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ARTICLE

Strong and fast-recovery Organic/inorganic hybrid AuNPs-supramolecular gels based on Loofah-like 3D networks

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A super strong and fast-recovery organic/inorganic hybrid gold nanoparticles (AuNPs)-supramolecular gels based on three-dimensional Loofah-like nanoscale network self-assembled by polyhedral oligomeric silsesquioxane (POSS) core supramolecular gelators was firstly reported. Two series of POSS core organic/inorganic hybrid gelators, POSS-BOC-L-Homophenylalanine (POSS-Hpy) and POSS-Boc-Cys(Bzl)-OH (POSS-Cys), with two kinds of peripherals that had different abilities of driving the self-assembly of AuNPs in gels were designed and synthesized respectively, both of which could self-assembly into three-dimensional Loofah-like nanoscale gel network through strong self-assembly abilities and so that the hybrid physical gels had fast-recovery behaviors. The mechanical properties of the resultant hybrid gel had been dramatically increased as 100 times higher in the system of sulfur contained POSS-Cys gelator without destroying the fast-recovery behaviors with addition of AuNPs, which had direct interaction with AuNPs to give S-Au non-covalent driving force to lead AuNPs self-assemble onto the 3D Loofah-like network nanofibers in the supramolecular hybrid gel system. While in the system of POSS-Hpy gelator without sulfur, no strong interaction with AuNPs existed and the POSS-Hpy nanocomposites showed no obviously changes of morphology, thermal stability or rheological properties, confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), tube-inversion and rotational rheometer measurements. Such obvious comparison indicated that organic/inorganic hybrid gelator POSS-Cys could be applied to the formation of soft materials in which AuNPs were self-assembled and closely arranged to a three-dimensional nanoscale networks. This hybrid material has great potential applications in self-recovery, nano- and micron- scale electronic devices for it has both a large mechanical strength and a fast-recovery capability.

Introduction

Supramolecular gels,¹ especially noble metal nanoparticles-supramolecular gels,² were soft materials which had generated enormous interest recently for basic scientific and advance applications in template materials, drug delivery agents, cosmetics, sensors, enzyme immobilization matrices and phase-selective materials.³ Supramolecular gels were generated by entrapment of large quantities of free flowing solvent within a reticulated superstructure made of intertwined fibrils of varying dimensions in a semisolid phase, which constituted by additives called gelators with only a tiny fraction of overall mass of gel system.⁴ Noble metal nanoparticles including gold nanoparticles (AuNPs) arising from

their high surface areas and the spatial confinement of electrons, biomedicine and electric fields in and around these particles had surprising optical, electronic, magnetic and catalytic properties, with vast potential applications in many fields.⁵ The new class of hybrid materials, gel-nanocomposites, integrating advantages of gels and nanoparticles, had surely inspired material scientists to systematically study the synthesis and characterization of NPs and gelators, fabrication of NPs-gel composites, formation mechanisms and applications during recent decades.⁶

The very early works always focused on utilizing of gel as templates to synthesize inorganic nanoparticles such as silica, TiO₂, CdS, Ag and Au nanoparticles via supramolecular self-assembly while rarely explored the mechanical property of gel-nanocomposites.⁷ Although the initial work intended the use of molecular gels as media for the preparation and stabilization of NPs, later reports suggested that combination of supramolecular gels with NPs had been found to be advantageous for both constituents. Tanmoy Kar et al. analysed the mechanical strength of in situ synthesized AuNPs-hydrogel nanocomposites by rheological measurement, noticed an increased mechanical strength of the gel through probable formation of more compact and dense fibers.⁸ However, nearly all these hybrid materials fabricated through in

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situ method had difficulty to remove the by-products that probably limited their further applications, and the final characteristics and properties depending on gel formation process⁹ were hardly to be predicted.

Recently, more and more reports focused on fabrication of gel-nanocomposites through addition of NPs synthesized externally, for whose intrinsic properties were largely predetermined and easier to achieve the desired effects.¹⁰ Designing and synthesizing different functional gelators, fabricating different capping agents protected NPs, making different functional hybrid materials had been taken to search for a new permutation matrix of AuNPs and seeking the advanced application of gel-nanocomposites. Kimura and co-workers had clearly demonstrated that strong interaction could be established between AuNPs and thiol groups to obtain NPs–gel materials where AuNPs could spatially assemble onto the gel fibers.¹¹ What's more, Bhattacharya and co-workers found that in the AuNPs–gel nanocomposites capping agents of AuNPs always had influence on morphological features and viscoelastic properties.¹² Another interesting relationship between NPs' dimensions and morphology had been revealed by Demirel and co-workers in a diphenylalanine (Phe–Phe) dipeptide gel, in which the increased dimensions of the nano-objects affected the gelator self-assembly process due to flatter NP surfaces so as to adsorb proteins better.¹³

The synergy of these self-assembled gels and nanoparticles could be advantageous for the composite itself in terms of the improvement of its mechanical properties as well as in biomedicine applications. Banerjee and co-workers reported on the modulation of the mechanical properties of hybrid hydrogel materials by incorporating AgNPs capped with cysteine and the cysteine-based dipeptides, and showed that AgNPs could directly interact with gelator nanofibres as a consequence of hydrogen bonding interactions between the two different nanoscale units and the mechanical strength of the gel could be modulated by varying the nature of the capping ligands.¹⁴ Del Guerso and co-workers noticed a similar behaviour that a gradual decrease in the stiffness of an organogel made of the anthracene derivative with increasing amounts of n-butanol protected AuNPs.¹⁵ However, most of the reported method to produce NPs–gel nanocomposites had either complicated preparation technology including polymerization and so on, or needed plenty a lot of gelator plus NPs to produce an opaque gel with mechanical properties not strong enough to be utilized so far. Despite large numbers of works being carried out on the development of gel-nanocomposites, rarely reports exhibited remarkably uses in improving the mechanical attributes of hybrid organogels.

Recently, we have reported a novel 3D radial symmetric organic/inorganic hybrid supramolecular gelator POSS-Lys which could form a unique loofah-like network structure and macroscopically manifest itself with a high efficiency in gelation, with a strong ability to resistant the external stress and exhibiting a distinct viscous flow state.¹⁶ The organization of NPs into well-defined and easily reproducible architectures was a particularly promising route not only for the construction of optoelectronic and biomedical devices, but also for the discovery of novel physico-chemical properties of organized matter. In this paper, we reported

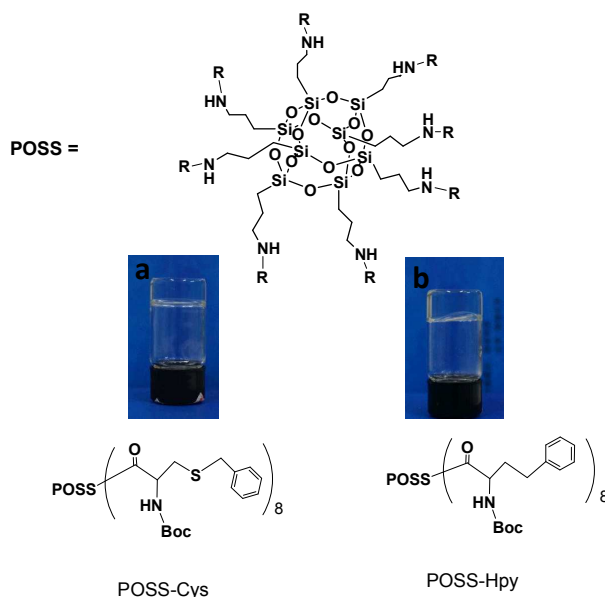


Fig. 1 Chemical structure and styrene gel of two POSS core based gelators: POSS-Cys (a) and POSS-Hpy (b).

a strong and fast-recovery organic/inorganic hybrid AuNPs-supramolecular gels based on three-dimensional loofah-like nanoscale network self-assembled by polyhedral oligomeric silsesquioxane (POSS) core supramolecular gelator through a quite simple sol-gel method with quite a few addition of gelators and NPs.

Experimental and methods

Synthesis and characterization of gelators (POSS-Cys and POSS-Hpy) and AuNPs

The details are present in section 1 in support information.

Preparation of AuNPs hybrid gels

An accurately measured mass of gelator was weighed and put into a 3 mL glass vial. The pure solvent or AuNPs solvent (1 mL) was then added. All the concentrations of gelators or AuNPs are expressed in % as the ratio of weight (mg) to liquid volume (mL). The sample was sonicated for 10 minutes (in the absence or presence of AuNPs stock solution, 0.1 mL), then shaken and dissolved in 110 °C oil bath. After standing for 24 h, a homogeneous nanoparticle-containing gel was obtained.

Gelation tests and gel-sol transition temperature (T_{gel})

A known weight of a tested compound and a measured volume (1 mL) of a chosen liquid were placed into a 3 mL glass vial as a test tube and the system was ultrasonic treated for 10 min at room temperature, then the test tube was inversed to observe if a gel had been formed. If the result was negative, the test tube was heated until the solid was dissolved completely, and then the system was cooled to room temperature. Finally, the test tube was inversed to observe the state of the materials inside. The gel-sol transition temperature (T_{gel}) was measured by using a simple tube-inversion method¹⁷. We defined the temperature at which the gels began to flow the gel-sol transition temperature (T_{gel}) as the gel

point. Considering such a simple tube-inversion method was not a rigorous test to examine the accurate gel point as Winter et al.¹⁸ and Negi et al.¹⁹ described, it was a working definition rather than the more strict definition for utilization.

Field emission scanning electron microscopy (FESEM)

The gels and the gel-NPs composites were carefully scooped onto the conducting resin on the platinum stubs and were allowed to dry overnight in the air. The samples were further dried in vacuum for 8 h. Then 10 nm-thick platinum films were deposited on the gels. Finally, the morphology of the gels was investigated by using a Hitachi S-4700 FESEM operated at 15 kV.

Transmission electron microscopy (TEM)

For both of the gel-nanoparticle mixtures, the material as a styrene sol was drop coated on amorphous carbon-coated Cu grids. In both cases, the concentration of the gelators were below the minimum gelator concentration, due to the resultant aggregates were too thick to get good-quality micrograph at higher concentrations. TEM images in Fig. 4 were recorded by using a JEM-1230 microscope at an accelerating voltage of 80 kV. For AuNPs dispersion liquid and POSS-Cys and POSS-Hpy solution, the styrene sol was drop coated on amorphous carbon-coated Cu grids. TEM images Fig. S1a, S5c, S5d were recorded by using a FEI-Tecni G2F30 microscope at an accelerating voltage of 200 kV.

Rheology

Rheological characterizations of gels were performed on an Anton Paar MCR302 Rheometer with plate geometry (PP 25). The gap distance between plate and plate was fixed at 0.5 mm. Rheological measurements were carried out on freshly prepared gels and were scooped onto the plate of the Rheometer. The following tests were performed: the samples were submitted to this parallel-plate very quickly to minimize solvent evaporation. Dynamic strain sweep tests were increased amplitude of oscillation from 0.1% up to 1000% apparent strain shear (kept a frequency $\omega=10$ rad s^{-1}) at 25 °C. Dynamic frequency sweep tests were between 0.1 and 100 rad s^{-1} (kept a strain $\gamma=1\%$) at 25 °C. Oscillatory frequency sweep experiments were performed in the linear viscoelastic region to ensure that calculated parameters correspond to an intact network structure. Dynamic time sweep tests were first given a small strain $\gamma=1\%$ for 100 s and then subjected to a strong strain $\gamma=200\%$ for 200 s, following a small strain $\gamma=1\%$ for its recovery. Then repeated twice to detect its reversibility, and frequency was kept in $\omega=6.28$ rad s^{-1} .

Results and Discussion

The characterisation of AuNPs

The morphology characteristics of the gold nanoparticles were determined by TEM as shown in Fig. S1 in ESI†, most of the particle shapes were homogeneously spherical. AuNPs had diameters in the range 1.5–5.5 nm and a maximum particle size distribution at 2.5–4 nm. The average diameter of the nanoparticles was $3.3(\pm 0.7)$ nm.

Gelation ability and thermal stability

To evaluate the gelation capacity of different gelator/solvent systems, tube-inversion experiments²⁰ were performed in a range

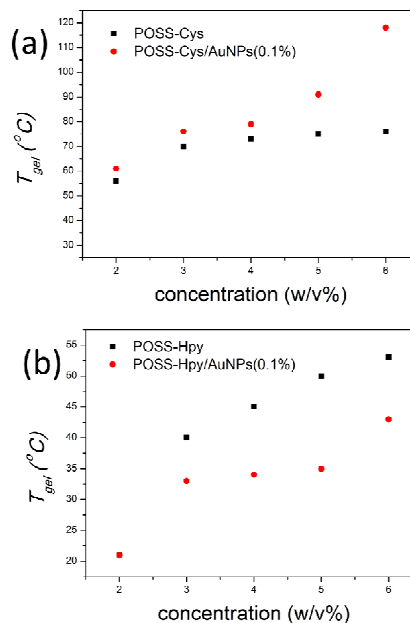


Fig. 2 Phase diagrams for gels. (a) Phase diagram of POSS-Cys gels and POSS-Cys/AuNPs hybrid gels, the concentrations of AuNPs in hybrid gels still keep in 0.1%. (b) Phase diagram of POSS-Hpy gels and POSS-Hpy/AuNPs hybrid gels, the concentrations of AuNPs in hybrid gels still keep in 0.1%.

of different solvents as shown in Table S1. The thermal stabilities of gels from solvents were also assessed by using a simple tube-inversion method. From the gelation behaviour research we could see that both of hybrid gelators POSS-Cys and POSS-Hpy had good gelation abilities in aromatic solvents, while the addition of AuNPs had quite opposite influences on the resultant gels. The gelation ability and thermal stability of novel hybrid gelators POSS-Cys and POSS-Hpy were discussed in section 2.2 in ESI†.

With the addition of AuNPs, the T_{gel} of POSS-Cys/AuNPs hybrid gels increased directly (Fig. 2a). Especially when the concentration of the gelator was 6% and the concentration of AuNPs was kept at 0.1%, the hybrid gel had a T_{gel} as high as 118 °C, which was 43 °C higher than pure POSS-Cys gel. It exerted that the thermal stability has been remarkably enhanced in AuNPs composite. While the POSS-Hpy/AuNPs hybrid gels had opposite results, with the addition of the AuNPs, the T_{gel} of hybrid gels were declined (Fig. 2b). All T_{gel} of POSS-Hpy/AuNPs hybrid gels were lower than pure POSS-Hpy gels, indicating the thermal stability had been weakened. Strong interaction of L-cysteine with naked gold nanoparticles (S–Au) via the sulfide group had been proved by Canepa et al.,²¹ so we suspected that gold nanoparticles could combine with the gel fibers by non-covalent bonds and enhance the binding force between gel fibers in the POSS-Cys/AuNPs hybrid gel, and the thermal stability of hybrid gels enhanced as a result. While in POSS-Hpy/AuNPs hybrid gels, gold nanoparticles played a different role and turned out only adverse influence were presented, which probably because there were no strong attraction between AuNPs and gel fiber without the

existence of sulphur atom. In this occasion the distance between gel fibers had been slightly enlarged with NPs filled in interspace and the interactions had been weakened, so the thermal stability of POSS-Hpy/AuNPs hybrid gels was diminished.

The morphology of the self-assembly and the self-arrangement

The network structures of the gels and AuNPs hybrid gels had been explored by SEM and TEM, both of novel gelators POSS-Cys and POSS-Hpy could self-assemble into loofah-like three-dimensional (3D) gel networks in which gel fibres have similar morphology of POSS-Lys (Figure S5 and discussions in section 2.3 in ESI[†]). While with the addition of AuNPs, the scale of the gel fibres and the morphology seems no obvious changes.

As shown in Fig. 3, POSS-Cys and POSS-Hpy molecules self-assemble into loofah-like three-dimensional (3D) gel networks with diameters of about 50-200 nm (POSS-Cys) and 0.5-1 μm (POSS-Hpy) gel fibres. With the addition of AuNPs (Fig. 3c, Fig. 3d), an almost the same 3D network with diameters of about 50-200 nm (POSS-Cys/AuNPs) and 0.5-2 μm (POSS-Hpy/AuNPs) can be observed. No obvious changes on the scale of the gel fibres and the morphology, which further demonstrated the network structure was not influenced by the addition of nanoparticles in AuNPs supramolecular hybrid gels.

The morphology of the hybrid xerogels have also been investigated by TEM. Gold nanoparticles arranged into an ordered network in POSS-Cys/AuNPs hybrid xerogel (Fig. 4a), most of which were adsorbed onto the gel fibres and formed as a continuous network with scarcely any aggregation. With the addition of AuNPs, the structure of the fibre network could be prominently observed, for which AuNPs closely adsorbed on gel fibers and formed a heavy

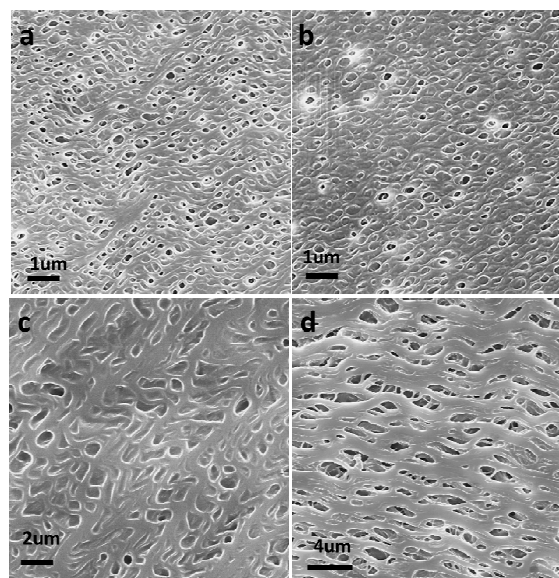


Fig. 3 SEM image of xerogel from styrene. The concentrations of the gelators were 5mg/mL, and the concentrations of AuNPs were 1mg/mL; (a) POSS-Cys xerogel, (b) POSS-Cys/AuNPs hybrid xerogel, (c) POSS-Hpy xerogel, (d) POSS-Hpy/AuNPs hybrid xerogel.

atoms network, and exhibited the constitutional features and structural information of gel in TEM investigation. Fig. 4b showed most of nanoparticles absorbed on (or in) the gel fibers arranged into a line, and very few nanoparticles in the regions existed

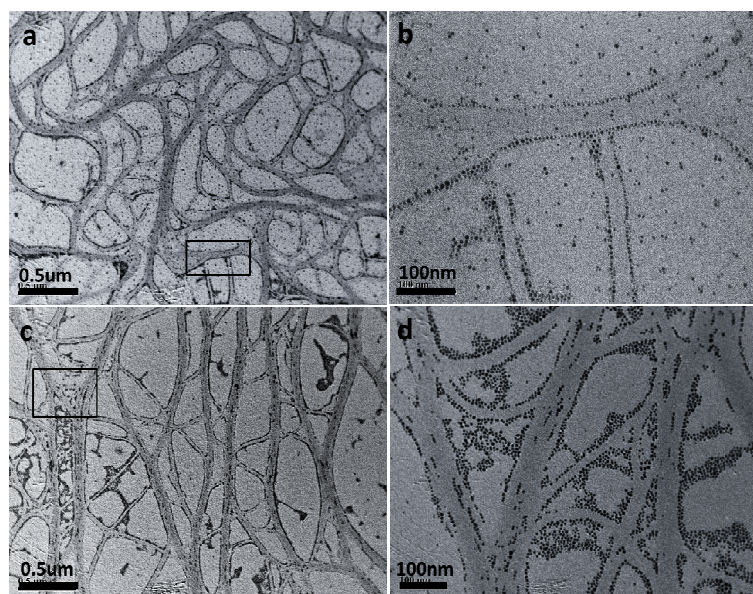


Fig. 4 TEM images of NPs interacting with gelator fibres composed of POSS-Cys and POSS-Hpy. (a) POSS-Cys/AuNPs hybrid xerogel. (b) POSS-Cys/AuNPs hybrid xerogel partial enlarged view. (c) POSS-Hpy/AuNPs hybrid xerogel. (d) POSS-Hpy/AuNPs hybrid xerogel partial enlarged view.

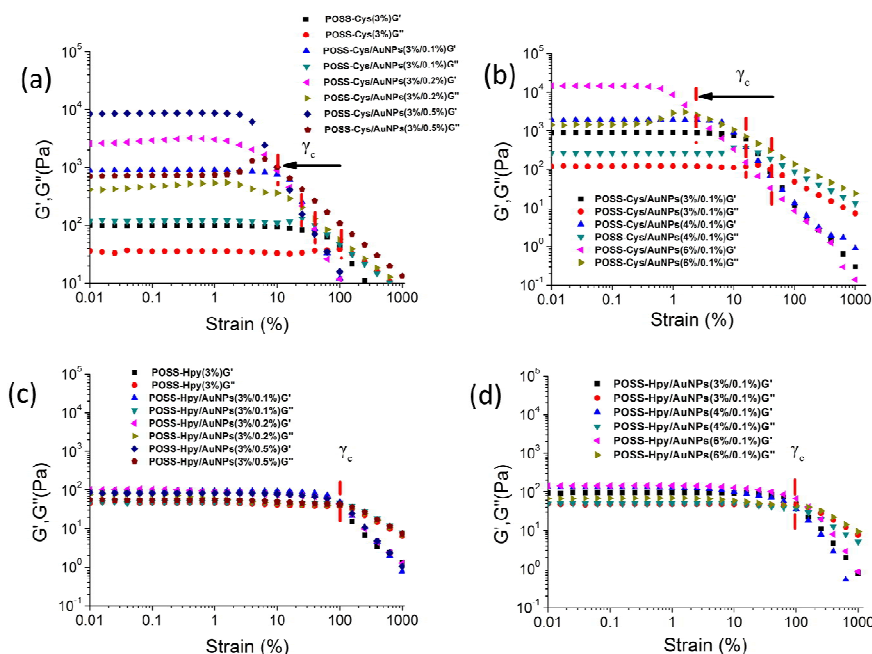


Fig.5 Strain dependence of G' and G'' for gels, measured at 25 °C with a strain from 0.01% to 1000% and frequency $\omega=10 \text{ rad s}^{-1}$; (a) (c) AuNPs hybrid gels in styrene with different concentrations of AuNPs. (b)(d) AuNPs hybrid gels in styrene with different concentrations of gelators.

without fibres. The high ratio of fibre-attached nanoparticles and little non-fibre-attached nanoparticles in Fig. 4b indicated that there were strong interactions between gel fibres and AuNPs. Although in POSS-Hpy/AuNPs hybrid xerogel (Fig. 4c) all fibres also connected to each other and formed a consecutive network, AuNPs appeared to a lot of nanoparticles aggregated in a flake, which was very different from that observed from POSS-Cys, as shown in Fig. 4d. Some of the nanoparticles just simply collected loosely around the gel nanofibres as a kind of simple 'negative staining' effect²² depending on weak electrostatic forces, which was much weaker than S-Au non-covalent bond. The formation of such a strange phenomenon may primarily because of a sample-drying effect made AuNPs pulls back towards the fibres during the solvent evaporation (Fig. 4c, 4d). So we speculated that with the help of S-Au non-covalent bonds and the networks assembled from POSS-Cys, AuNPs could form a highly organized new network, which benefited the dispersion of nanoparticles, mechanical property, further catalysis, biological applications and micro/nano conductive.

Rheological studies of AuNPs hybrid gels

Rheological measurements were carried out to investigate the mechanical properties and self-recovery properties of these gels. Dynamic strain sweep data showed that the uppermost boundary of the linear viscoelastic region (LVR) of POSS-Cys and POSS-Hpy gels were about 10% strain, and could keep its elasticity (storage modulus $G' >$ loss modulus G'') to an extremely large strain of 100%, a value of which was the same as POSS-Lys and one order of magnitude larger than reported one²³ (Fig. S6a, S6b). The results noticeably indicated that a relatively stable gel network could be

self-assembled in solvent at a quite low concentration of POSS-Cys and POSS-Hpy with a strong ability to resist the external stress²⁴, as discussed in section 2.4 in ESI†. The points at which the G' values always deviated by more than 5% from the plateau values indicated departure from linear viscoelastic behaviour and therefore were defined as the critical strains (γ_c) for each sample²⁵. With the addition of AuNPs, POSS-Cys hybrid gels lost the ability to keep its elasticity to a strain of 100%. With the concentration of POSS-Cys increased (Fig. 5b), G' value increased and had a plateau of value storage modulus $G' > 10000 \text{ Pa}$ (POSS-Cys/AuNPs=6%/0.1%) which were more than 100 times higher than POSS-Cys gel (POSS-Cys =6%) about 100 Pa, while γ_c of POSS-Cys hybrid gels rapid decreased which from $\gamma_c=100\%$ (POSS-Cys=6%) to $\gamma_c=3\%$ (POSS-Cys/AuNPs=6%/0.1%), as shown in Fig. 5b. As expected, the addition of a small amount (0.1-0.5% in Fig. 5a) of AuNPs pronouncedly increased the viscoelasticity and stiffness of hybrid gels, which had a same tendency as Fig. 5b. In generally, the LVR was the shortest when the sample in its most solid form. Comparing with pure POSS-Cys gel, POSS-Cys/AuNPs hybrid gels presented a much higher G' max, a shorter LVR and therefore a lower γ_c . This phenomenon indicated that AuNPs had direct interactions with the POSS-Cys networks, and vastly increased the strength of hybrid gels but with an expense of its elasticity, in which a rather higher G' max, a shorter LVR and therefore a lower γ_c was observed. While with the composite of gold nanoparticles, POSS-Hpy hybrid gels showed no differences from POSS-Hpy gels (Fig. 5c, 5d). This result further demonstrated that the POSS-Cys/AuNPs hybrid gels were stronger gels.

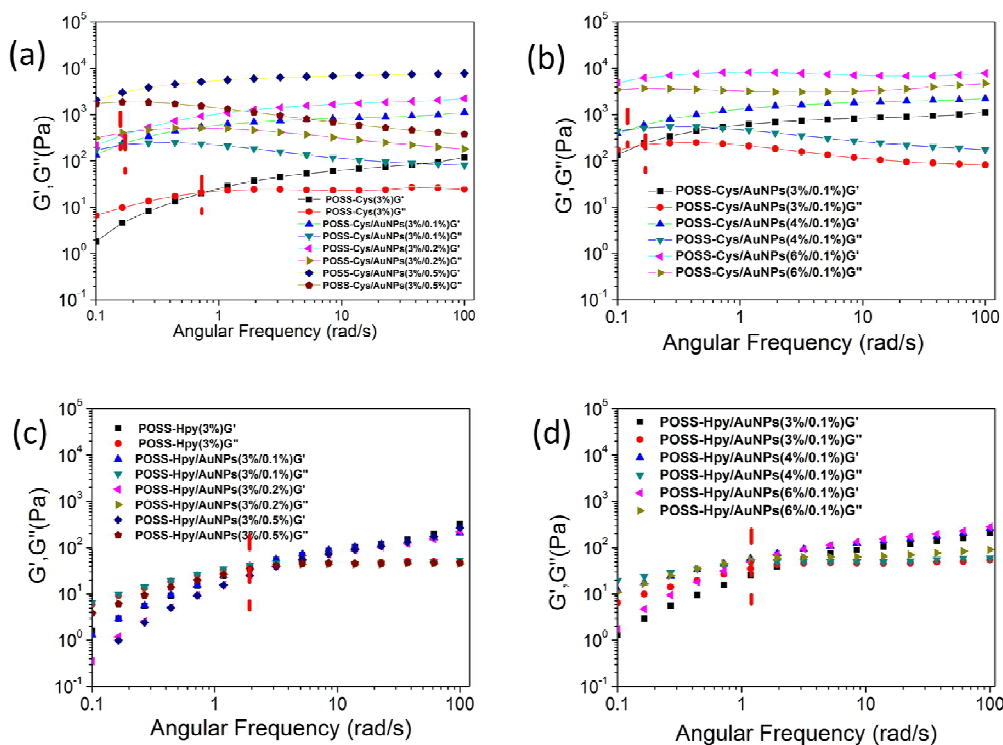


Fig. 6 Frequency dependence of G' and G'' for gels, measured at 25 °C with a frequency from 0.01 to 100 rads^{-1} and strain $\gamma=1\%$. (a)(c) AuNPs hybrid gelin styrene with different concentrations of AuNPs. (b)(d) AuNPs hybrid gels in styrene with different concentrations of gelators.

The G' (elasticity) and G'' (viscosity) as a function of ω for gels within linear deformation range were illustrated in Fig. 6 and Fig. S7. POSS-Cys and POSS-Hpy gels showed a kind of elastic gel network²⁶ properties as discussed in section 2.4 in ESI†. According to its viscoelastic properties and the trend of moduli curves of the pure gels, the crossover point ($G' = G''$) of POSS-Cys/AuNPs (keep POSS-Cys in 3%) hybrid gels shifted to a lower ω ($\omega < 0.2$). $G'(\omega)$ substantially increased to a plateau region, while $G''(\omega)$ had a high value at low ω and then slightly decreased (Fig. 6a, 6b). The substantial increasing of moduli indicated that the hybrid gel fibres network structure were enhanced to form rather stable and strong networks, the hybrid gel soft materials exhibited typical solid-like elasticity, evidenced that AuNPs improve the mechanical strength of gels. While in POSS-Hpy/AuNPs (0.1%) hybrid gels (Fig. 6c, 6d), the moduli curves showed no obvious difference from pure gels which the moduli curves were almost entirely coincidence, evidencing that AuNPs had no interaction with POSS-Hpy, and further confirmed the AuNPs could hardly improve the mechanical strength of POSS-Hpy/AuNPs hybrid gels.

Self-recovery of the gels under continuous step strain

The self-recovery was one of the most amazing properties in nature, an ability of biological or artificial systems spontaneously repaired their damage and restored their original state²⁷. Different from most soft materials, self-recovery gels could regenerate the integral network after being damaged. This property endowed these

materials vast applications in the fields of drug delivery, 3D cell proliferation and tissue engineering.²⁸ However, the materials with self-recovery properties reported till now are mainly polymer gels.²⁹ In contrast, low-molecular mass (LMMG) based gels and AuNPs hybrid gels are scarcely reported.³⁰ Interestingly, we noted that our novel gels exhibited very rapid recovery of its mechanical properties after a large-amplitude oscillatory break-down, known as thixotropic nature³¹ (Fig. 7 and Fig. S8). Under the application of a large-amplitude oscillatory force (strain, $\gamma=200\%$; frequency, $\omega=6.28$ rad/s) the G' value decreased from 700 Pa to 2 Pa (POSS-Cys/AuNPs=3%/1%) (Fig. 7a), resulted in a quasi-liquid state. However, when the amplitude decreased ($\gamma=0.1\%$) at the same frequency, G' recovered to its initial value immediately and the system returned to a quasi-solid state. Using the same test method we investigated the other AuNPs hybrid gels, all gels had the excellent recovery properties (Fig. 7b, 7c, 7d). Though high mechanical strength AuNPs hybrid gels had a low γ_c , they also had excellent self-recovery properties (Fig. 7c, 7d), which further demonstrated the hybrid gels both had a large mechanical strength and fast-recovery ability. These characteristic made it possible to be applied to the self-recovery soft materials.

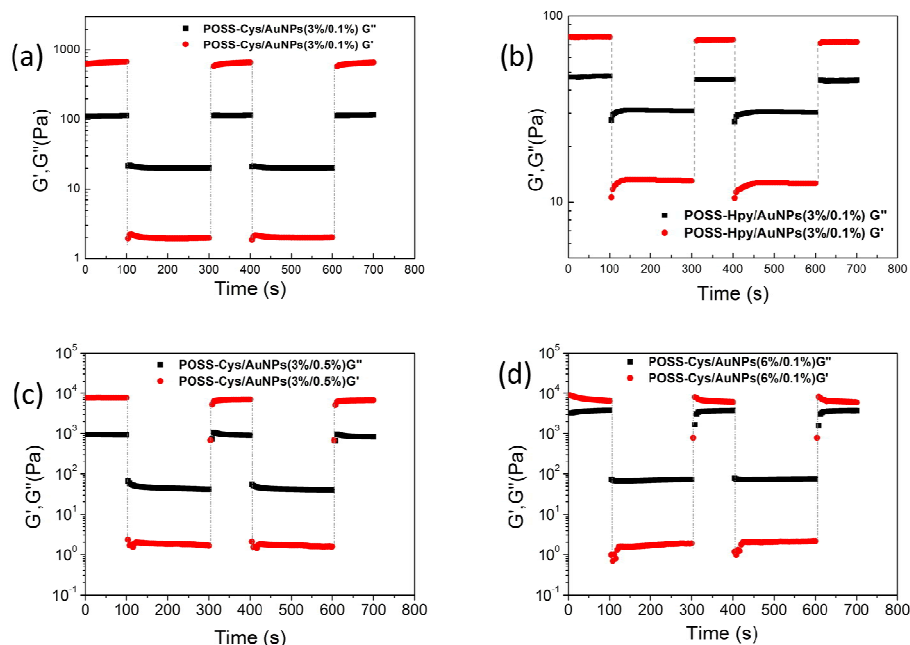


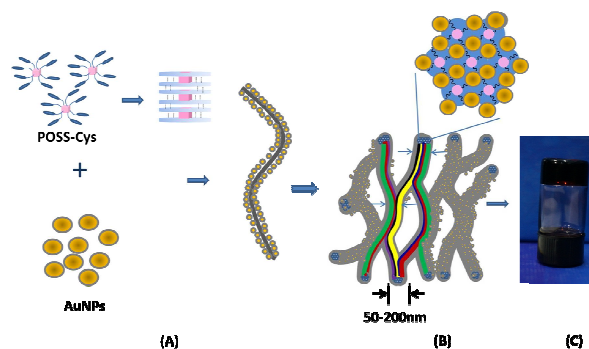
Fig. 7 The G' and G'' dependence of time in continuous step strain measurements for gels; (a), (b), (c), (d) were recovery property of the hybrid gels: the gel was first given a small strain of 1% for 100 s and then subjected to a strong strain of 200% for 200 s, following small strain of 1% for its recovery. Then repeat twice to detect its reversibility, frequency keep in 6.28 rad s^{-1} .

Proposed mechanism for the formation of gel-nanocomposites

The driving forces of gelators had been proved by $^1\text{H-NMR}$ spectroscopy and fluorescence spectral. As shown in Figure S9, S10, the initially peaks of amide H, carbamate H gradually got upfield shifted at higher varying volume fraction of CCl_4 , which attributed to the weakening of hydrogen bonding interactions³² proved the hydrogen bonding interaction involving amides and carbamate groups was the driving force for the gelation of POSS based hybrid gelators.³³ What's more, studies on the polarity of the interior of the aggregate were carried out by using the fluorescence emission of pyrene in the gel state.³⁴ The observed changes in I_1/I_3 value (Figure S11) demonstrated the formation of π - π stacking.³⁵

On the basis of the above findings and discussions, we proposed a model for the self-organization of the 3D organic/inorganic hybrid gel-nanocomposites as presented in Scheme 1. Presumably, in AuNPs dispersions, in the initial time, a unidirectional plane-to-plane stacking of the building blocks was promoted by a more favourable alignment of hydrogen bonds and π - π interactions³⁶. Later, the single column was able to form and grow smoothly and meandered without endpoint with AuNPs closely adsorbed on it by S-Au interactions. At the same time, single columns aggregated to form a hexagonal columnar bundle structure¹⁶ with AuNPs messily adsorbed on it, so as to achieve the thermodynamic stable state. However, as shown in Scheme 1B, the endless and flexuous column orders itself in a sectional type fibre, thus the furcate and continuous structure with AuNPs in or on its fibers was formed. Plenty of these fibres therefore underpinned the loofah-like gel-AuNPs network. With AuNPs distributing around the

single column or in the junction part of fibers enhance the interaction force between fibres, the mechanical strength of hybrid gels had been markedly improved.



Scheme 1 Proposed mechanism for the formation of 3D loofah-like organic/inorganic hybrid AuNPs-supramolecular gels. (A) Free molecules and particles formed single column via the plane-to-plane stacking of POSS-Cys and S-Au interactions; (B) Loofah-like networks; (C) Optical image of hybrid gel.

Conclusions

Strong and fast-recovery organic/inorganic hybrid AuNPs-supramolecular gels based on loofah-like 3D networks were reported here through design and synthesis new kinds of

organic/inorganic hybrid gelators. Both POSS-Cys and POSS-Hpy had the ability to self-assemble into loofah-like 3D gel networks. Test-tube-inversion method, rheological measurements, SEM, TEM obviously showed that the strong interaction of sulphur in the structure of gelators and AuNPs was the key factor of giving the resultant gel special thermal and mechanical properties. The gel-nanocomposites obtained from sulphur contained gelator POSS-Cys and AuNPs had a morphology of which AuNPs closely absorbed onto the gel fibers to form a loofah-like metal 3D nanoscale network, which provided a 43 °C higher T_{gel} and a more than 100 times greater G' than the reference gel without AuNPs. While in the system of POSS-Hpy without sulphur, neither morphology nor rheological properties showed clear changes. Such hybrid gels with high mechanical strength and strong fast-recovery ability could have potential applications in self-recovery and nano-conduct soft materials.

Acknowledgements

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