Supporting Information

Experimental section

Materials

All glasswares were stored in a drying oven for several hours at 120 ^{o}C prior to use. Compounds including 2,2'-azo-bis(isobutyronitrile) (AIBN), chloroauric acid ($HAuCl_4.3H_2O$), lithium borohydride ($LiBH_4$), cholesterol (96%), 3,3,5,5′-tetramethylbenzidine (TMB), cetyltrimethylammonium bromide (CTAB), ascorbic acid, and n-butylamine were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Triethylamine (TEA) and dimethyl formamide (DMF) were purchased from Fisher Scientific (Boston, MA, USA). Polyethylene oxide methyl ether (MW= 2000), 1,4-dioxane (99.8%, extra dry), dichloromethane (DCM) (99.9%, extra dry), methacryloyl chloride (>97%) were purchased from Acros Organics USA. Monomer, cholesteryl 6-methacryloyloxyhexaneoate (C5MA), was synthesized according to a published report.[1] The RAFT agent, S-1-dodecyl-S'-(α,α'-dimethyl-α"-acetic acid) tricarbonate (CTA), was synthesized according to a published procedure.[2] All chemicals used were analytical grade and used without purification. The thiol functionalized liquid crystalline brush block copolymer (LCBBC) and the AuNPs-grafted LCBBC were synthesized according to our published work.[3] To determine the bands of LCBBC/AuNPs as a nanocomposite hydrogel control, the UV-visible plasmon resonance spectroscopy was used and the quantitative elemental composition of Au atom within LCBBC/AuNPs nanocomposite ~ 2.9 wt % was confirmed by energy dispersive X-ray (EDX) spectroscopy (Figure S4).

Preparation of LCBBC/AuNRs hydrogel

Gold nanorods (AuNRs) were synthesized by seed-mediated method.[4] In a typical experiment, 9.9 mL of 0.2 M CTAB was mixed with 98.5 μL of 25.4 mM $HAuCl_4.3H_2O$ followed by

addition of 1 mL ice-cold $NaBH_4$ (0.006 M). After 5 min of stirring, the raw seed solution was stored at room temperature, forming the gold seed solution. The grow solution of AuNRs was prepared by adding 5 mL of $HAuCl_4.3H_2O$ (1 mM) to 5 mL of CTAB (0.2 M) and 270 μL of $AgNO_3$ (4 mM). After that, 70 μL of ascorbic acid (78.8 mM) was added, followed by gentle mixing to form the growth solution. The seed solution (12 μL) was then added to the growth solution and allowed to react for 6 h till the solution turned deep pink color, indicating the formation of AuNRs. The solution was stirred for 30 min, and then polymer solution (LCBBC, 200 mg in 10 mL DMF) was injected dropwise over 15 min. The solution was further stirred for 30 min, and then transferred into dialysis bag (MWCO: 6,000-8,000 Da), followed by dialysis against distilled water for 48 h to remove byproducts. Dry LCBBC/AuNRs nanocomposites were obtained upon freeze-drying.

To prepare LCBBC/AuNPs nanocomposite, LCBBC (0.15 g, 0.025 mmol) and $HAuCl_4.3H_2O$ (0.01 g, 0.05 mmol) were dissolved in DMF (10 mL) and stirred in the dark under nitrogen blanket at room temperature for 24 h. Freshly prepared 0.25 M $LiBH_4$ (1.2 mL, 0.25 mmol) was then added quickly to the solution with vigorous stirring. The reaction mixture immediately turned from yellow to dark purple; violent gas evolution was observed. The solution was stirred for 4 h at room temperature. The reaction mixture was then transferred into dialysis bag (MWCO: 6,000-8,000 Da), followed by dialysis against DMF for 48 h to remove byproducts. Dry LCBBC/AuNPs nanocomposite was also obtained through freeze-drying process.[3]

The LCBBC/AuNRs and LCBBC/AuNPs nanocomposite was placed in distilled water of 25 ^oC and allowed to swell till there is no further weight gain and LCBBC/AuNRs and LCBBC/AuNPs nanocomposite hydrogels were obtained, respectively.

Catalysis and H_2O_2 detection

In a typical experiment, LCBBC/AuNRs nanocomposite hydrogels containing 15 μg AuNRs were immersed in acetate buffer (5 mL, 0.5 M, pH 4.0), in the presence of 150 mM H_2O_2 and 250 mM TMB at 40 °C for 10 min. Afterwards, the nanocomposite hydrogel were removed using tweezers and the remaining solution was examined by a wavelength-scan mode of 650 nm, using a UV-VIS spectrophotometer (Shimadzu, Japan). This method was used to detect varying concentrations (4 μM–150 mM) of hydrogen peroxide.

Polymer composition characterization

The ^{1}H NMR spectra (Bruker DMX 400 MHz NMR spectrometer) of macromonomer and polymers were recorded in $CDCl_3$ and the 7.24 ppm peak was used as an internal standard. Molecular weight and polydispersity indices (PDI) of the polymers were determined by gel permeation chromatography (GPC) by using a Waters 150-C ALC/GPC equipped with Evaporative Light Scattering Detector. THF was used as the eluent with a flow rate of 2.0 mL/min at 40 ^oC with polystyrene as the standard.

Rheology Analysis

The rheological properties of LCBBC hydrogel and LCBBC/AuNRs nanocomposite hydrogel were analyzed using the AR-G2 rheometer (TA Instruments, Minimum Torque Oscillation: 0.003 μN.m and Torque Resolution: 0.1 μN.m) with peltier plate-temperature control. A cone-plate geometry with a diameter, d = 40.0 mm and cone angle (deg: min: sec = 1:59:24), was used for more fluid-like samples with approximately 2 ml of sample added at experimental temperatures. Parallel plate geometry (20 mm diameter) was used for more solid-like samples. Dynamic frequency sweep experiments were performed from 10^{-2} to 10^2 $rads^{-1}$ between 10 and 100 °C while cooling the samples. Only linear viscoelastic properties were measured for dynamic frequency and temperature ramp experiments and the linear range was determined using

strain sweep experiments. Strength of the hydrogels was qualitatively ascertained by running dynamic strain sweeps at oscillation frequency (ω) of 6.283 $rads^{-1}$. In each experiment 30 minutes conditioning time was allowed for thermal equilibration and to get rid of any shear history introduced while transferring the copolymer solutions to the appropriate geometry.

Microstructure Analysis

The freeze-dried LCBBC/AuNR nanocomposite was further subjected to compression molding process at 80 ^{o}C for 1 h to give discoid sheet sample for further analysis.

Cryo-SEM study was performed on FEI Nova NanoSEM 450 with an accelerating voltage of 120 KV. The LCBBC/AuNRs hydrogel sample was placed on a silicon wafer and quickly plunged into liquid nitrogen and stored 24 h before imaging and observed under cryo-SEM without further staining. The morphologies of the nanorods were imaged by Tecnai T12 TEM with accelerating voltage of 120 kV. Specimens were prepared by dropping solution of the nanorods on to copper grid coat with Formvar film, followed by air-drying. The LCBBC/AuNPs sample was synthesized and characterized according to our published work.[3]

References

1. I. W. Hamley, V. Castelletto, P. Parras, Z. B. Lu, C. T. Imrie and T. Itoh, *Soft Matter* 2005, **1**, 355-363
2. J. Lai, D. Filla and R. Shea, *Macromolecules* 2002, **35**, 6754-6756
3. C.T. Nguyen, T.H. Tran, X. Lu and R.M. Kasi, *Polym. Chem.* 2014, **5**, 2774-2783
4. B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.* 2003**, 15***,* 1957-1962
5. C. T. Nguyen, Y. Zhu, X. Chen, G. A. Sotzing, S. Granados-Focil and R. M. Kasi, *J. Mater. Chem. C,* 2015, **3**, 399-408

Table S1. Molecular characterization of as-synthesized LCBBC[5]

Polymer	M_n (g/mol)	PDI	Weight fraction [c] (%)		Conversion [d] (%)
	GPC [b]		PMA-*g*-PEO	PC5MA	
PMA-*g*-PEO-thioester	29 150	1.21	100	-	82
LCBBC-thioester	38 420	1.31	70	30	90
LCBBC[a]	38 540	1.35	70	30	95 [e]

LCBBC comprised of PEO block (2000 g/mol), and poly(cholesteryl 6-methacryloyloxyhexaneoate) (PC5MA) block, where the cholesteryl mesogen was attached to the polymerizable methacrylate moiety via 5 methylene spacer.

[a] LCBBC was obtained from reduction of LCBBC-thioester by *n*-butylamine in THF, [b] Determined by GPC calibrated at 40 ^{o}C with THF as the mobile phase with polystyrene standards, [c] The ratio of the integrals of peaks by ^{1}H-NMR spectra at 5.33 ppm (olefin group in cholesteryl moiety) and 3.64 ppm (PEO repeating unit) is used to calculate the weight fraction of the LCBBC, [d] Conversion of monomer to polymer was determined using ^{1}H- NMR analysis, [e] Conversion of reduction was determined using UV-visible spectra;

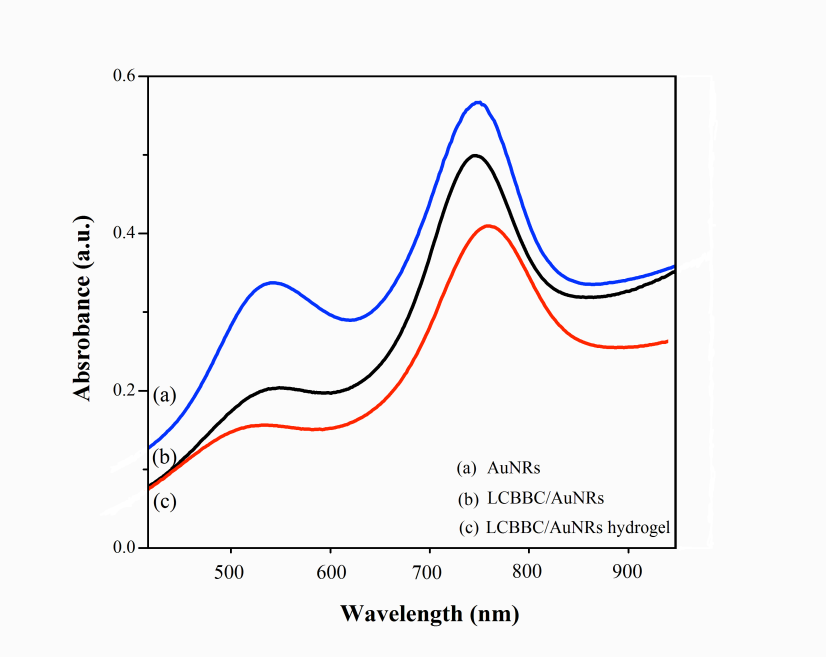


Figure S1. UV-visible absorption spectra of AuNRs, LCBBC/AuNRs in DMF solution, and LCBBC/AuNRs nanocomposite hydrogel. The absorbance of these samples exhibited two plasmon bands including shorter wavelength (transverse plasmon oscillation) at 520 nm and longer wavelength (longitudinal plasmon oscillation- LSPR) at 740 nm

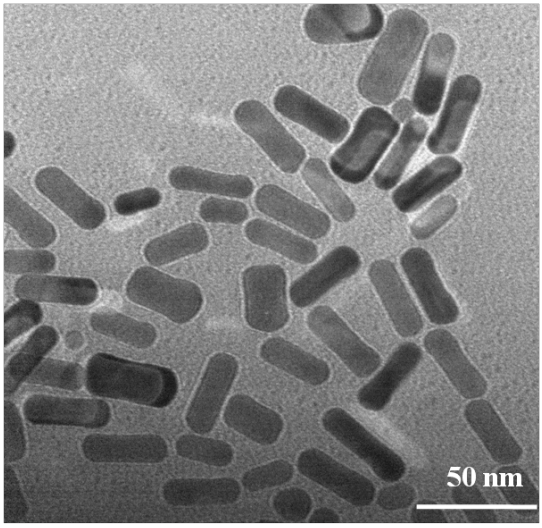


Figure S2. TEM image of ligand protected AuNRs by seed-mediated method with an average dimension of 25 x 5 nm, obtained by dropping solution of the nanorods on to copper grid coat with Formvar film, followed by air-drying

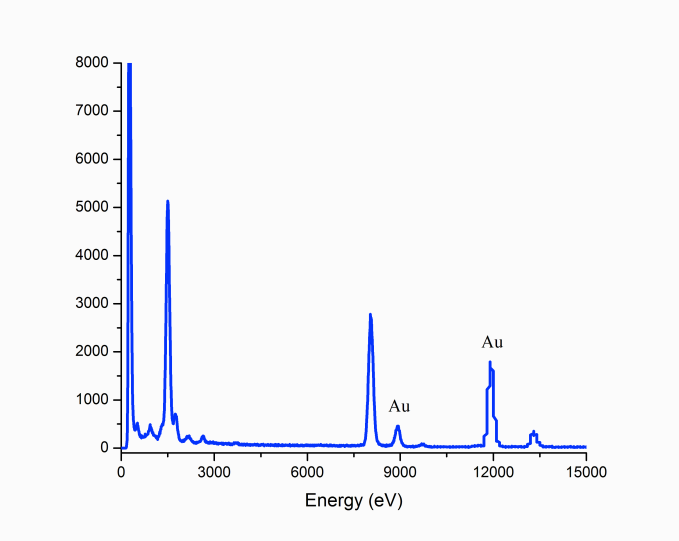
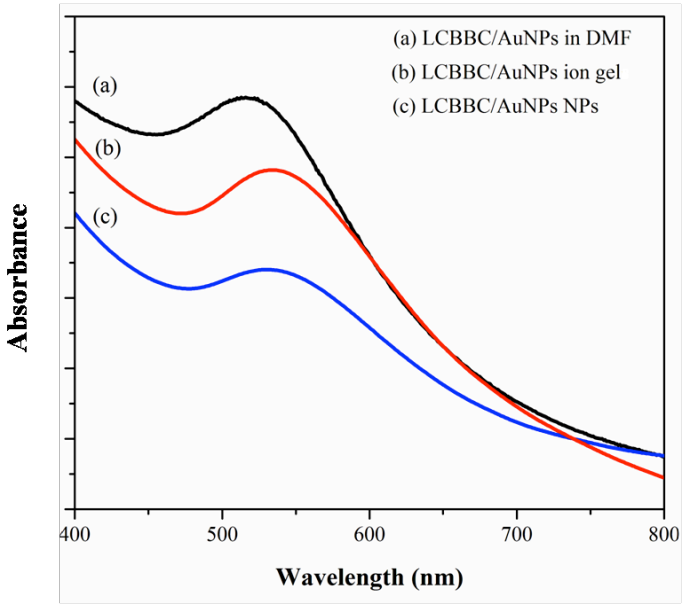


Figure S3: EDX spectroscopy of LCBBC/AuNRs nanocomposite hydrogel with a quantitative elemental composition of Au atom about 3.78 wt %

(A)



(B)

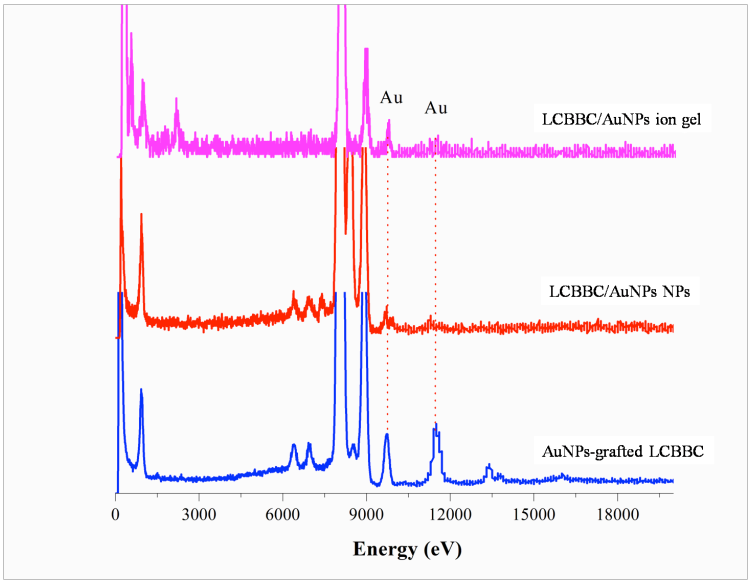


Figure S4: (A) UV-visible absorption spectra of (a) LCBBC/AuNPs in DMF, (b) LCBBC/AuNPs nanoparticles in ILs, and (c) LCBBC/AuNPs ion gels; (B) EDX spectroscopy of AuNPs within AuNPs-grafted LCBBC, LCBBC/AuNPs NPs in IL, and LCBBC/AuNPs ion gel.[3,5]

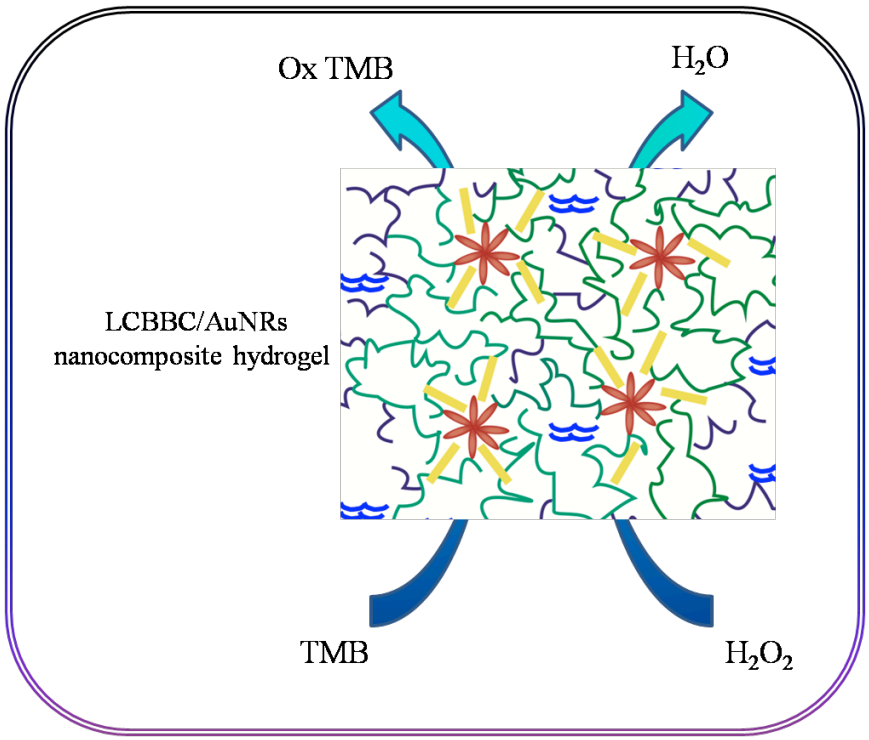


Figure S5. A schematic for catalytic activity based on LCBBC/AuNRs nanocomposite hydrogel in which LCBBC/AuNRs was used as peroxidase mimics to catalyze oxidation of peroxidase substrate 3,3,5,5-tetramethylbenzidine (TMB) in the presence of H_2O_2 as oxidized

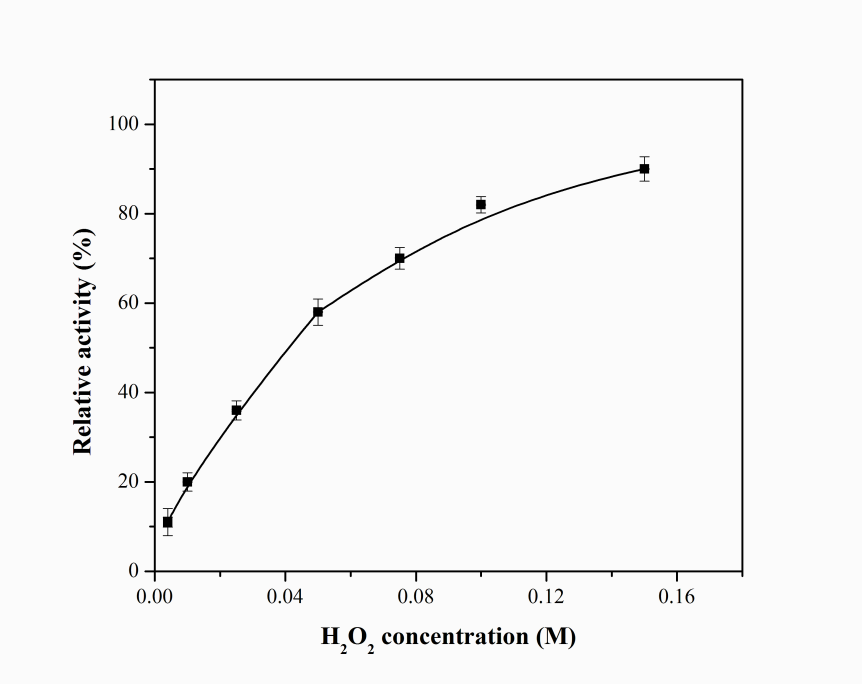


Figure S6. A H_2O_2 concentration–response curve using the LCBBC/AuNRs nanocomposite hydrogel with a various H_2O_2 concentration range from 4 μM- 150 mM at 40 °C for 10 min