Supporting information for

‘Coating and dispersion of ceramics nanoparticles by UV-ozone etching assisted surface-initiated living radical polymerizations’

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1. Experimental details:

Materials:

Commercially available nanoparticles (NPs) were purchased from NanoAmor®, NanoTek™, DENKA and SHOWA DENKO. The detailed information was listed in Table S1.

Styrene (99 %, WAKO) and methyl methacrylate (MMA, 99 %, WAKO) and 2-hydroxyethyl methacrylate (HEMA, 99 %, Aldrich) were purified by passing through a column filled with basic Al₂O₃. N-isopropylacrylamide (NIPAM, 99%, WAKO) was used as received.

2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 99%, WAKO), capper chloride (CuCl, Aldrich), dinonyl bipyridine (dnbipy, Aldrich), Bipyridine (bipy, WAKO) and ATRP initiators; ethyl 2-bromoisobutyrate (EBIB, 98%, TCI) and methyl 2-chloropropionate (MCP, 96%, TCI), were used as received. Tris(2-(dimethylamino)ethyl)amine (ME₆TREN) was prepared as described in the literature.¹ Tetrahydrofuran (THF, HPLC grade, WAKO) and dimethyl formamide (DMF, HPLC grade, WAKO) were used as eluents in size-exclusion chromatography. Methanol (dehydrated grade, WAKO), chloroform (CHCl₃, 99%, WAKO), THF (99%, WAKO) for solvents for polymerization and washing of NPs were used as received.

Initiator installing and graft polymerization on ceramics nanoparticles:

Commercially available powdery ceramic NPs were prepared and spread on the glass schale. The shale was introduced into the UV-ozone etcher (TC-003/C, MeiwaFosis Co., Ltd.) and exposed to UV-ozone radiation for 45 min. After the exposure, the surface layer of the powders were immediately transferred into a test tube with screw cap and transferred into the oxygen- and moisture- free glove box. Then, the beforehand prepared solution for living radical polymerization
(LRP) was added to the test tube and inserted into aluminum block heater previously heated to the desired temperature. After scheduled time was passed, the test tube was removed from the glove box and the polymerization was totally quenched by adding the oxygen rich good solvent of the synthesized polymer. The NPs were washed with the good solvent of the polymer by dispersion and centrifugation method at least five times to perfectly remove the unbound polymers from the solution. The characterization of the NPs were carried out by transmission electron micrography (TEM), dynamic light scattering (DLS), Fourier transfer infrared spectroscopy (FTIR), thermo gravimetry (TG) X-ray photoelectron spectroscopy (XPS) and Gel permeation chromatography (GPC).

Nitroxide mediated polymerization (NMP) of styrene:
9.6 mM of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) styrene solution was prepared and stored in the refrigerator in the moisture and oxygen free glove box. 0.5 g of UV-ozone treated NPs powder was immersed into 3 mL of the stocked solution and stirred very well. Then, the test tube with screw cap was placed in the aluminum block heater previously heated to 125 °C for 12 hours. After the polymerization, the test tube was removed from the heater and the glove box, then oxygen rich CHCl₃ was added to terminate polymerization and dissolve the NPs.

In the most cases, the molecular weight of the PS synthesized by this procedure had the mean number molecular weight as \( M_n = 45,000 \text{ g mol}^{-1} \) with the polydispersity index \( (M_w/M_n) \) as PDI = 1.24.

Atom transfer radical polymerization (ATRP) of methylmethacrylate (MMA):
The surface initiated ATRP of MMA was carried out by immersing 0.5 g of UV-ozone treated NPs powder into 3 mL of Ar-purged MMA solution of Ethyl 2-bromoisobutyrate (EBIB, 7 mM), CuCl (35 mM) and 4,4'-dinonyl bipyridine (dNbipy, 75 mM). The ATRP was carried out at 80 °C for 2 h. After the polymerization, the test tube was removed from the heater and the glove box, then oxygen rich CHCl₃ was added to terminate polymerization and dissolve the NPs.

In the most cases, the molecular weight of the PMMA synthesized by this procedure had \( M_n = 108,000 \text{ g mol}^{-1} \) with PDI = 1.17.

Atom transfer radical polymerization (ATRP) of 2-hydroxyethylmethacrylate (HEMA):
The surface initiated ATRP of HEMA was carried out by immersing 0.5 g of UV-ozone treated NPs powder into 3 mL of Ar-purged methanol solution of Ethyl 2-bromoisobutyrate (EBIB, 20 mM), CuCl (25 mM), bipyridine (bipy, 55 mM) and HEMA (4.4 M). The ATRP was carried out at 80 °C for 15 min. The reaction temperature was reduced to 40 °C, and kept for 1.5 h. After the polymerization, the test tube was removed from the heater and the glove box, then oxygen rich THF
was added to terminate polymerization and dissolve the NPs.

In the most cases, the molecular weight of the PHEMA synthesized by this procedure had $M_n = 32,000 \text{ g mol}^{-1}$ with PDI = 1.22.

**Atom transfer radical polymerization (ATRP) of N-isopropyl acrylamide (NIPAM):**

The surface initiated ATRP of NIPAM was carried out by immersing 0.5 g of UV-ozone treated NPs powder into 3 mL of Ar-purged methanol solution of methyl 2-chloropropionate (MCP, 0.45 M), CuCl (0.53 M), tris(2-(dimethylamino) ethyl)amine (M6TREN, 0.53 M) and NIPAM (5.3 M). The ATRP was carried out at 80 °C for 15 min. The reaction temperature was reduced to 40 °C, and kept for 24 h. After the polymerization, the test tube was removed from the heater and the glove box, then oxygen rich THF was added to terminate polymerization and dissolve the NPs.

In the most cases, the molecular weight of the PNIPAM synthesized by this procedure had $M_n = 17,000 \text{ g mol}^{-1}$ with PDI = 1.20.

**Characterization of NPs:**

The average size, size distribution and morph of polymer grafted NPs were measured by transmission electron microscopy (TEM, H7650, Hitachi). The solution of polymer grafted NPs was dropped on a standard carbon coated copper grid and dried. Electron micrographs were taken by a micrometer at an accelerating voltage of 100kV. Attenuated total reflection Fourier transfer infrared (ATR FT-IR) spectrometer (Digilab, FTS-7000) was employed to analyze the status of the surface of NPs. The spectra were measured at a resolution of 1 cm$^{-1}$. The amount of grafted surface modifier was measured from the weight loss of the thermo gravimetry (TG, Rigaku, TG8120). The temperature dependent weight loss of NCs was recorded under Air flow with the rate of heating and cooling at 10 °C/min. 20 mg of the polymer grafted NPs were used for single TG measurements. Because of the large amount of the polymer grafted NPs, 2 % of weight loss was calculated to be 0.4 mg. This amount is enough large to regard accurate measurement was done for the TG measurement. The dispersity of NPs in solvents was also measured through our eyes (taking photographs by RICOH digital camera GX200).

**Size exclusion chromatography:**

Gel permeation chromatographic (GPC) analysis was carried out at 35 °C on a JASCO GPC-900 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-803L, exclusion limit: $7\times10^4$ and KF-805L, exclusion limit: $4\times10^5$), and a differential refractometer. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min. The GPC system was basically calibrated by PS and PMMA standards (Polymer Standard Service, PSS-Kit, (PS): Mp. 682 - $1.67\times10^6$ D, (PMMA): $M_p$. 102 - $9.81\times10^5$ D). In the
case of DMF was used as an eluent, the column set was changed to a guard column (Shodex GPC KD-G), two 30-cm mixed columns (Shodex GPC KD-804, exclusion limit: $4 \times 10^5$ and KD-805, exclusion limit: $4 \times 10^6$), the flow rate was set to 1 mL/min and the calibration was complemented by polyethylene oxide standards (Polymer Laboratories, $M_p$: $2.0 \times 10^3$ - $1.0 \times 10^6$ D).

The free polymer sample for the GPC were corrected by the following method.

2. List of the NPs used in this study.

Table S1. The list of the polymer grafted NPs investigated in this study.

<table>
<thead>
<tr>
<th>Core</th>
<th>Supplier</th>
<th>APS (nm)</th>
<th>UV-O3 or Plasma</th>
<th>Polymer</th>
<th>$M_n$ (D)</th>
<th>PDI</th>
<th>PSchais n/NP</th>
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<tr>
<td>$\alpha$-Al_{2}O_{3}</td>
<td>NanoAmor™, 40-80, UV-O3</td>
<td>PS</td>
<td>PMMA</td>
<td>45,000</td>
<td>1.24</td>
<td>154</td>
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<tr>
<td>$\alpha$-Al_{2}O_{3}</td>
<td>NanoAmor™, 30-40 UV-O3</td>
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<td>PMMA</td>
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<td>1.18</td>
<td>12.9</td>
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<td>NanoAmor™, 10 UV-O3</td>
<td>PS</td>
<td>PMMA</td>
<td>45,000</td>
<td>1.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$-Al_{2}O_{3}</td>
<td>NanoAmor™, 25 UV-O3</td>
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<td>CeO_{2}</td>
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<td>PMMA</td>
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<td>PMMA</td>
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<td>$\alpha$-Fe_{2}O_{3}</td>
<td>NanoTek™, 39 UV-O3</td>
<td>PMMA</td>
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<tr>
<td>$\gamma$-Fe_{2}O_{3}</td>
<td>NanoAmor™, 20-40 UV-O3</td>
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<tr>
<td>Fe_{3}O_{4}</td>
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<td>NiO</td>
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<td>SiO_{x}</td>
<td>NanoAmor™, 15 UV-O3</td>
<td>PS</td>
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<tr>
<td>TiO_{2}(A)</td>
<td>NanoAmor™, 5 UV-O3</td>
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<td>TiO_{2}</td>
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3. The images of the NPs dispersant synthesized in this study.

Some examples of polymer grafted NPs dispersion are shown in Figure S1. The dispersion was stable at least several tens of hours depending on the core size of NPs (because of the magnetic interaction between Fe₃O₄ NPs, the dispersion of polymer grafted Fe₃O₄ NPs was not stable long time comparing with the other NPs).

![Image of NPs dispersant](image-url)
**Figure S1.** Images of the PS-grafted NPs dispersion in chloroform. Approximated concentrations of the NPs in the suspension were depicted in the image.

For example, the concentration dependence of DLS sizes of PS-grafted $\gamma$-$\text{Fe}_2\text{O}_3$ and TiN NPs in chloroform were depicted in Figure S2. The size of the dispersant was increased with increasing the concentration of the NPs. As it mentioned in main text, one of the magnetic NPs, $\gamma$-$\text{Fe}_2\text{O}_3$-$b$-PS showed worse dispersion than TiN-$b$-PS.

![Figure S2](image)

**Figure S2.** DLS sizes of the PS-grafted TiN (left) and $\gamma$-$\text{Fe}_2\text{O}_3$ (right) NPs dispersions in chloroform. With increasing the concentration, the DLS sizes increased.

### 4. TG weight loss of the mixture of TiN and PS.

The mixture of PS and TiN NPs was prepared for the sake of comparison. The mixture was prepared by the same method as the graft polymerization of styrene without having the UV-ozone exposure process. This implies that the difference between the PS-grafted TiN NPs and the mixture is the PS-grafted TiN NPs may have grafted polymer on the surface, on the other hand, the mixture may not. The TG curve shown in Figure S3 clearly depicts that the weight loss attributed to PS decomposition was much smaller than that of the PS-grafted TiN NPs (it was 2 wt%). This will be another strong proof that the method developed here has successfully grafted polymer chains on the ceramics NPs. In other word, the unbound (free) PS chains were effectively eliminated by dispersion and centrifugation method.
Figure S3. TG curve of the mixture of PS and TiN NPs. The mixture loaded for the measurement polymer grafted NPs. It is apparent that weight loss attributed to polymer (PS) was one order of magnitude smaller than that of the PS grafted TiN NPs (2 wt%).
5. XPS spectra of the TiN, TiO$_2$ and AlN NPs.

XPS spectra shown in Figure S4 indicates the graft polymerization of PS shields the Ti, N and O signals of TiN NPs and the signal attributed to carbon of PS chains was increased. This is consistent with the operation to grafting PS to TiN NPs. For the UV-ozone treatment, there was no effective change observed in the XPS spectra shown in Figures S4, S5 and S6. The chemistry change, possibly the author expects numbers of peroxide groups that can generate active free radical species, was not observed by XPS. Because of the very small concentration of the surface change, it was difficult to detect the change by XPS.

![XPS spectra of untreated (black), UV-O$_3$ treated (red) and PS grafted (blue) TiN NPs.](image)

Figure S4. XPS spectra of untreated (black), UV-O$_3$ treated (red) and PS grafted (blue) TiN NPs. Because all the samples for the XPS measurement are the powder so that, in principle, quantitative determination is difficult. For instance, the amount of the UV-O$_3$ treated TiN sample for the XPS would be smaller than the others. The powdery sample might be lost during the evacuation of the XPS spectrometer.
Figure S5. XPS spectra of untreated (black) and UV-O₃ treated (red) TiO₂ NPs.

Figure S6. XPS spectra of untreated (black) and UV-O₃ treated (red) AlN NPs.

References (for Supporting information):