Results

Synthesis:

For better visualization of the synthesis procedure, a photograph of the used 1L stainless steel autoclave (Parr Instruments) is given in Figure S1.

![Figure S1. Photograph of the autoclave used for nanoparticle synthesis (1L stainless steel reaction vessel, Parr Instruments).](image)

The sample was obtained in form of a slightly yellowish suspension as presented in Fig. S2 A. Figure S2 B shows about 2 g of the obtained product as dried powder. As mentioned in the main text, however, for preparation of functionalized nanoparticles the samples at no stage were dried completely as otherwise the redispersion properties were significantly aggravated.
Thermogravimetric Analysis:

For thermogravimetric analysis, the stable dispersions obtained through post-functionalization were dried at room temperature prior to the measurement and then heated to 950°C at a rate of 20 K min$^{-1}$. All the obtained results are presented in Figure S3. For all samples, three decomposition steps are visible, with the finally remaining weight amounting to 75-78 wt %. The weight loss in the first step below 150°C can mainly be attributed to adsorbed moisture and low-boiling solvents; hence the content of organic stabilizers was calculated to be about 15 wt % in all cases. Monolayers of fatty acids adsorbed onto Fe$_3$O$_4$ nanoparticles were reported to decompose below 400°C,$^{11}$ and therefore, we attribute the second weight loss step to the decomposition of the acid stabilizer, whilst the weight loss above 420°C is assigned to surface-adsorbed benzyl alcohol. Comparison between samples OA 10 and OA 7.5 illustrates that the amount of fatty acid introduced has no influence on the total organic content on the particle surface: although sample OA 10, which was prepared using the 1.33-fold concentration of the fatty acid in chloroform as for OA 7.5, exhibits higher weight loss at lower temperatures (by about 1.2 wt %), the residual weight of both samples after the decomposition of benzyl alcohol, at temperatures above 600°C, is equal.
Characterization details:

The X-ray diffraction (XRD) measurements were performed on a Nonius PDS120 powder diffractometer in reflection geometry with CuKα radiation. The obtained data for Rietveld refinement calculations performed on the diffractogram as shown in the main text, Figure 1, are presented in Table 1.

<table>
<thead>
<tr>
<th>ZrO₂</th>
<th>cubic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Fm-3m (225)</td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>5.1098(7)</td>
</tr>
<tr>
<td>Volume-weighted average crystallite size (nm)</td>
<td>2.8</td>
</tr>
<tr>
<td>Average maximum microstrain e (×10⁴)</td>
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</tr>
<tr>
<td>B(Zr) (Å²)</td>
<td>1.33(2)</td>
</tr>
<tr>
<td>B(O)(Å²)</td>
<td>2.24(7)</td>
</tr>
<tr>
<td>R_wp (%)</td>
<td>6.6</td>
</tr>
<tr>
<td>R_B (%)</td>
<td>2.6</td>
</tr>
<tr>
<td>GoF- index</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Table 1. Structural data and refinement parameters obtained from Rietveld calculations performed on the XRD plot of dried as-prepared ZrO₂ nanoparticles.

Figure S3. Thermogravimetric analysis of nanoparticles after surface modification with various fatty acids, obtained from stable particle dispersions in CHCl₃ after solvent removal (see text for details).
From the obtained average crystallite size of 2.8 nm, the weight of one “average” nanoparticle core is calculated to $6.77 \times 10^{-20}$ g (assuming the density of the ZrO$_2$ cores to be close to the bulk density of 5.89 g cm$^{-3}$). Therefore, in 50 mg sample (taking into account the thermogravimetry results, this amounts to 39 mg nanoparticle cores), there are about 1 µmol of particles. These are stabilized by 0.625 mg OA (or 2.2 µmol), which gives a ratio of 2.2 molecules OA per nanoparticle.

For transmission electron microscopy (TEM) studies, one drop of the diluted (1:20) dispersion of the nanoparticles in CHCl$_3$ was deposited on an amorphous carbon film. A Zeiss EM 912Ω instrument at an acceleration voltage of 120 kV was used for the measurement. $^{13}$C NMR measurements were performed under $^1$H-BB-decoupling on a Bruker DPX 400 spectrometer at 100 MHz, at a sample spinning rate of 20 Hz and a ZG30 pulse program. Thermogravimetric analysis was carried out on a Netzsch thermoanalyzer TG 209 instrument under N$_2$ atmosphere.

$^{13}$C NMR characterization – reaction mechanism (100 MHz, CDCl$_3$, 25°C): Benzyl ether: $\delta$ = 138.1 (C$_{Ph}$, other aromatic signals superimposed by the benzyl alcohol solvent), 72.0 ppm (-CH$_2$-). Isopropanol: $\delta$ = 64.3 (-CH-$\cdot$), 25.1 ppm (-CH$_3$). 4-phenyl-2-butanol: $\delta$ = 142.2, 125.9 (C$_{Ph}$, other aromatic signals superimposed), 67.4 (-CH-$\cdot$), 40.7, 32.0 (-CH$_2$-$\cdot$), 23.3 ppm (-CH$_3$); only detected in traces.
Holography details:

A standard two-beam interference setup based on an Ar-ion laser (Spectra-Physics) emitting at 364 nm (s-polarisation) was used for holographic recording of the transmission unslanted gratings. The overlap of two expanded coherent beams (1.5 cm diameter) with equal intensities resulted in a spatial periodicity ($\Lambda$) of the interference pattern (and the gratings) $\sim 1\mu$m. The samples were exposed to achieve steady-state value of the diffraction efficiency (typically for 10-40 s.); the total recording intensity ($I$) was ranging from 5 up to 20 mW/cm$^2$. The intensity of the recording beams was selected to obtain the highest grating diffraction efficiency. Post flood-exposure of the gratings was performed using Philips PL 10W-10 lamp to reach a complete polymerization of the monomers around the grating area. For all the gratings recorded in the nanocomposites only two diffracted orders (0 and $-1^{st}$) were observed, indicating that thick (volume) gratings were formed (the Klein-Cook parameter\textsuperscript{[2]} for the gratings was of about 50). The diffraction efficiency ($\eta$) of the gratings was calculated as $\eta = I_{\text{dif}} / (I_{\text{tr}} + I_{\text{dif}})$, where $I_{\text{tr}}$ and $I_{\text{dif}}$ are the intensities of the transmitted and the diffracted beams, respectively. For a real-time monitoring of the grating formation ($\eta(t)$) a He-Ne laser beam ($\lambda_{\text{tr}}=633$ nm, s-polarization) placed at the Bragg angle was used since the photoinitiator used in the nanocomposites is not sensitive to red light.

A typical angular selectivity curve of the grating ($\eta$ as a function of the incident angle of the readout beam at the detuning from the Bragg angle) is plotted in Figure S4 (gray squares; the material of the grating was 15 wt % of AA modified nanoparticles in the monomeric mixture). A diffusion light pattern was observed around the diffracted spot, indicating the distortion and some light-scattering of the gratings that explains the uplifted nulls of the curve.\textsuperscript{[3]} A good agreement of the experimental curve with the fit using Kogelnik coupled-wave theory\textsuperscript{[2,4]} (Figure S4, solid line) was obtained. The thickness of the grating was measured with the profilometer after the removal of one substrate; the fitting parameters:
\[ \Lambda = 1 \mu m, \lambda = 633 \text{nm}, d = 19.5 \mu m, n \approx 1.52. \] Therefore the refractive index modulation amplitude, \( n_1 \), was calculated using the formula of the coupled-wave theory for the diffraction efficiency of a volume phase sinusoidal transmission unslanted grating at the readout by \( s \)-polarized light under Bragg conditions: \( \eta = \sin^2(\pi n_1 d / \lambda \theta_B) \), where \( \theta_B \) is the Bragg angle within the grating, \( d \)- thickness of the grating. The diffraction efficiency is a periodic function of \( \nu \), where 
\[ \nu = \pi n_1 d / \lambda \cos \theta_B. \] So, \( \eta \) first increases from 0 up to 1 if \( \nu \) grows from 0 to \( \pi/2 \) (a typical one-peak angular selectivity of such a grating is shown in Figure S4). A further rise of \( \nu \) from \( \pi/2 \) to \( \pi \) causes a decrease in \( \eta \) from 1 to 0, and so on. This phenomenon is known as an overmodulation. If the thickness and the spatial period remain constant, the overmodulation evidences the increase in \( n_1 \) beyond the value needed to attain 100\% \( \eta \). The angular selectivity curve of such gratings changes substantially in dependence on the overmodulation value obtained. Optical losses (OL) due to light- scattering of the grating were estimated from the balance of intensity of the incident (\( I_0 \)), reflected (\( I_{Fr} \)), diffracted (\( I_{dif} \)) and transmitted (\( I_tr \)) beams as 
\[ \text{OL} = 1 - ((I_{dif} + I_{tr} + I_{Fr}) / I_0). \] Refractive indices of the composites were measured using an Abbé refractometer.

![Figure S4. Angular selectivity curve for a grating containing 15 wt % of AA-modified nanoparticles.](image-url)
References


