

## Supporting Information

### Enzymatic Catalysis at Nanoscale: Enzyme-coated Nanoparticles as Colloidal Biocatalysts for Polymerization Reactions

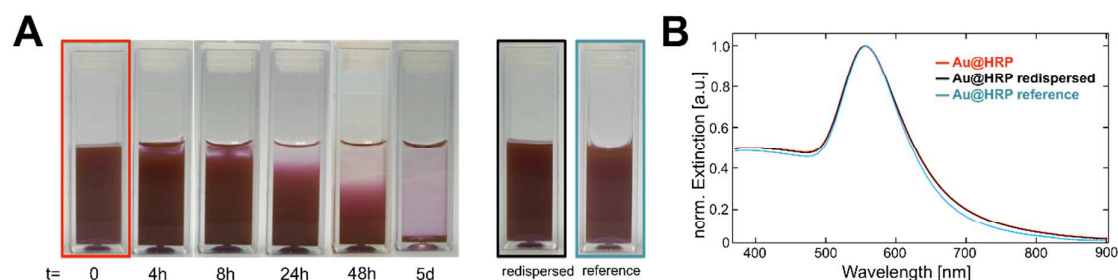
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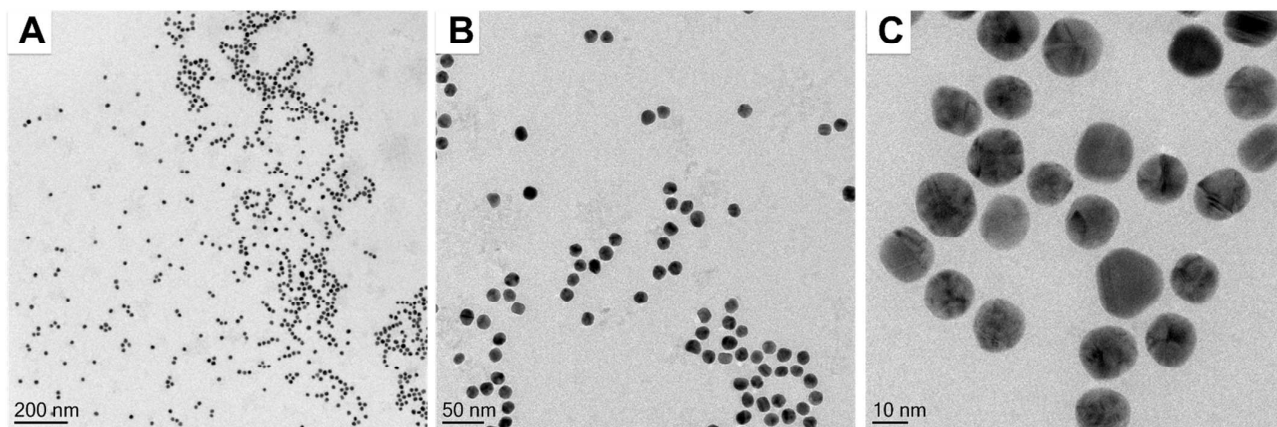
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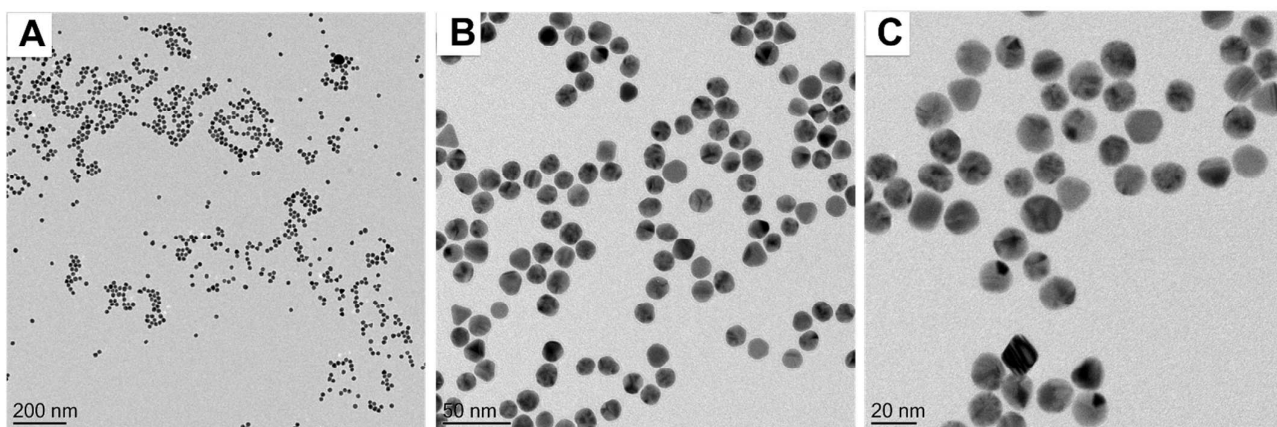


**Figure S1.** Sedimentation behavior of larger Au@HRP NPs ( $d \sim 100$  nm). A) Sedimentation of Au@HRP NPs that were used for the ATRP reaction over time. After 5 days, the gold NP sediment completely and can be redispersed completely, without any aggregation, as revealed by the LSPR band (B). UV-Vis spectra of Au@HRP (red), redispersed Au@HRP (black) and a reference (light blue). The reference is the Au@HRP dispersion that was not used for the ATRP reaction. The corresponding images of the nanoparticle dispersions are framed with the color of the graphs.



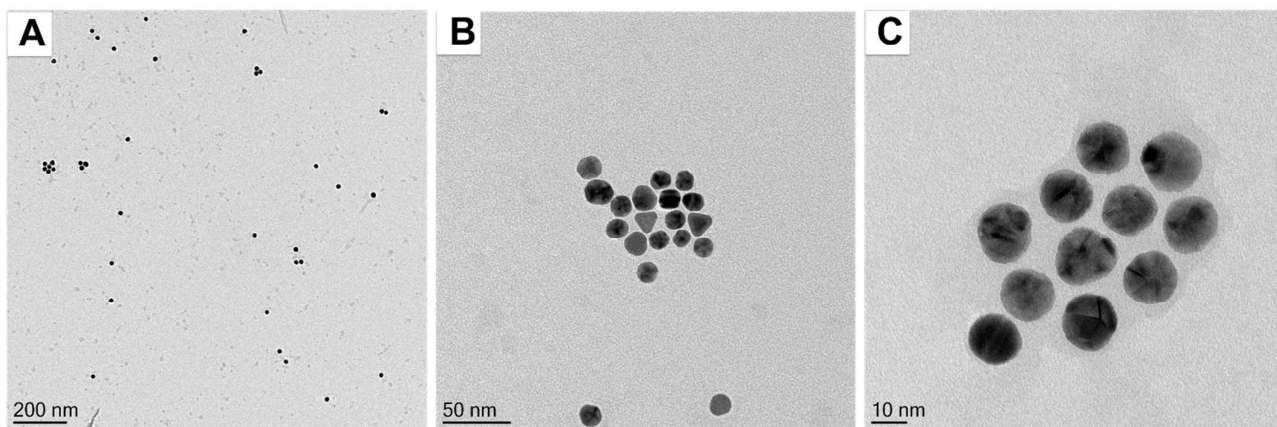


**Figure S2.** TEM images of citrate-stabilized 15 nm gold nanoparticles. The scale bar corresponds to 200 nm (A), 50 nm (B) and 10 nm (C).

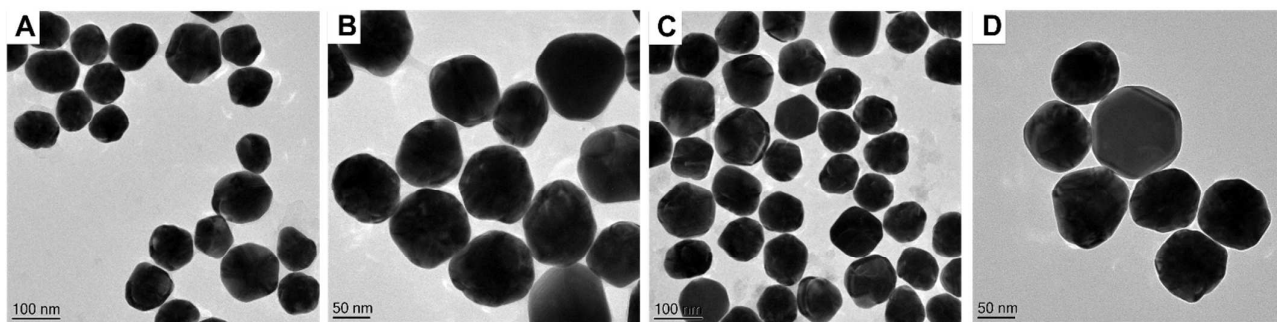


**Figure S3.** TEM images of HRP-coated 15 nm gold nanoparticles. The scale bar corresponds to 200 nm (A), 50 nm (B) and 20 nm (C).



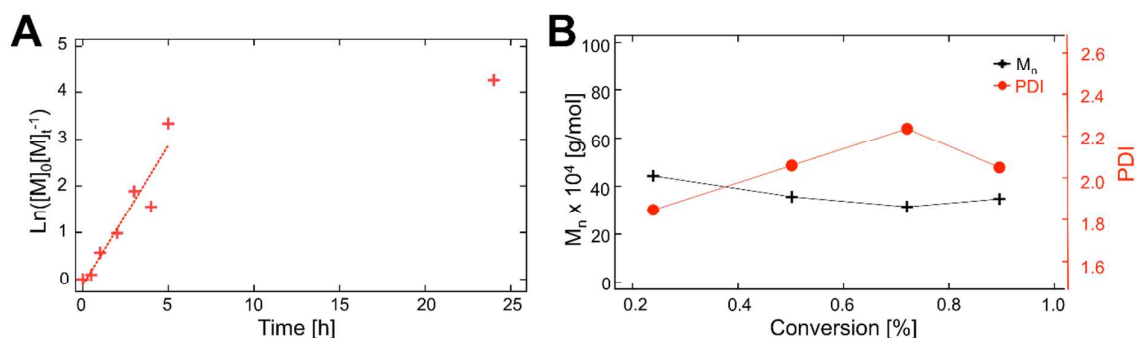


**Figure S4.** TEM images of HRP-coated 15 nm gold nanoparticles after 3 full polymerization and recovery cycles. The scale bar corresponds to 200 nm (A), 50 nm (B) and 10 nm (C).



**Figure S5.** TEM images of HRP-coated ~100 nm gold nanoparticles before (A and B) and after 3 full polymerization and recovery cycles (C and D). The scale bars corresponds to 100 nm (A, C) and 50 nm (B, D). The average size of the nanoparticles is  $98.7 \pm 18.74$  nm.





**Figure S6.** Kinetic measurements of ATRP of PEGA: A) Kinetic plot. Negative normal logarithm as function of reaction time. B) Molecular weight (+) and PDI (●) as function of conversion. <sup>1</sup>H-NMR data: <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, δ): 6.25 (d, J=15Hz, 1H, C=CH<sub>2</sub>), 6.10 (m, 1H, CH<sub>2</sub>=CH), 5.90 (d, J=9Hz, 1H, C=CH<sub>2</sub>), 3.58-3.45 (m, 32H, [-O-CH<sub>2</sub>-CH<sub>2</sub>-O]<sub>8</sub>), 3.2 (s, 3H, CH<sub>3</sub>)

**Table 1.** GPC results of the ATRP of NIPAAM and DEGMA using Au15@HRP (overall 3 polymerization cycles)

	PNIPAAM			PDEGMA		
cycle	M <sub>n</sub> [g/mol]	M <sub>w</sub> [g/mol]	PDI	M <sub>n</sub> [g/mol]	M <sub>w</sub> [g/mol]	PDI
1	42900±5750	104000±16000	2.4±0.1	20000±2780	35700±5850	1.8±0.1
2	28300±6510	77100±19500	2.7±0.3	20100±2930	28800±12300	1.9±0.1
3	35200±3260	81900±11500	2.3±0.1	21000±1130	36900±2090	1.8±0.2

The constant values for molecular weight and PDI, the high colloidal stability as well as the nearly full recovery of the Au15@HRP NPs suggest clearly that more than three ATRP cycles can be realized with the same HRP-coated gold NP dispersions.