Electronic Supplementary Information

Asymmetric Surface Modification of Yeast Cell for Living Self-Assembly

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**Experimental section**

**Materials**

The polystyrene serving as film matrix (PS, molecular weight: 349 kg /mol) was obtained from Sigma-Aldrich. Didodecyldimethylammonium bromide (DDAB) that was used as the stabilizer of water droplets and modifier of inner wall of voids was from Aladdin. The recognition agent of cells 3-aminophenylboronic acid hydrochloride (APBA) for a linker, and the coupling agent 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) for esterization reaction, were purchased from J&K Scientific Ltd. The dye alizarin red (ARS) was obtained from the Tianjin Guangfu Fine Chemical Research Institute, China. The mercaptopropionic acid modified CdTe (QDs) nanoparticles were synthesized according to the literature in this lab [1].

**One-pot preparation of QDs modified porous polymer film**

A mixture of PS (6 mg/mL) and DDAB (0.2 mg/mL) was prepared by simply adding them to a certain volume of dichloromethane (DCM). For the preparation of the microemulsion solution, a typical procedure was to add distilled water (18.2 MΩ/cm) with 0.5 mM QDs with red emission, to the DCM solution of PS mixed with DDAB while maintaining the volume of water fraction at 5%. The resulting mixture was shaken for 1 min to disperse the aqueous solution in the organic phase, forming a translucent microemulsion. Then, 20 μL of the microemulsion was cast onto a glass substrate under a relative humidity of 30–40% at ca. 27 °C. With the solvent evaporation, the porous PS hybrid films in which the QDs modified on the inner wall of voids was obtained in one-pot.

**Surface reaction of APBA onto the inner wall of patterned voids**

For the incorporation of APBA into the cavities, porous PS film with QDs on the cavities was put into a mixture of 1 mg/mL APBA and 5 mg/mL EDC in pH=7.4 phosphate buffered saline (PBS) solution for 3 h, followed by washing with water three times and drying in air. For the verification of covalent incorporation, the APBA contained film was dipped into an aqueous solution of 1mg/mL ARS for 3 h, followed by washing with water three times and drying in air.

**Adsorption of yeast cells into the patterned voids**

As a typical procedure, the yeast Saccharomyces cerevisiae cells (BY4741, 4 mL) that are in their stable period were dropped onto the patterned porous polymer film whose inner wall of voids were initially modified with QDs and then APBA at 30 °C. After 1 h of incubation, the film was rinsed three times with PBS solution (pH=7.4) to remove unspecific adsorbed yeast cells. Then the film containing the adherent yeast cells were incubated in 4 ml of fresh yeast extract peptone dextrose (YPD) media for another 6 h at 30 °C.

**Preparation of green luminescent QD complex with APBA**

For the modification of APBA on the surface of QDs, the QDs with green emission in solution was added into a mixture buffer solution (pH=7.4, PBS) of 2 mg/mL APBA and 10 mg/mL EDC, in which the concentration of QDs is maintained at 2 mM. After a 3 h gentle stirring at room
temperature, the reaction mixture was centrifuged (5000 rpm, 5 min) to remove unreacted residues, giving APBA modified QDs product. The obtained samples were stored in dark place for the following use.

Asymmetric surface modification of yeast cells

For the half-face modified cells on the bottom of voids, the cell assembled porous polymer film mentioned at “Adsorption of yeast cells into the patterned voids” was immersed into a 0.6 M sodium chloride (NaCl) solution for 40 min. Because of the breaking down of the salt for the electrostatic interaction between DDABs and QDs at the interface of inner voids, the modified cells release from cavities, followed by three times of washing with pH 7.4 PBS aqueous solution. For the whole surface modification toward Janus cells, the initially cell assembled porous polymer film was further treated with 0.5 mM QDs-APBA complex (with green emission) in pH 7.4 PBS solution for 3 h, followed by washing with PBS solution for three times. Then, the cell assembled film was immersed into a 0.6 M NaCl solution for 40 min, following by washing the films three times. The resultant solution undergoes a centrifugation (12000 rpm, 5 min) to collect the modified cells in the solution.

Covalent self-assembly of yeast cells

There are two ways for the interaction between cells, the fully modified Janus cells with half-modified Janus cells and virgin cells. As an example, the fully modified cells, after releasing from the porous polymer film, were mixed together with the half decorated cells from another film under the condition of controlling ratio of them at ca. 1:1 in PBS aqueous solution. The mixture was allowed to culture for 5 h. The co-assembly of fully modified cells with the virgin cells were performed under the same condition. For the co-assembly of free cells onto the cells fixing on porous polymer film, the free half-decorated cell solution were dropped onto the porous polymer film that accommodated the cells in the voids for 5 h. After washing with PBS solution three times to remove the unreacted cells, the cells’ co-assembly was then released from the cavities on the polymer film by emerging in NaCl solution, as mentioned above.

The detection of yeast activity

To identify the activity of yeast cells that encountered half-face and whole-face modification, as well as assembly process, the half-face modified yeast with QDs in red emission, the whole-face decorated yeast with QDs half in red and the other half in green emission, and the dimer assembly, were placed into the YPD media for 5 min. And then they were washed quickly with PBS solution following a procedure of centrifugation (5000 rpm, 5 min). The obtained samples were detected by CLSM.

Disassembly of yeast cell assemblies

To a 0.5 mL solution of cells’ dimer assembly was added 20 μL 10 mM glucose solution and the mixture was cultured 100 min for measurement. 2 mM and 5 mM glucose solutions were also selected to investigate the disassembly behavior. Similarly, 2 mM ARS was also added to test the
behavior, but the culture time was set at 0.5, 1.0, and 3.0 h, respectively.

**Measurements**

Scanning electron microscopic (SEM) images were collected using a Jeol JSM-6700F field emission scanning electron microscope. X-ray photoelectron spectroscopic (XPS) analysis was performed on a VG Escalab MKII spectrometer with Al Ka (1486.5 eV) from an achromatic X-ray source. Confocal laser scanning microscopic (CLSM) images were obtained using an Olympus FluoView FV1000. Analysis of CLSM data was carried out by using a FV10 ASW software.

**Data of characterizations**

![Histograms referring to the size-distribution of cavities in (a) width and (b) depth of pores on polymer film.](image1)

*Fig. S1* Histograms referring to the size-distribution of cavities in (a) width and (b) depth of pores on polymer film.

![CLSM images of APBA and QDs modified porous polymer film (a) without and (b) with their immersion in ARS dye solution, and (c) XPS spectrum of APBA and QDs decorated porous film of (a).](image2)

*Fig. S2* CLSM images of APBA and QDs modified porous polymer film (a) without and (b) with their immersion in ARS dye solution, and (c) XPS spectrum of APBA and QDs decorated porous film of (a).
Fig. S3 XPS spectra of the porous polymer film with the voids modified with (a) QDs and (b) QDs and then APBA, where the peaks (402.3 and 299.8 eV) source from N1s of DDAB and APBA.

Fig. S4 CLSM images of half-face modified cells on optical mode.

Fig. S5 CLSM images of cells anchored on porous film, which have been modified on bottom with QDs in red-emission and on top surface with QD-APBA complex in green-emission, taken on (a) optical, (b) green fluorescent, and (c) green and red emission merged modes.
Scheme S1. The schematic procedures of asymmetric modification and release of yeast cells.

Fig. S6 CLSM images of double-face modified cells performed on (a) red and (b) green fluorescent mode.

Scheme S3. The schematic drawing for the surface groups on the area of half-face modified cell surface covered with QDs in red emission.

Scheme S4. The schematic drawing for the surface groups on area of double-face modified cell surface after modification by APBA and QDs with green emission and another QDs with red
emission.

**Fig. S7** CLSM images for assemblies of whole-face decorated cells (QDs in red and green emission) fixing on the porous polymer film interacting with half-face modified cells (QDs in red emission) and then released, taken on (a) optical and (b) fluorescent modes.

**Fig. S8** CLSM image of the assembly of double-face modified cells interacting with virgin cells in solution under the condition for nearly equal amount of these two cells.
**Fig. S9** CLSM image of assemblies for double-face modified cells interacting with virgin cells in solution under the condition for a little excess of double-face modified cells.

**Fig. S10** CLSM image of assemblies for double-face modified cells interacting with virgin cells in solution under the condition for larger excess of double-face modified cells.
Fig. S11 CLSM images of assemblies from combination of double-face modified Janus cells interacting with unmodified cells (excess).

Fig. S12 CLSM images of assemblies from double-face modified Janus cells (excess) interacting with unmodified cells. The top right pictures are the simulated packings for corresponding observed results. The scale bar is 5 μm.

Scheme S5. The schematic drawing of (a) close packing and (b) unfolding modes for rigid balls with identical diameter, (c) maximum number packing mode for flexible Janus cells.
Scheme S6. The schematic drawing for the possible assembly fashions of whole-face modified cells with half-face decorated cells.
Fig. S13 CLSM images of (a) half-face modified, (b) whole-face modified Janus yeast cells, and (c) Janus cell assemblies of (a) and (b) after encountering a further culture.
**Fig. S14** Growth curves based on the OD$_{600}$ at 600 nm for (a) initial yeast cells in (as control), (b) double-face modified Janus cells, and (c) Janus cell assemblies (dimer).
Scheme S7. The chemical reactions occurred on the disassembly process of yeast cell assemblies.
**Fig. S15** CLSM images of dimer yeast cell assemblies (double-face modified cells with virgin cells) in the presence of (a) 2, (b) 5, and (c) 10 mM glucose after encountering a 100 min of
Fig. S16 CLSM images of dimer yeast cell assemblies (double-face modified cells with half-face modified cells) after adding 2 mM Alizarin Red and culturing for (a) 0.5, (b) 1, and (c) 3 h.

Reference
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