SUPPORTING INFORMATION

to

Mesoporous titanium zirconium oxide nanospheres

with potential for drug delivery applications

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Figure S1. Selected area electron diffraction pattern (a) and XRD pattern (b) of the calcined mesoporous TiZr30 oxide nanospheres. The featureless electron diffraction pattern and XRD trace reveal the amorphous nature of the resultant oxide nanospheres.
Figure S2. Variation in the zeta potentials of the mesoporous TiZr oxide nanospheres with different compositions. Inset is a magnification of the data around pH 5.0.
Table S1. Physical properties of calcined mesoporous TiO$_2$ and ZrO$_2$ nanospheres with a diameter of ~360 nm.$^a$

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-360nm</td>
<td>106 ± 2</td>
<td>14</td>
<td>0.34</td>
</tr>
<tr>
<td>ZrO$_2$-360nm</td>
<td>116 ± 2</td>
<td>6.1</td>
<td>0.20</td>
</tr>
</tbody>
</table>

$^a$ $S_{\text{BET}}$ = BET specific surface area obtained from nitrogen adsorption data in the P/P$_0$ range from 0.05 to 0.20; Pore diameter was determined by using the Barrett-Joyner-Halenda model from the nitrogen adsorption data; and pore volume was calculated from the adsorption isotherm at P/P$_0$ = 0.98.

Such TiO$_2$ and ZrO$_2$ nanospheres possess relatively low specific surface areas as compared to the TiZr oxide nanospheres listed in Table 1. The substitution of Ti$^{4+}$ ions by the Zr$^{4+}$ could effectively retard the crystallization of TiO$_2$, thus giving rise to mixed oxide nanospheres with high surface area and uniform mesopores, promising properties for drug delivery.
Table S2. Physical properties of the calcined mesoporous Ti-Zr oxide spheres with a diameter of ~780 nm.6

<table>
<thead>
<tr>
<th>Sample name</th>
<th>S(_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiZr30-780nm</td>
<td>413 ± 4</td>
<td>3.4</td>
<td>0.39</td>
</tr>
<tr>
<td>TiZr50-780nm</td>
<td>315 ± 3</td>
<td>3.9</td>
<td>0.34</td>
</tr>
<tr>
<td>TiZr70-780nm</td>
<td>306 ± 3</td>
<td>3.9</td>
<td>0.33</td>
</tr>
</tbody>
</table>

6\(S_{\text{BET}}\) = BET specific surface area obtained from nitrogen adsorption data in the P/P\(_0\) range from 0.05 to 0.20; Pore diameter was determined by using the Barrett-Joyner-Halenda model from the nitrogen adsorption data; and pore volume was calculated from the adsorption isotherm at P/P\(_0\) = 0.98.

Comparison between the current spheres and previously published spheres (Ref. 26 in manuscript): Such large Ti-Zr oxide spheres (~780 nm in diameter) were synthesized with a mole ratio of H\(_2\)O/(Ti+Zr) = 3, while the smaller Ti-Zr oxide nanospheres investigated in this study were fabricated using an increased water content (H\(_2\)O/(Ti+Zr) = 8 in mole). The increased water content can significantly accelerate hydrolysis of the metal alkoxides and subsequent condensation of the titanium or zirconium oligomers derived from the hydrolysis process.\(^{[1,2]}\) It is worth noting that these small Ti-Zr oxide nanospheres were intentionally fabricated using this carefully updated synthesis to obtain mixed oxide nanospheres suitable for drug delivery application. As shown in the above Table S2, the TiZr30-780nm and TiZr50-780nm spheres possess comparable physical properties to the counterpart spheres with diameters of ~360 nm. TiZr70-780nm spheres have a relatively higher specific surface area than the ~360 nm counterparts, probably due to the relatively low hydrolysis and condensation kinetics which results in a more homogeneous Ti-Zr-O matrix when the mole ratio of H\(_2\)O/(Ti+Zr) is 3.

References