Modulating the photo-exciting process of photosensitizer to improve *in vitro* phototoxicity by preparing its self-assembly nanostructures

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being left to stand for 3 days. The absorption intensity of the characteristic absorbance bands of nanostructures displayed no obvious change but that of the HA aqueous solution sharply decreased. As shown in Fig. S3A, HA and nanostructures showed a remarkable difference after compared with their original spectra. If there were sedimentation, their absorbance intensity would were kept in dark for 3 days. The absorption spectra of their supernatant fluid were detected and by UV-Vis spectra (we added these part in ESI). The aqueous solution of HA and nanostructures

Fig. S1. The process detection for HA-nano-1 (2), HA-nano-2 (3), HA-nano-3 (4) and HA-nano-4 (1) using CD spectra (A) and UV-Vis spectra (B) at their self-assembly pH condition.

Fig. S2. Time-dependent bleaching of ADPA caused by $^1$O$_2$ generated by HA-nano-1 (A), HA-nano-2 (B), HA-nano-3 (C) and HA-nano-4 (D) upon 470 nm photo-irradiation was monitored as a function of time.

The stability of the nanostructures were not obtained by naked eye observation, but obtained by UV-Vis spectra (we added these part in ESI). The aqueous solution of HA and nanostructures were kept in dark for 3 days. The absorption spectra of their supernatant fluid were detected and compared with their original spectra. If there were sedimentation, their absorbance intensity would decreased. As shown in Fig. S3A, HA and nanostructures showed a remarkable difference after being left to stand for 3 days. The absorption intensity of the characteristic absorbance bands of nanostructures displayed no obvious change but that of the HA aqueous solution sharply
decreased in intensity. We compared their stability (Fig. 5) by calculating the absorption intensity decreased percent.

Besides, the nanostructures in the supernatant were not formed aggregates or but still kept the well-dispersed condition. We detected their TEM image of the nanostructures in the supernatant fluid after keeping for 3 days in dark. And results indicated that no obvious aggregation were detected (Fig. S3B).

**Fig. S3.** (A) Absorption spectra changing of aqueous solutions of free HA (1), HA-nano-1 (2), HA-nano-2 (3), HA-nano-3 (4) and HA-nano-4 (5) left to stand for 3 days (black line: origin absorbance spectra; red line: the absorption spectra of their supernatant fluid after keeping for 3 days in dark); (B) TEM image of HA nanostructures in the supernatant fluid after stand for 3 days, HA-nano-1 (1), HA-nano-2 (2), HA-nano-3 (3) and HA-nano-4 (4).

The fluorescence quantum yield of all samples were directly detected using Horiba Jobin Yvon Fluoro Max-4 spectrofluorometer equipped with an integrating sphere accessory (Horiba Jobin Yvon). The fluorescence quantum yield of HA and nanostructures were not high, which indicated after been excited by light, few singlet excited HA molecules (\(1^{\text{PS}}\)) can relax back to the ground state (\(0^{\text{PS}}\)) via the emission of fluorescence. Most \(1^{\text{PS}}\) participated the photosensitive process to generate singlet oxygen as photosensitizer.

**Table S1.** Fluorescence quantum yield of HA, HA-nano-1, HA-nano-2, HA-nano-3 and HA-nano-4 in aqueous solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HA</th>
<th>HA-nano-1</th>
<th>HA-nano-2</th>
<th>HA-nano-3</th>
<th>HA-nano-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence quantum yield</td>
<td>4.02%</td>
<td>3.95%</td>
<td>3.33%</td>
<td>3.54%</td>
<td>4.15%</td>
</tr>
</tbody>
</table>
**Fig. S4.** Fluorescence decay curves of HA (A), HA-nano-1 (B), HA-nano-2 (C), HA-nano-3 (D) and HA-nano-4 (E) associated with the lamp profile. (Time calibration = $2.194787 \times 10^{-10}$ s/channel)