SUPPORTING INFORMATION

Homogenous photopolymerization of acrylic monomers initiated with ZnO-methacrylate in non-aqueous medium and production of luminescent nanocomposites

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Experimental Section

Materials

Zinc dimethacrylate (Zn(MA)₂, 99%), poly(ethylene glycol) diacrylate (PEGDA, Mₙ = 575) and triethylene glycol dimethacrylate (TEGDMA, 95%) was purchased from Sigma Aldrich. Methyl methacrylate (MMA, >99%) was purchased from Merck. All monomers were passed through aluminium oxide column to remove the inhibitor before use.

Methanol (MeOH, >99%, Prolabo), 1-butanol (≥99.5%, Merck), sodium hydroxide (NaOH, >97%, Merck) and methyl ethyl ketone (MEK, ≥99.5%, Tekkin) were used without further purification. For washing steps, ultra-pure water (MilliQ, Millipore, 18.2 MΩ/cm) was used.

Synthesis of ZnO-MAA

Procedure was adopted from Gabriela et al. with minor modifications in the reaction duration. Zinc dimethacrylate was sonicated in 1-butanol for 1 hour. The mixture was placed in a pre-heated oil bath at 80°C. 1.2M NaOH was added to the reaction mixture and stirred for 11 h. Then, the reaction mixture cooled down to room temperature and the product was precipitated in cold MeOH, washed with water, and dried in a lyophilizer (Labconco FreeZone 2.5 Liter Cascade Benchtop Freeze Dry System). The final product was obtained as a white powder.

Photopolymerization

Bulk and solution polymerizations were performed with Black-Ray UV lamp (UVP, B-100AP High Intensity UV Lamp, 365nm, 100 Watt) keeping the polymerization mixture at 10cm distance from the lamp.

Bulk photopolymerization

Dry ZnO-MAA powder was dispersed in MMA (0.42% (w/w)) and the mixture was degassed for 5 minutes with Ar. Polymerization mixture was excited with Black Ray UV lamp for 5 hours.

Solution Polymerization

Dry ZnO-MAA powder was dispersed in methyl ethyl ketone (MEK) (1.5% (w/w)) by sonication. MMA was added and the mixture was degassed for 5 minutes with Ar. Polymerization mixture was excited with Black Ray UV lamp for 5 hours. The product was precipitated in cold MeOH, washed with dH₂O and lyophilized.

photoDSC studies

Dry ZnO-MAA were dispersed in the monomer at the ratios given in table 1. Kinetics of the photopolymerization was studied with Photo Differential Scanning Calorimetry (photoDSC) (TA Q2000 equipped with Omnicure 2000s) using three band pass filters (320-390nm, 320-480nm and 400-500nm) at 30°C under 50.0 ml/min Nitrogen flow. Usually, samples were purged with nitrogen 1 min before irradiation was started and continued for another minute once the light was turned off.

Rate was calculated from the heat flow using the following equation:

\[ Rate = \frac{m}{3} \times \frac{M_w}{m} \times \frac{1}{n \times \Delta H \times 10^3} \]

\( \Delta H \) is taken as 86000 J for acrylates and 54400 J for methacrylates, \( M_w \) is the molecular weight of the monomer, \( m \) is the weight of the monomer used and \( n \) is the number of double bonds per monomer. Monomer conversion is calculated from the integrated area under the Rate-time curve.
Decarboxylation experiment
ZnO-MAA in MEK (1.23 mg/ml) was de-oxygenated with Ar and then irradiated 5h with Blackray UV lamp (365 nm). This flask was connected to another one containing 9.4x10^{-4} M Na_{2}CO_{3} and phenolphthalein in water.

Characterization
X-Band spectrometer (EMXplus Bruker) was used for the ESR-ST experiments. ZnO-MAA dispersed in nitrogen saturated tert-butylbenzene with sonication and irradiated with a LED@365 nm (Thorlabs M365L2, 190 mW) at room temperature. Photogenerated free radicals were trapped with phenyl-N-tert-butynitrone (PBN). 10 scans were performed for data acquisition at 1.10^{15} receiver gain, 1 G modulation amplitude, 20.48 ms time constant and 6.325 mW (15 dB) power. WINSIM (a NIEHS Public EPR Software Tool) was used for the simulation of data. Crystal structure of ZnO-MAA NPs was determined by X-ray diffraction (Bruker D8 Advance X-Ray Diffractometer). Hydrodynamic sizes of the nanoparticles were measured by dynamic light scattering (DLS) (Malvern ZS–Zetasizer). Absorbance and photoluminescence spectra were recorded on a UV-Vis-NIR Spectrophotometer (Shimadzu UV-3600) and Spectrofluorometer (Horiba Jobin Yvon- Fluoromax 3), respectively. Fourier transform infrared spectroscopy (FTIR) analysis was performed with Thermoscientific Nicolet iS10 instrument (ATR-FTIR). Glass transition temperature (T_{g}) was determined from the second heating cycle of 1.5 mg sample at a heating rate of 10°C/min between 25-150°C using TA Differential Scanning Calorimetry (DSC) Q200.

Table S1 Time to peak maximum

<table>
<thead>
<tr>
<th>Figure #</th>
<th>ZnO (wt%)</th>
<th>Monomer</th>
<th>Excitation Filter</th>
<th>Time (sec)</th>
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<td>TEGDMA</td>
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<td>320</td>
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<td>400-500 nm</td>
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Fig. S1  (a) FTIR spectra of ZnO-MAA and the ZnO-MAA/PMMA, (b) DSC thermogram of ZnO-PMMA (second heating cycle)
**Fig. S2** Three replica of HDDA photopolymerization initiated with ZnO-MAA (0.5 wt%) at 320-390 nm with 40 mW/cm$^2$ light intensity. Average double bond conversion = 40.26 ±2.18

**Fig. S3** Rate of polymerization and double bond conversion of PEGDA autopolymerization versus ZnO-MAA initiated photopolymerization upon irradiation between 320-390 nm. Time to peak is 168 s for the autopolymerization and 24 sec with ZnO-MAA.

**Fig. S4** Rate of polymerization and double bond conversion of PEGDA autopolymerization versus ZnO-MAA initiated photopolymerization upon irradiation at 400-500 nm.
Fig. S5 Rate of polymerization and double bond conversion of PEGDA autopolymerization versus ZnO-MAA initiated photopolymerization upon irradiation at 320-480 nm.

Fig. S6 ESR spectrum of ZnO-MAA registered after 840 sec of light irradiation at 365 nm. (—) experimental, (—) simulated.

Fig. S7 Generation of carbon based radical by decarboxylation reaction of the coating molecules.

ZnO

\( \text{OCR} \)

\( \xrightarrow{h\nu} \)

ZnO (e\(^{-}\), h\(^{+}\))

\( \text{OCR} \)

\( \xrightarrow{} \)

ZnO + \( \cdot \text{OCR} \)

Polymer

\( \xleftarrow{M} \)

CO\(_2\) + \( R\cdot \)
REFERENCES