report a method to enhance the stiffness in the rheological yield strain of cucurbit[8]uril (CB[8])-based hydrogels by introducing inorganic nanowires (NWs) into the supramolecular networks. The supramolecular hydrogel is comprised of methylviologen-functionalised poly(vinyl alcohol) (PVA-MV), hydroxyethyl cellulose with naphthyl moieties (HEC-Np) and CB[8] macrocyclic hosts. The gel structure can be effectively enhanced by the framework supporting effects of cerous phosphate NWs and additional hydrogen bonding interactions between the NWs and the PVA-MV/HEC-Np polymers. The high aspect ratio NWs there serve as a "skeleton" for the network providing extra physical crosslinks, resulting in a single continuous phase hybrid supramolecular network with improved strength, presenting a general approach to reinforce soft materials.

Hybrid materials composed of organic molecules (small molecules or polymers) and inorganic nanostructures typically exhibit enhanced mechanical properties and display multifunctionality on account of their molecular scale interactions and synergistic effects.[1–3] In such materials the inorganic components can act as a rigid skeleton while the organic constituent parts serve as a flexible entangled mesh to generate an extended network of interactions.[4] Among different nanostructures, 1D nanowires (NWs) are of particular interest as they can link multiple binding sites along their extended dimension, which induce the formation of 3D network structures.[5,6] The ductility of NWs arising from their unique 1D geometric characteristics drives them to form 3D networks, which enables them to be utilised in the preparation of reinforced hybrid materials.[7–9] The intrinsic mechanical strength of inorganic NWs, however, has not been extensively studied for reinforcement of organic soft materials.

Supramolecular chemistry is a growing field,[10–12] where supramolecular hydrogels have arisen as a new class of soft materials[13] and serve as attractive alternatives to covalent hydrogels on the account of their unique properties including stimuli-responsiveness, shear-thinning and self-healing, which arise from their dynamic physical crosslinks.[14–18] Several fabrication methods of supramolecular hydrogel systems have been reported by utilising the host-guest chemistry of cyclodextrins (CD)[19,20] and cucurbit[n]urils (CB[n]s).[21–23] However, the scope of supramolecular hydrogel applications is typically limited to applications requiring soft properties.[24] When compared to covalently crosslinked hydrogels,[25–28] supramolecular hydrogels prepared by host-guest interactions have proven difficult to reinforce, as the host-guest interactions are very sensitive to external stimuli.[29] Therefore, few samples have been reported to date that utilise extended 1D inorganic structures to reinforce CB[8]-based supramolecular hydrogels.[30–32]

Inspired by the fascinating geometric structure of NWs, we present here a method to enhance the stiffness of supramolecular hydrogels based on host-guest interactions. By employing inorganic NWs as skeletal constructs, CB[8]-based supramolecular hydrogels exhibit a 50 % increase in storage modulus. This prominent reinforcement is achieved from two simultaneous components, firstly, CePO$_4$ NWs provide extra crosslinks through hydrogen bonds between the polymer chains and the hydroxy-rich NW surfaces (Figure 1d). Secondly, as shown in Figure 1c, the polymer networks replicate "soft" tissue, holding a high content of water through CB[8]-mediated supramolecular crosslinks. Additionally, the NWs serve as an extended scaffold for the polymeric network.

CePO$_4$ NWs were synthesised by a hydrothermal reaction at 170 °C from Na$_3$PO$_4$ and CeNO$_3$ precursors, under acidic conditions (pH = 2, HCl aq, 1M) (Figure 1b).[33] A clear colloidal suspension was obtained after a 10 h reaction without the appearance of any large aggregates. The morphology of
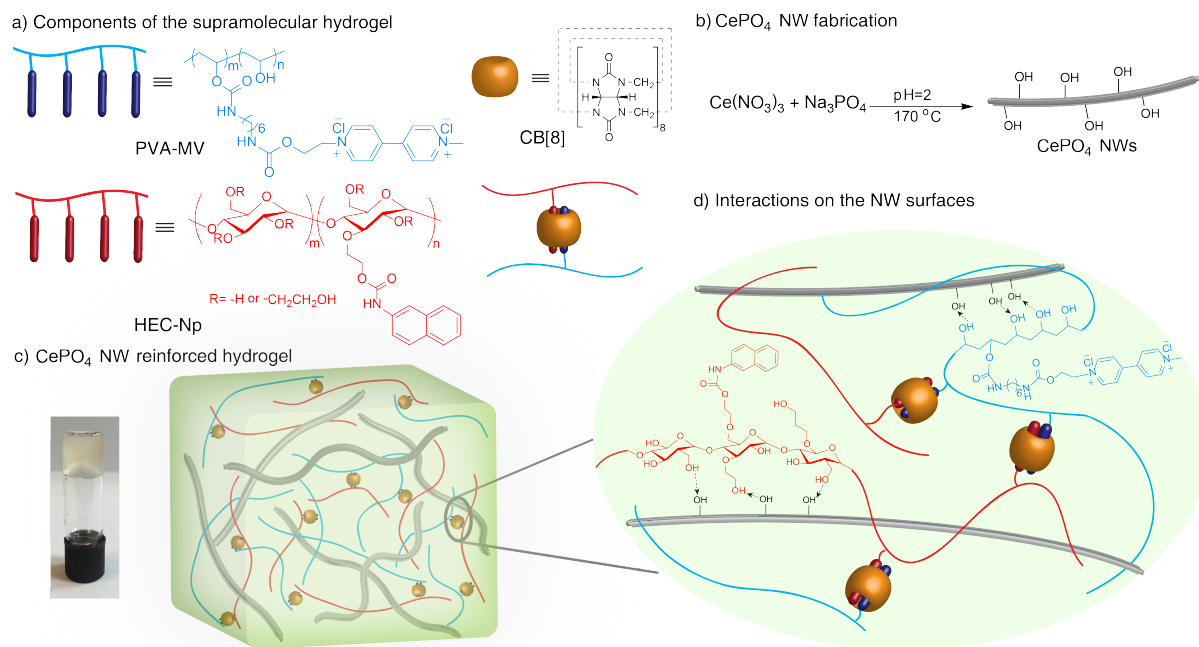
Fig. 1 a) The chemical structure of PVA-MV, HEC-Np, cucurbit[8]uril (CB[8]) and the highly dynamical 1:1:1 ternary complex formed by CB[8] host-guest chemistry between first guest viologen and second guest naphthyl. b) Schematic representation of cerous phosphate NWs prepared by a hydrothermal method, with hydroxyl groups on the surface. c) The structure of the NW-reinforced organic-inorganic hybrid supramolecular hydrogel based on CB[8] host-guest interactions. d) NWs were employed as a "skeleton" to bridge polymers through hydrogen bonds between NWs and PVA-MV/HEC-Np polymers.
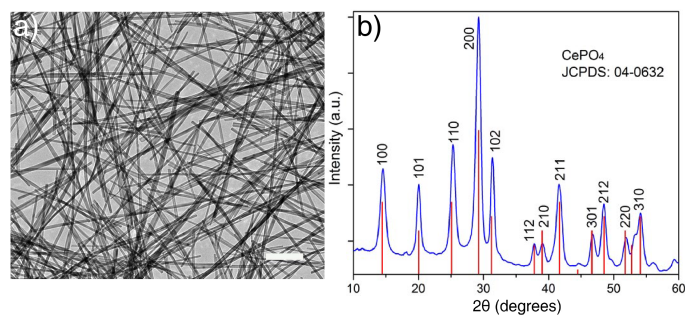

Fig. 2 a) TEM image of CePO$_4$ nanowires (Scale bar: 200 nm). b) Powder X-ray diffraction results of CePO$_4$ nanowires.

the product was characterised by transmission electron microscopy (TEM), which indicated that pure nanowires were successfully fabricated (Figure 2a). The average diameter of the NWs was 15 nm with an average length of 3 μm. Since the nanowires were prepared in the absence of any capping ligands, their surfaces are highly hydrated in water and thus, were covered with hydroxyl groups, resulting in a highly hydrophilic surface. The hydroxyl groups on the NW surface were confirmed by FT-IR spectroscopy (see ESI, Fig. S7). The density of OH groups was quantified by thermal gravimetric analysis (TGA, see ESI, Fig. S8) and found to be

24 nm^{-2}. The hydrophilicity of the NWs enable them to be dispersed in aqueous solutions. Furthermore, crystallinity of the nanowires were characterised using powder X-ray diffraction (PXRD) and is shown in Figure 2b. The pattern indicates pure CePO$_4$, which can be indexed to a JCPDS card of 04-0632.

We have previously shown that naphthyl-functionalised cellulose (HEC-Np, 1.3 MDa, 5 mol% Np loading) and viologen-functionalised poly(vinyl alcohol) (PVA-MV, 205 KDa, 5 mol% MV loading) are able to form a dynamic hydrogel *via* CB[8] host-guest interactions (Figure 1a).[21] The composition of the hydrogel can be varied from 0.25 wt% HEC-Np, 0.05 wt% PVA-MV@CB[8] to 1.5 wt% HEC-Np, 0.3 wt% PVA-MV@CB[8], with the storage modulus increased from 10 Pa to 500 Pa (10 rad/s frequency and 1% oscillation strain).[21] Here the supramolecular hydrogel composed of HEC-Np (0.5 wt%), PVA-MV (0.05 wt%) and CB[8] (0.05 wt%) was enhanced simply by the addition of a very small amount of CePO$_4$ NWs (0.001-0.030 wt%).

Amplitude dependent oscillatory rheology of the hydrogel was investigated to understand the dependence of the material strength (Figure 3a) on increasing amounts of CePO$_4$ NWs from 0.001 wt% to 0.002 wt%. Hydrogel samples with 0, 0.0010, 0.0015, 0.0020 and 0.0300 wt% CePO$_4$ NWs were
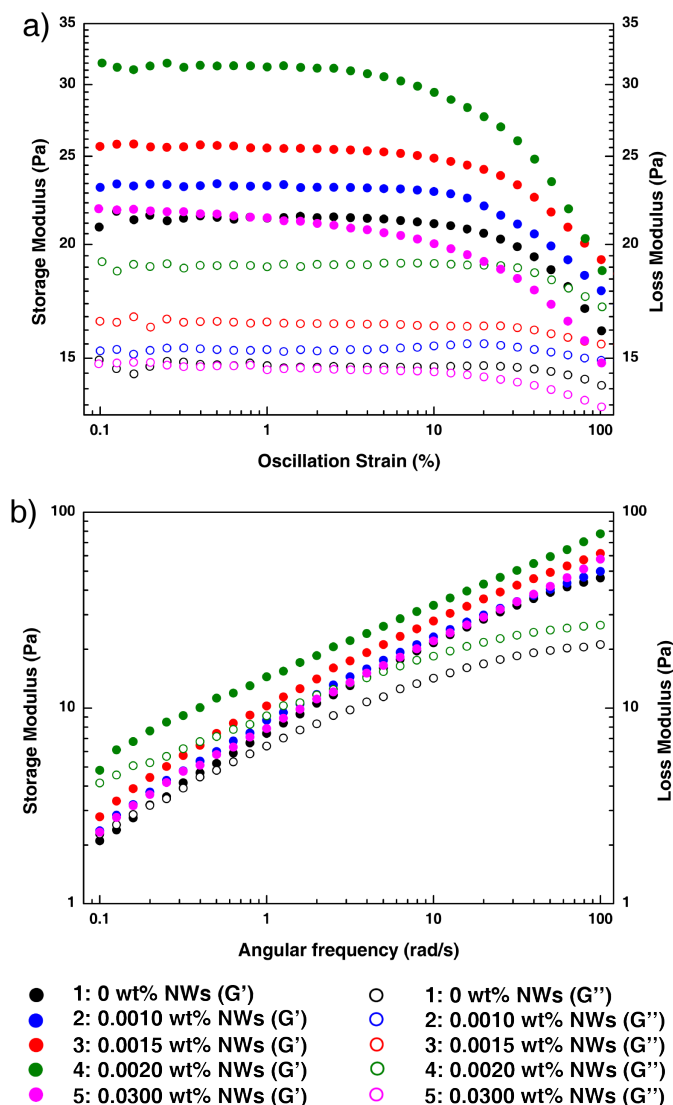
Fig. 3 Storage (G') and loss (G'') moduli from a) amplitude dependent and b) frequency dependent oscillatory rheology of CePO$_4$ NWs enhanced hybrid supramolecular hydrogels at 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.05 wt% CB[8] with NW concentration ranges from 0 to 0.0300 wt% (labelled as sample **1-5**).

labelled as **1-5**, respectively. All the samples displayed broad elastic properties up to 50% of oscillatory strain, where G' (storage moduli)$>G''$ (loss moduli), indicating the elastic hydrogel behaviour of the hybrid materials. The material strength can be investigated by the value of G', the moduli difference (G'-G'') and tan δ (the ratio of G''/G').[22] The G' values display a 48% increase (from 21.3 ± 0.3 Pa to 31.5 ± 0.3 Pa) upon addition of the NWs. Moreover, tan δ before the critical strain point (90 % strain) of sample **1** was 0.69, and decreased to 0.59 with the addition of NWs (sample **4**), highlighting that hydrogel strength was enhanced upon addition of the NWs.

Hydrogels fabricated by non-covalent interactions typically exhibit frequency dependence on account of finite crosslink lifetimes.[34] The frequency sweep results (ESI, Fig. S10) illustrate that for all samples, G' is dominant over G'' at higher angular frequencies, indicating that all samples have gel-like structures with lengthy crosslink lifetimes. At frequencies below 0.2 rad/s, G'' is slightly dominant over G' in sample **1** as shown in Figure 3b, this is likely due to its bulk relaxation being longer than that in the other samples, resulting in viscous flow behaviour.[22] However, for sample **4**, across the range of frequencies tested, G' exceeds G'', implying an enhanced crosslinked structure. Even at lower frequencies when the crosslink off rate is faster than the oscillation periods, the hybrid material still retains a gel structure. This is likely due to the supporting effect of the NW network.

The microstructure of cryo-dried and lyophilised hydrogel samples was observed by scanning electron microscopy (SEM). Figure 4a and b reveal that the hybrid hydrogel retains a similar gel structure to that of a pure supramolecular hydrogel after addition of the NWs. At higher magnification, the NW structures are clearly dispersed and embedded within the polymer network, as shown in Figure 4c (inset). The strength-reinforced behaviour of CePO$_4$ NW hydrogels may be attributed to two mutually occurring interactions. Compared with the soft polymer chains, the inorganic CePO$_4$ NWs have a larger aspect ratio and remain in an extended conformation with excellent ductility. This enables the polymer chains to complex with the NWs through hydrogen bonding and the NWs can serve as a supporting skeleton to reinforce the 3D network. The hydrogen bonding interactions between the hydroxyl groups on the polymer chains and the surface of the cerous phosphate NWs provide many more physical crosslinks in addition to the CB[8] mediated 3D network. Furthermore control experiments (ESI, Fig. S13) with the same composition of HEC-Np and PVA-MV polymers but without any CB[8], containing nanowire concentration of 0, 0.0020 and 0.0025 wt% showed G^* (complex moduli, $|G^*|=[G'^2+G''^2]^{1/2}$) increased with addition of the NWs, confirming a stiffening effect of NWs on the polymer networks.

When the amount of NWs exceeded 0.0020 wt%, the strength of hydrogels decreased (Figure 3a, ESI, Fig. S9). We hypothesise that excess NWs over a critical value lead to aggregation. As a consequence, the polymer-NW interactions decrease and result in a weaker internal network. Aggregates of the NWs were indeed observed by SEM (ESI, Fig. S12) 0.0020 wt%. In addition, a decrease of G^* of the polymer solution with "excess" NWs, but without any CB[8], was observed (ESI, Fig. S13).

The NW-reinforced hybrid hydrogels retained their shear-thinning and self-healing properties, allowing for potential applications in injectable delivery systems. Dynamic viscosity
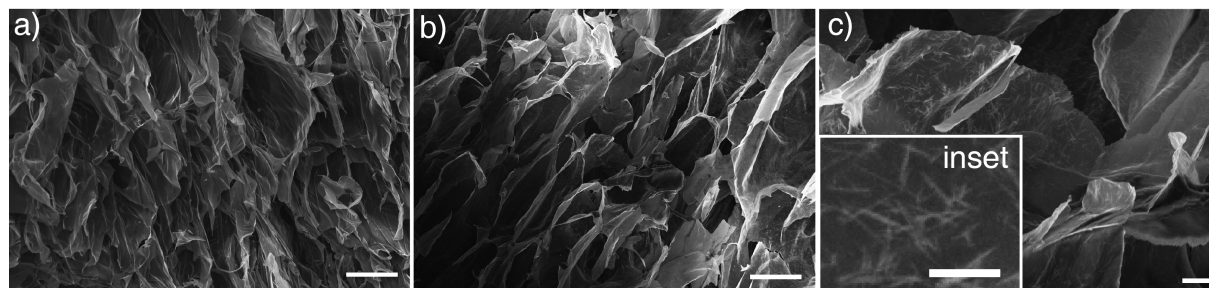
Fig. 4 SEM image of cryo-dried and lyophilised samples of hydrogels a) in absence of NWs (scale bar: 20 μm); b and c) with 0.0020 wt% NWs (scale bar of b: 20 μm, scale bar of c: 2 μm, inset scale bar: 1 μm); while NWs in the hybrid gel can clearly be seen in c.
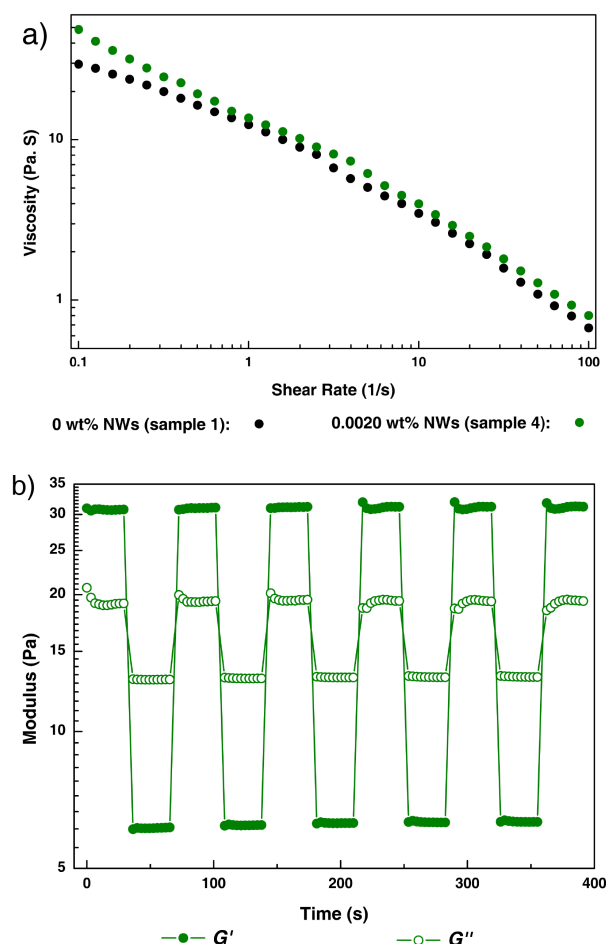

Fig. 5 a) Shear dependent rheology of CePO$_4$ NW-enhanced hybrid supramolecular hydrogels at 0.5 wt% HEC-Np, 0.05 wt% PVA-MV and 0.05 wt% CB[8] without CePO$_4$ NWs (sample **1**) and with 0.0020 wt% NWs (sample **4**). b) Alternating strain experiment on NW-enhanced hybrid hydrogel. The oscillatory strain alternated between 1 and 1000% every 30 s. G'' dominates at high strain whilst G' recovers rapidly when the applied strain reverts back to 1% and the original viscoelastic property is recovered. This process was repeated 5x, demonstrating good recyclability.

rheology with different shear rates indicates the hybrid hydrogels exhibit shear-thinning, viscoelasticity and non-Newtonian behaviour on the account of various non-covalent interactions within the material. As shown in Figure 5a, the viscosity of both sample **1** and **4** decreases to a low level around 0.6-0.8 Pa·s with the shear rate rising to 100 s^{-1}; the high shear rate breaks most CB[8]-facilitated crosslinks and the materials tend to express liquid behaviour with a much lower viscosity.[22] However, at a low shear rate (0.1 s^{-1}), sample **4** has the highest viscosity value of 48.6 Pa·s, while a value of only 29.6 Pa·s is obtained for sample **1**, which further confirms that hydrogel **4** has a deformation resistant structure. In addition, the hybrid gel shows its self-healing nature as a supramolecular network (Figure 5b). Control experiments suggest the responsive properties of the hybrid hydrogel have been retained while without host-guest interactions, gel-like properties would not exist (ESI, Fig. S14-S17).

In conclusion, the mechanical properties of CB[8]-based supramolecular hydrogels were significantly enhanced by the formation of hybrid hydrogels with extremely small quantities of CePO$_4$ NWs. The addition of CePO$_4$ NWs generated physical interactions resulting from the hydrogen bonding between the NW surface and the polymer network. The NWs were found to act as a "skeleton" resulting in an enhanced continuous phase hybrid network and allowed for the supramolecular hydrogels to retain their attractive properties, including stimuli-responsivity, shear-thinning and self-healing. This work outlines a general approach for the use of inorganic NWs as frameworks to enhance the mechanical properties of organic soft materials through the formation of organic-inorganic hybrid networks. Further investigations into the function of these hybrid supramolecular hydrogels are currently underway.

Acknowledgements

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