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ARTICLE TYPE

# Nanocomposite Hydrogel based on Liquid Crystalline Brush-like Block Copolymer/Au nanorods and its Application in H<sub>2</sub>O<sub>2</sub> Detection

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**New nanocomposite hydrogels from liquid crystalline brush-like block copolymers (LCBBC) and gold nanorods (AuNRs) were synthesized and characterized. The hydrogel protected and stabilized AuNRs, which presented peroxidase-like activity and catalysed the oxidation of a substrate in the presence of H<sub>2</sub>O<sub>2</sub> and elicited a sensitive chromogenic response. This reusable, table-top stable, free-standing nanocomposite hydrogel platform can be used to develop a simple and reproducible method to detect H<sub>2</sub>O<sub>2</sub>.**

Noble metal nanomaterials like spherical gold nanoparticles (AuNPs) have received extensive attention due to their fascinating and special optical/plasmonic properties.<sup>1, 2</sup> However, anisotropy in shapes of these nanoparticles presents more interesting properties.<sup>3</sup> For example, anisotropic gold nanorods (AuNRs) afford unique localized surface plasmon resonance (LSPR).<sup>4</sup> The LSPR properties can be tailored using AuNRs of different aspect ratios for applications in bio-imaging, sensing, photothermal therapy, and optical storage.<sup>5-9</sup> More interestingly, because of high surface-to-volume ratio and high surface energy of AuNRs, the surface atoms function as efficient catalysts and peroxidase mimics for the oxidation of chromogenic substrate in the presence of H<sub>2</sub>O<sub>2</sub>.<sup>10</sup> Thus, AuNRs are attractive catalyst for hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) oxidation reaction in biotechnology and agriculture wherein accurate and rapid determination of H<sub>2</sub>O<sub>2</sub> is important. Also, as an artificial enzyme mimetic, AuNRs has some advantages over natural enzymes such as the ability to maintain high catalytic activity under a wide range of environmental conditions and ability to be stored under ambient conditions for a long period.<sup>11</sup> Liu and co-workers prepared Au nanorods @ Pt nanodots core/shell nanostructures that exhibited dual functional enzyme-like (peroxidase and oxidase-like) activities.<sup>12</sup> Recently, Li and co-workers fabricated graphene-gold nanorod composite with high intrinsic peroxidase-like sensitivity for detecting H<sub>2</sub>O<sub>2</sub> through an electrocatalytic mechanism.<sup>13</sup> Interestingly, the presence of AuNRs in conjunction with graphene allowed the decomposition of H<sub>2</sub>O<sub>2</sub> without aggregation of the rods. However, several challenges remain in using these systems as catalysts including complicated synthetic protocol, low catalytic activity of the nanorods and ability to recover the catalysts.

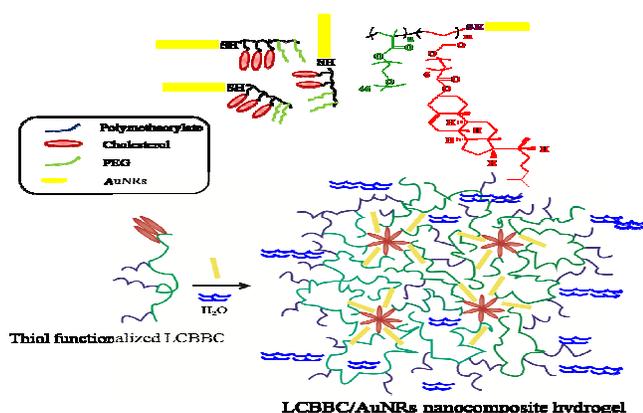
The three-dimensional network structures of polymer hydrogels and ionic gels are regarded as ideal supports for

immobilization of catalytic enzymes (i.e. glucoseoxidase, horseradish peroxidase) as well as catalytic inorganic nanoparticles enzyme mimetics (i.e. Pt, Au, Ag, Fe<sub>3</sub>O<sub>4</sub>).<sup>14</sup> These gels bearing catalysts are robust nanocomposites endowed with the properties of polymers including stability and recover ability as well as unique optical, magnetic, electric and biological properties of the nanoparticle.<sup>13-15</sup> In addition, the networks of hydrogels form a good template for the in situ immobilization, which helps overcome aggregation and degradation issues associated with bare nanocatalysts.<sup>14, 15</sup> While polymer protected AuNRs have been widely used for photonics,<sup>16</sup> polymer protected/passivated AuNRs as catalysts and peroxidase mimics is an unexplored field.

We recently reported the synthesis of new amphiphilic thiol functionalized liquid crystalline brush-like block copolymer (LCBBC) comprised of polymethacrylate bearing cholesterol mesogen (poly(cholesteryl 6-methacryloyloxy hexaneate) (PC5MA)) and polymethacrylate bearing PEO block (PMA-g-PEO) with hemitelechelic thiol groups attached at the end of the PC5MA block.<sup>17</sup> The LCBBC was used to encapsulate AuNPs and generate well-defined LCBBC/AuNPs nanocomposites ion gels.<sup>18</sup>

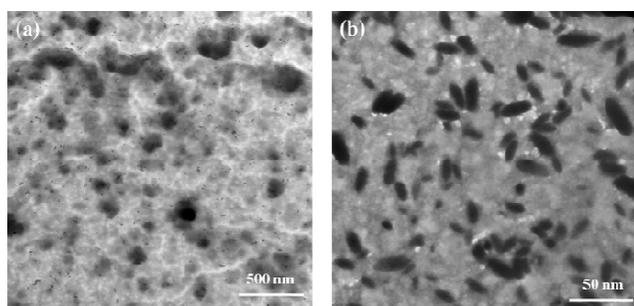
In the current study, we exploit LCBBC properties and report a facile and modular approach for the preparation of free-standing liquid crystalline brush-like block copolymer/Au nanorods (LCBBC/AuNRs) nanocomposite hydrogels. The peroxidase-like activity of the AuNRs within hydrogel was used to catalyze the oxidation of the substrate 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of H<sub>2</sub>O<sub>2</sub> and a platform to detect H<sub>2</sub>O<sub>2</sub> was developed. In addition, free-standing nanocomposite hydrogel can be recovered easily and effectively. As a control, LCBBC/AuNPs nanocomposite hydrogel was prepared and compared. This is a versatile and general approach to nanocomposite gels with unique catalytic properties.

Gold nanorods (AuNRs) were synthesized by seed-mediated method.<sup>19</sup> The as-synthesized LCBBC served as macromolecular ligands to stabilize AuNRs *in situ* and resulted in LCBBC/AuNRs nanocomposites (see the ESI†, Experimental Procedure and Table S1). This LCBBC/AuNRs nanocomposite gelled in water to form free standing nanocomposite hydrogel, in which the LC domains and AuNRs

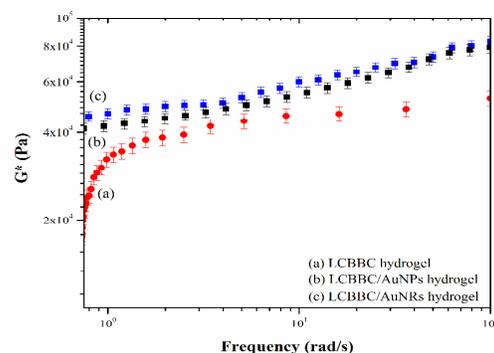


**Scheme 1** LCBBC/AuNRs nanocomposite hydrogel with a network structure connected by LC domain and AuNRs. The LCBBC brush-like block copolymer comprised of poly(cholesteryl 6-methacryloxy hexanoate) with 5 methylene spacer block and brush-like poly ethylene oxide (MW 2000 g/mol).

served as physical crosslinkers or network junctions that lead to mechanically robust hydrogel (Scheme 1). The morphology of LCBBC/AuNRs nanocomposite hydrogel was examined by cryo-SEM (Figure 1), which showed presence of network structure. Interestingly, numerous AuNRs with an average dimension of 25 x 5 nm were distributed within nanocomposite hydrogel matrix. UV-visible plasmon resonance spectroscopy (see the ESI†, Fig.S1) was used to determine the bands of LCBBC/AuNRs nanocomposite hydrogel. The absorbance of LCBBC/AuNRs hydrogel exhibited two plasmon bands including shorter wavelength (transverse plasmon oscillation) at 520 nm and longer wavelength (longitudinal plasmon oscillation- LSPR) at 740 nm, which is similar with LCBBC/AuNRs in DMF solution and AuNRs bands.<sup>4</sup> This indicated the presence of strong interaction between Au and thiol group and retention of AuNRs within the polymer scaffold upon hydrogel formation, which is important for plasmonic sensing and catalytic applications. The presence of AuNRs in LCBBC/AuNRs nanocomposite hydrogel was also confirmed by energy dispersive X-ray (EDX) spectroscopy. The EDX spectrum with peaks at 2100, 9300 and 12 000 eV<sup>20</sup> revealed the presence of Au within the LCBBC/AuNRs nanocomposite hydrogel, and showed a quantitative elemental composition of Au atom about 3.78 wt % (see the ESI†, Fig. S3). This result is comparable with our results of nanoparticles and nanocomposite gels formed by LCBBC/spherical AuNPs<sup>17, 18</sup> (see the ESI†, Fig. S4).



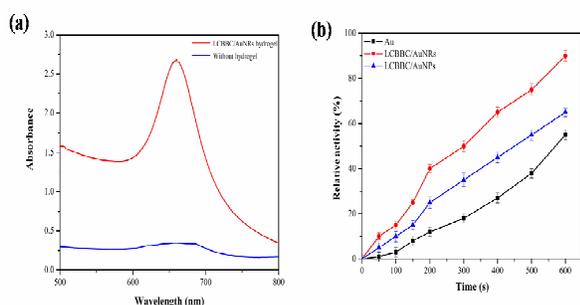
**Fig.1** Cryo-SEM image of LCBBC/AuNRs hydrogel (a) broad range and (b) zoom in.



**Fig.2** Comparison dynamic frequency sweep of all hydrogel samples at 25 °C: (a) LCBBC hydrogel, (b) LCBBC/AuNPs hydrogel, and (c) LCBBC/AuNRs hydrogel. All the samples were prepared with same LCBBC brush-like block copolymer. The LCBBC/AuNPs and LCBBC/AuNRs nanocomposite hydrogels contained ~ 3 wt% of gold nanomaterial.

To assess the effect of AuNRs and AuNPs incorporation on the thermomechanical properties, oscillatory frequency sweep experiments at 25 °C of nanocomposite hydrogels were performed and compared with the hydrogels under constant stress. From Figure 2, it was observed that the LCBBC/AuNRs nanocomposite hydrogel showed the modulus higher than the plain polymer hydrogel (without AuNRs) and comparable with LCBBC/AuNPs nanocomposite hydrogel containing ~ 3 wt% AuNPs. This is indicative of high degree of elasticity of nanocomposite hydrogel. We expect that the LC units within both LCBBC/AuNRs and LCBBC/AuNPs nanocomposite hydrogel will retain smectic ordering during the gelation process based on our previous work with LCBBC/AuNPs nanocomposite ion gels.<sup>18</sup> Thus, the presence of both AuNRs (and/or AuNPs) and LC smectic layered mesophases within the nanocomposite hydrogel enhanced their mechanical properties.

To demonstrate the peroxidase-like activity of the AuNRs and AuNPs within nanocomposite hydrogel, the nanocomposite hydrogels was used to catalyse the oxidation of 3,3,5,5-tetramethylbenzidine (TMB) in the presence of H<sub>2</sub>O<sub>2</sub> (see the ESI†, Fig. S5). The catalytic reaction can be detected by monitoring absorbance change at 650 nm, which originates from the oxidation of TMB. In the absence of LCBBC/AuNRs hydrogel, the solution containing TMB and H<sub>2</sub>O<sub>2</sub> showed negligible absorption in the range of 500 nm to 800 nm. In contrast, in the presence of the nanocomposites hydrogel, the blue colored solution exhibited characteristic absorbance peak at 650 nm (Fig. 3a), indicating that the intrinsic peroxidase-like activity of the AuNRs can still be preserved after *in situ* fabrication within a hydrogel matrix. Furthermore, the obtained nanocomposite hydrogel can be easily and effectively recovered, suggesting the LC domains served as physical crosslinkers that were sufficient strong to lead to mechanically robust hydrogels. Interestingly, the catalytic performance of the nanocomposite hydrogel was affected by shape and morphology of the gold nanomaterial embedded within the hydrogel. Figure 3b compared the catalytic activity of LCBBC/AuNRs with LCBBC/AuNPs and with only AuNRs.



**Fig.3** (a) UV-visible spectra of the TMB–H<sub>2</sub>O<sub>2</sub> mixed solution in the absence and in the presence of LCBCC/AuNRs hydrogel at 40 °C for 10 min; (b) Comparison the relative activity of the LCBCC/AuNRs nanocomposite hydrogel and LCBCC/AuNPs with only AuNRs using TMB as substrate in the presence of H<sub>2</sub>O<sub>2</sub>.

The improved catalytic activity of LCBCC/AuNRs over LCBCC/AuNPs might be attributed to the higher active site at the interface of AuNRs and differences in electronic structures of gold atom.<sup>21</sup> In addition, the catalytic activity of nanocomposite hydrogel were much higher than plain AuNRs due to interaction between AuNRs and LCBCC matrix which prevented aggregation of bare nanorods.<sup>22</sup> Besides the morphology and shape of AuNRs, the concentration of H<sub>2</sub>O<sub>2</sub> was also directly impacted the catalytic activity of nanocomposite hydrogel. The catalytic activity increased with increase in H<sub>2</sub>O<sub>2</sub> concentration. Furthermore, H<sub>2</sub>O<sub>2</sub> can be detected at concentration range of 4 μM to 150 mM with the detection limit of 2 μM, comparable with results obtained from graphene-AuNRs composite (see the ESI†, Fig. S6).<sup>13, 23</sup> Therefore, these results suggest that the LCBCC/AuNRs hydrogel is a good platform to sense H<sub>2</sub>O<sub>2</sub>. An additional benefit of the LCBCC/AuNRs nanocomposite hydrogel is that can be recovered easily due to its free standing nature and effectively using the hydrogel as a platform. Thus, the consolidation of AuNRs and LCBCC features within the framework of nanocomposite hydrogel is promising enzyme mimics with advantages of easy preparation, robustness, and durability.

## Conclusions

In this study, we reported a modular, versatile and unique strategy leading to LCBCC/AuNRs nanocomposite hydrogel in which amphiphilic thiol functionalized liquid crystalline brush copolymers (LCBCC) served as macromolecular ligands to stabilize AuNRs *in situ*. The AuNRs and liquid crystalline mesophases functioned as junctions within the network structure resulting in mechanically robust hydrogels. This is a first report on nanocomposite hydrogel comprising new copolymer passivated gold nanorods that possess intrinsic peroxidase-like activity for H<sub>2</sub>O<sub>2</sub> detection. Thus, LCBCC/AuNRs are promising enzyme mimics due to their ease of preparation and stability for use as catalysts and sensors.

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† Electronic Supplementary Information (ESI) available: Experimental procedures and additional data. See DOI: 10.1039/b000000x/  
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