Supporting Information

ZnO@silica core-shell nanoparticles with highly luminescence and stability in cell imaging

Hua-Juan Zhang, a Huan-Ming Xiong, * b Qing-Guang Ren, * a Yong-Yao Xia b and Ji-Lie Kong c

a Center of Analysis and Measurement, Fudan University, 220 Hand Road, Shanghai 200433, P. R. China, E-mail: qgren@fudan.edu.cn
b Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, 220 Hand Road, Shanghai 200433, P. R. China, E-mail: hmxiong@fudan.edu.cn
c Department of Chemistry and Institutes of Biomedical Sciences, Fudan University, 220 Hand Road, Shanghai 200433, P. R. China
Figure S1. Photoluminescence spectra in water of (A) ZnO-A@silica NPs, (B) ZnO-B@silica NPs and (C) ZnO-C@silica NPs versus the standard rhodamine 6G ethanol solutions (QY = 95%) when evaluating the quantum yield of ZnO@silica nanoparticles. (A) ZnO-A@silica NPs and rhodamine 6G ethanol solutions were excited at 340 nm. (B) ZnO-B@silica NPs and rhodamine 6G ethanol solutions were excited at 350 nm. (C) ZnO-C@silica NPs and rhodamine 6G ethanol solutions were excited at 350 nm.

In general, the quantum yield values were determined by the following formula according to the method described by Crosby and Demas (J. Phys. Chem., 1971, 75, 991.).
QY_x = QY_r[A_x(λ_x)/A_r(λ_r)](n_x^2/n_r^2)(D_x/D_r)

where A(λ) is the absorbance of the solution at the exciting wavelength λ, n is the average refractive index of the solution to the luminescence, D is the integrated area under the corrected emission spectrum, and subscripts x and r refer to the sample and reference solutions, respectively (For water, n = 1.33; For ethanol, n = 1.36.). Rhodamine 6G ethanol solution (QY = 95%) was chosen as reference solution. First, we diluted the R6G solution and the ZnO sample solution to suitable concentrations. Secondly, we measured their UV-Vis absorption spectra and find a proper wavelength at which both solutions had the same absorbance intensity (make λ_r = λ_x). Thirdly, we conducted the PL measurements on both solutions using the above wavelength as the excitation wavelength. Finally, we calculated the QY according to the above formula.

Figure S2. Photoluminescence spectra of (A) ZnO-A@silica, (B) ZnO-B@silica and (C) ZnO-C@silica in RPMI Medium 1640. After mixing each ZnO sample with RPMI Medium 1640 at a ratio of 1:10 for one day, the photoluminescence spectra of the mixture and RPMI Medium 1640 was recorded on a Varian Cary Eclipse fluorescence spectrophotometer. RPMI Medium 1640 exhibited blue emission peak at 400 nm under 330 nm and 340 nm excitation, while under the excitation of 360 nm, RPMI Medium 1640 exhibited a weak emission at 530 nm. The PL spectra of ZnO@silica nanoparticles in cell culture were similar with those in water, except that there was a weak emission peak at 400 nm for ZnO-A@silica and ZnO-B@silica samples. This phenomenon is ascribed to the contribution of RPMI Medium 1640.
Figure S3. Photoluminescent spectra of (A) ZnO-A@silica NPs, (B) ZnO-B@silica NPs and (C) ZnO-C@silica NPs in PBS; After mixing each ZnO sample with PBS at a ratio of 1:10 for one day, the photoluminescence spectra of the mixture and PBS was measured. PBS exhibited no fluorescence emission under 310 nm to 360 nm excitation. The PL spectra of ZnO@silica nanoparticles in cell culture were similar with those in water.
<table>
<thead>
<tr>
<th>Control 0min</th>
<th>Control 10min</th>
<th>Control 20min</th>
<th>Control 30min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 40min</td>
<td>Control 50min</td>
<td>Control 60min</td>
<td>Control 70min</td>
</tr>
<tr>
<td>Control 80min</td>
<td>Control 90min</td>
<td>Control 100min</td>
<td>Control 110min</td>
</tr>
<tr>
<td>Control 120min</td>
<td>Control 130min</td>
<td>Control 140min</td>
<td>Control 150min</td>
</tr>
<tr>
<td>Control 160min</td>
<td>Control 170min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Figure S4.** Confocal luminescence images of Hela cells incubation with 50 mg/L ZnO@silica NPs at 37 °C. The cells treated with (A) ZnO-A@silica NPs, (B) ZnO-B@silica NPs and (C) ZnO-C@silica NPs were excited at the wavelength of 365 nm. The control experiment was conducted at the same conditions without ZnO NPs. The actual fluorescence intensity of the sample = F(t) - F(0), where F(t) represented metrical fluorescence intensity of the sample and F(0) represented metrical fluorescence intensity at the time of t = 0 min.

The cellular fluorescence can be observed after 40 min treatment with ZnO-A@silica NPs or ZnO-C@silica NPs and 60 min with ZnO-B@silica NPs. There were no obvious changes of cellular morphology within 170 min except that there were several blebs forming on the cellular membrane in the treatment group of ZnO-C@silica NPs. A gradual growth in the fluorescence intensity indicates the uptake of the NPs by the Hela cells.

**Figure S5.** HRTEM images and size distribution graphs of (A) ZnO-A@silica, (B) ZnO-B@silica and (C) ZnO-C@silica. See below.