Supporting Information

Evaluation of the Photo-degradation of Alzheimer's Amyloid Fibrils with a label-free approach

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Materials and Chemicals

Aβ42 powder was purchased from Abbiochem Co., Ltd. (amino acid sequence: DAEFRRHDSGY EVHHQKLVFFAEDVGSNKGAIIGLMVGGVVIA). The meso-tetra (4-sulfonatoph-enyl) porphyrin used in this experiment was purchased from Frontier Scientific, Inc (Logan, Utah, USA). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Ethanol was purchased from Sinopharm Chemical Reagent Co.,Ltd., (Shanghai, China). The Au-coated QCM chips (AT-cut, 5 MHz) were purchased from Dongwei Biotech (Hangzhou, China).

Preparation of Aβ42 aggregates

2 mg of Aβ42 power was dissolved in 2 mL of HFIP, followed by sonication for 10 s. After repeating the sonication 3 times, the solution was placed in a thermo-shaker (PHMT, Grant Instruments, England) at 350 rpm/min at 25℃ overnight. Finally the solution was stored at -20℃ until use. After 20 μL of Aβ42 solution was taken into a 1.5 mL tube and sealed with the parafilm, the tube was put in a vacuum drying oven for 1 hours at 25 ℃ in order to evaporate HFIP fully. Subsequently, 200 μL of MilliQ water was added to the tube, to make a final Aβ42 concentration of 20 μM. Then the solution was sonicated for 5 seconds and vortexed for 5 seconds (repeated for 3 times). Finally, the Aβ42 solution was incubated on a thermo-shaker at 350 rpm/min and at 37 ℃ for 72 hours.

Quartz crystal microbalance (QCM) measurement

We used a QCM apparatus and Au-coated QCM chips (Qsense E4, Biolin Ltd., Sweden) for the measurement of the degradation efficiency of Aβ42 fibrils. The Au-coated QCM chips were loaded into the QCM chamber. The Aβ42 fibrils in Milli-Q water was introduced into the chamber. After establishing the baseline, 200 μL of 20 μM Aβ42 fibrils (which had been incubated for 72 hours at 37℃ before QCM measurements) was injected into the flow channel of the QCM at 37℃ at a flow rate of 50 μL/min. The Aβ42 fibers deposited on QCM chip and induced a resonant frequency change(Δf).Next, we detected the degradation efficiency of Aβ42 fibrils by porphyrins upon UV irradiation. After establishing the baseline of Aβ42 fibrils, 200 μL of porphyrin solution (20μM) was injected into the QCM at 37℃ at a flow rate of 50 μL/min.

Circular dichroism (CD) spectroscopy

Circular dichroism measurements were performed in a spectropolarimeter JASCO PTC-348W1 (Jasco, Gross-Umstadt, Germany) at room temperature. CD spectra were performed between 200 and 250 nm with a 0.1 cm quartz cells. The slit-width was set at 2 nm with scan speed of 50 nm/min. The signal of the MilliQ water has been subtracted as the background noise. Measurements were carried out with a sample volume of 200 μL.

Thioflavin T (ThT) fluorescence assay

25 μL of amyloid fibrils solution (20μM), 100 μL MilliQ water and 25 μL ThT (1 mM) was mixed together. Then the ThT fluorescence of the mixed solution was measured by a fluorescence spectrophotometer (F-4500; Hitachi) with the excitation light at 450 nm and the emission light at 485 nm with a 1 cm quartz cells.

Atomic force microscopy (AFM)

The gold chip was taken out after the QCM experiment and then dried for 10 min in the air, and the residue liquid on the surface was removed. All AFM were performed on MultiMode VIII SPM (Bruker Company, United States) in tapping mode with an ultra-sharp silicon cantilever with a nominal spring constant of 26 N/m

in the air (OMCL-AC160TS-R3; Olympus). AFM imaging was gained at a scan frequency of 1 Hz and with 512×512-pixel resolution.

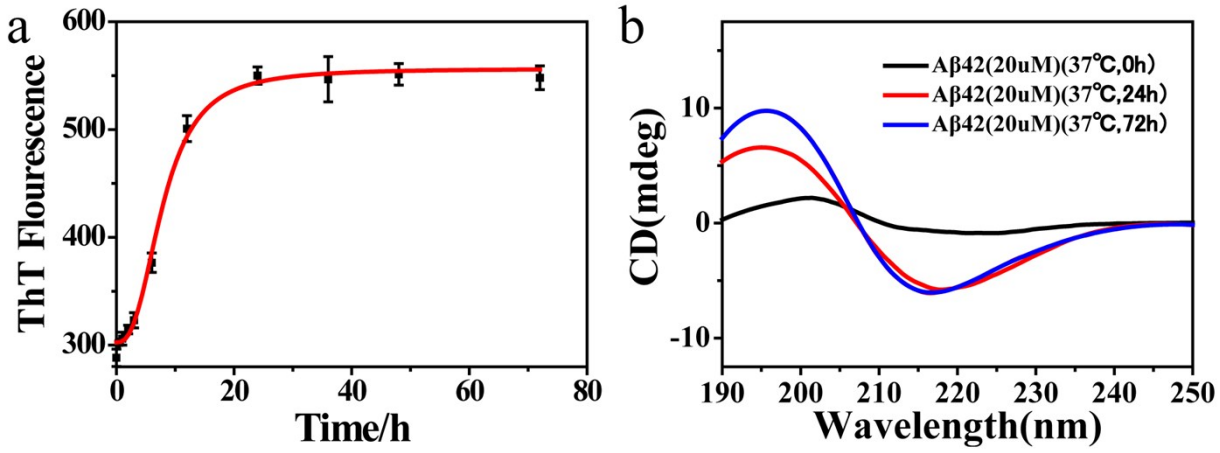

Fig. S1. Characterization of Aβ42 self-assembly (20 μM). (a) ThT assay of Aβ42 self-assembly process over time; (b) Circular dichroism (CD) spectra of Aβ42 assemblies with different incubation time of 0, 24, and 72 hours.

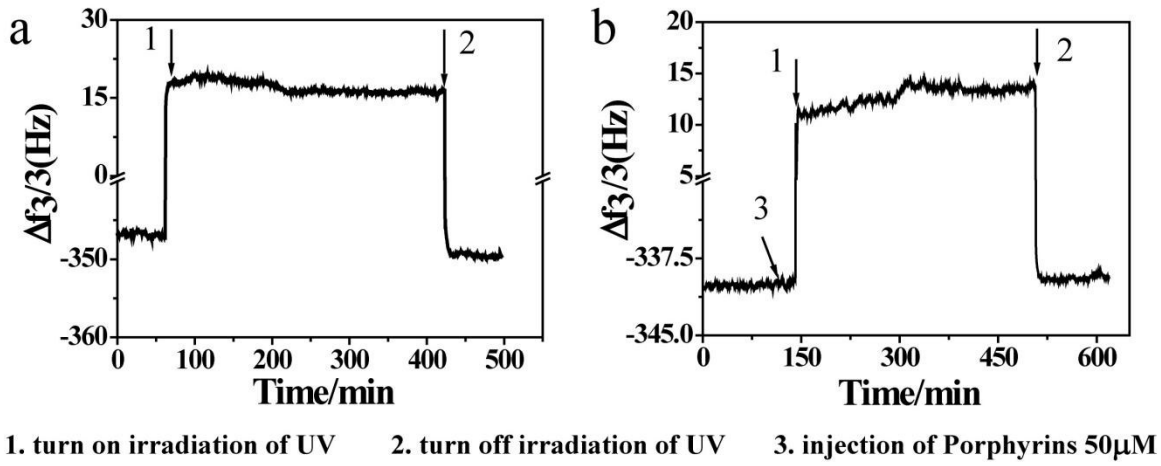

Fig. S2. QCM signal obtained in aqueous solution under 6-hours UV irradiation without (a) and with porphyrin (b), respectively. The minor fluctuation (~2 Hz) can be ignored compared to the frequency change caused by fiber deposition.

We found that the baseline enhancement by photoirradiation might be ascribed to the mass variation of water layer on the interface of QCM by the light irradiation, in the previous research, the observed frequency increase (mass decrease) can be ascribe to the photo-induced reversible desorption of water molecules from Au electrode surface of the QCM due to the interfacial property changes. (Anal Sci, 2009, 25 (9): 1069-1075.) Under the light irradiation on/off, the water-layer on the QCM Au chip would be disassociated/associated irreversibly from the QCM chip surface, inducing the baseline shifting dramatically. Therefore, minor fluctuation of the frequency change is feasible, and it can be also ignored compared to the frequency change caused by fiber deposition.

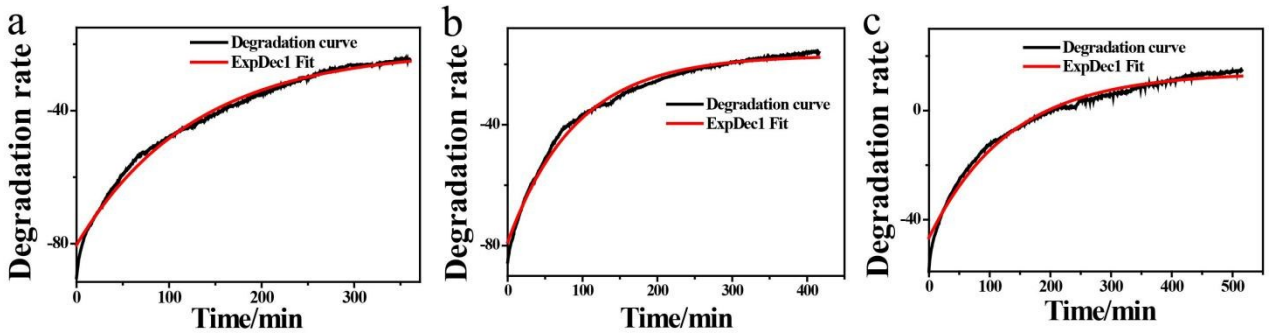

Fig. S3. (a—c) The curve equation of the degradation process can be obtained by nonlinear fitting, The black line represents the degradation curve between 1 and 2 (Fig. 2b). The red line is the nonlinear fitting curve of the black line (a—c). (a) when the porphyrin concentration is 1μM, The curve equation is y=-21.71 - 58.67*exp(-x/126.49). (b) when the porphyrin concentration is 2.5 μM, The curve equation is y=-17.05 - 61.79*exp(-x/91.09). (c) when the porphyrin concentration is 5 μM, The curve equation is y=13.88 - 60.54*exp(-x/132.55) .