Supporting Information

Generation of fluorescent silver nanoscale particles in reverse micelles using gamma irradiation

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Materials Reagents were obtained as follows and used without further purification: 3-(N-morpholino) propanesulfonic acid (MOPS), $AgNO_3$, and spectroscopic grade toluene were purchased from Sigma-Aldrich. The PS-PAA block co-polymer was purchased from Polymer Source Inc. (Quebec, Canada). The rhodamine 590 dye was purchased from Exciton.

Preparation In a typical two-phase synthesis of reverse micelles containing an aqueous core, commercially available PS-PAA having a polystyrene block (n = 50, MW 5200) and a polyacrylic acid (n = 65, MW 4800) block was dissolved at a concentration of 2 mg/mL in 10 mL toluene. The solution was placed into a 20 ml vial. A 10 mM morpholine sulfonic acid (MOPS) buffer (pH 7.2) was prepared and silver nitrate was added in the appropriate amount in the dark to form a 10 mM solution. The solution was shielded from light. Next, 10 mL of this aqueous solution was added to the toluene solution, a stir bar was placed in the vial, the vial was shielded from light and stirred at 30 RPM for 16 hours at room temperature. Afterwards, the stirring was stopped and one mL aliquots were then removed from the toluene phase, which was the top phase.

Radiation Some of the aliquots were subjected to gamma irradiation from a ^{60}Co source at various distances and times, and the total doses were recorded. Other aliquots were used for control experiments. Irradiation experiments were performed using a ^{60}Co source at the Naval Research Laboratory (Washington, DC). Samples were irradiated with the ^{60}Co source at dose rates ranging from 103 Gy/min to 508 Gy/min.

Characterization The set of aliquots were characterized using UV-visible and fluorescence spectrometry, thermogravimetric analysis (TGA), voltammetric stripping, and TEM imagery/analysis. UV-visible measurements were made with an Agilent 8453 diode array spectrometer and referenced against a solvent blank. Fluorescence measurements were made with a Fluoromax-3 (Horiba) fluorimeter, using a bandpass of 5 nm for the excitation and emission monochromators. Emission spectra were corrected using correction factors supplied by the manufacturer. For spectroscopy, 1 mL fluorescence quartz cuvettes were used. TGA was performed using a Thermogravimetric Analyzer (Model 2950, TA Instruments, New Castle, DE). Voltammetric stripping was performed using a CH Instruments (Austin, TX) Model 700D potentiostat.

Quantum yield calculations were made using eq 1 with rhodamine 590 as the fluorescent standard. Emission spectra were recorded for rhodamine 590 in EtOH with excitation at 500 nm corrected for lamp intensity. Emission spectra for the $AgNO_3$ samples were recorded in toluene with excitation at 565 nm corrected for lamp intensity.

$$\Phi_x = \Phi_{ST}\,(\mathrm{Grad}_x/\mathrm{Grad}_{ST})(\eta_x^2/\eta_{ST}^2) \qquad \text{eq 1}$$

The subscripts ST and X denotes the standard and sample respectively. Φ is the fluorescence quantum yield. Grad is the slope from the plot of integrated fluorescence intensity vs. absorbance, and η is the refractive index of the solvent.

TEM Imagery The Ag nanoparticles were imaged using a JEOL JEM-2200FS field emission electron microscope. A SPI 200 mesh holey carbon coated on Cu TEM grid was placed onto a Teflon sheet in a fume hood. Three 5 μl droplets of toluene containing the Ag nanoparticles were placed onto the grid at 60 second intervals, allowing for the toluene to evaporate between each drop.

Table 1S. Characterization of the RM.

Conditions	Amount polymer in the organic layer (TGA)	Amount of Ag^+ in the organic layer (TGA)
10 mL of 2 mg/mL polymer in toluene and 10 mL of 10 mM $AgNO_3$ in pH 7.2 MOPS buffer	0.57 mg/mL (± 6%) Polymer = 0.057 mM	0.061 mg/mL (± 6%) Ag^+ = 0.57 mM

TGA Studies Prior to irradiation, TGA studies were performed on aliquots of the toluene phase of the two phase system. This was done to determine the concentrations of block copolymer and Ag^+ that arise there after the system was allowed to stir for 16 hrs and experience mass transport between the two phases. In this study, 400 μL of the toluene phase was carefully concentrated to ~ 30 μL in a 2 mL conical glass sample vial using nitrogen gas. Next, the walls of the vial were carefully rinsed with the concentrated solution to ensure that all solids were retained. The solution was then transferred to a tared platinum TGA pan and the solution was evaporated in the TGA using a heating rate of 10 ˚C/min over the temperature range 30 ˚C – 600 ˚C, under nitrogen. After complete evaporation of the toluene, which occurred in the range 30 ˚C to ~ 170 ˚C, the additional weight loss arising from the decomposition of the polymer was recorded. This took place over the temperature range 200 ˚C to 500-550 ˚C. The weight loss corresponded to the amount of polymer that was in the original sample of toluene solution. After the final temperature of 600 ˚C was reached, the amount of residue in the pan was recorded, which corresponded to the amount of Ag^+ that was in the original sample of toluene solution. This data allowed us to calculate the concentration of polymer and Ag^+ in the toluene phase, which were found to be 0.57 ± 0.03 mg/mL (0.057 mM) and 0.061 mg/mL ± 0.003 mg/mL (0.57 mM), respectively. Thus, in the toluene phase the mass of the Ag+ is 10-fold lower than that of the polymer, but the molar concentration of the Ag+ is 10-fold higher than that of the polymer.

Voltammetric Stripping Studies For determination of residual unreacted Ag^+ in the toluene phase after gamma irradiation, standard voltammetric stripping studies[1-3] were performed wherein the Ag+ was converted to Ag^0 on the working electrode at a reducing voltage, and then removed ("stripped") from the electrode by increasing the voltage to oxidizing levels using a series of square-wave pulses from the potentiostat. For this study, 400 μL of the toluene phase was removed and added to 3.0 mL 10 mM MOPS buffer in a 20 mL glass vial, and gently agitated for 16 hrs at 30 RPM. The excess aqueous phase used in this procedure caused virtually all of the reverse micelles to partition out of the toluene phase, as shown by TGA studies on the latter that indicated a negligible amount of solid residue after heating to 600 °C. After extraction, 300 μL of the aqueous phase was diluted into 700 μL of fresh 100 mM MOPS buffer, and the resulting 1 mL solution was subjected to the voltammetric stripping studies. These utilized a Pt wire button working electrode (0.50 mm diameter) with a silver wire quasi-reference electrode, and a Pt wire counterelectrode (4 cm in length, .350 mm diameter). The studies were conducted using a shot-glass type glass vessel with a stir bar, which was placed on a stirrer. To convert the Ag^+ in solution to Ag^0 on the working electrode, the latter was held at -1.0 V for 30 seconds while stirring at 60 RPM. The stirring was then stopped, the test solution was removed, and fresh 100 mM MOPS buffer was added to the vessel. The Ag^0 was then stripped from the electrode by using a square wave voltage sweep from -1.0 V to +1.0 V, (0.004 V step, 0.025 V amplitude, frequency 15 Hz). The area (in VA) and height (in mA) of the oxidation peak that resulted from the oxidative stripping was recorded. Finally, the electrode was cleaned by subjecting it to + 1.0 V for 60 seconds, and the next 1.0 mL sample was introduced. A standard curve (Figure S1) showing the relationship between peak areas and mg/mL Ag^+ in solution was constructed by using 100 mM MOPS solutions with known amounts of $AgNO_3$. Using this method we constructed Figure S2, which shows the amount of Ag^+ that was reacted as a function of gamma ray dosage in Gys. The amount of Ag^+ present in the toluene phase before irradiation was determined using voltammetric stripping, and found to be 0.081 ± 0.003 mg/ml MOPS.

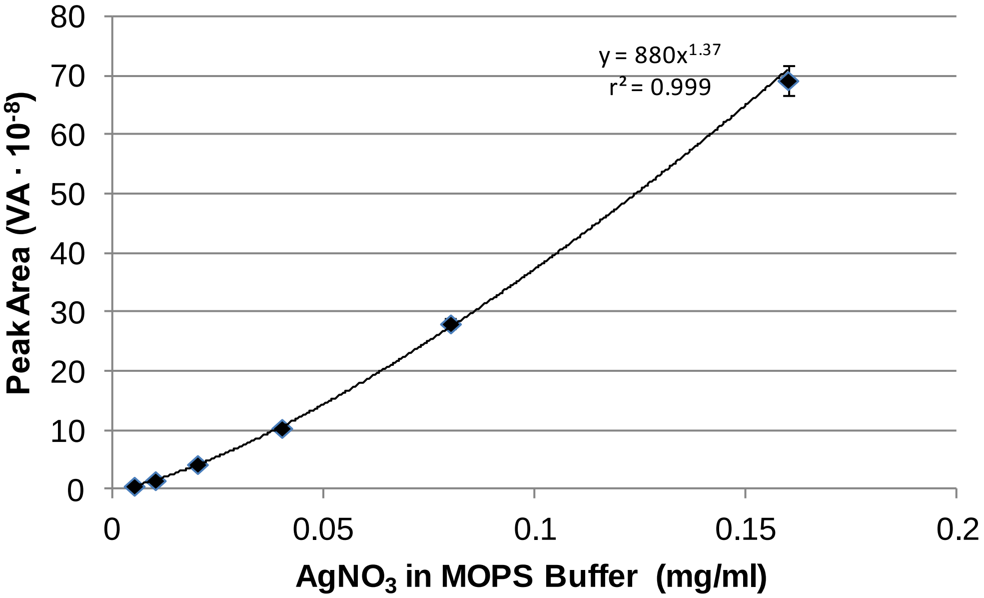

Figure S1. Standard curve for determination of unreacted Ag^+. Peak area units = Volts · Amps.

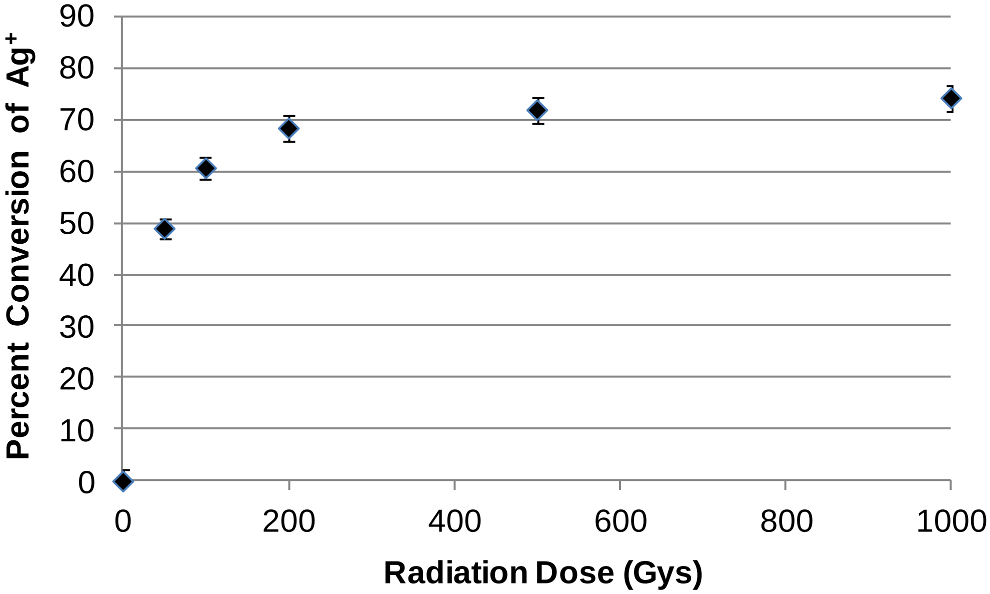

Figure S2. Percent conversion of Ag^+ vs. radiation dose in Gys.

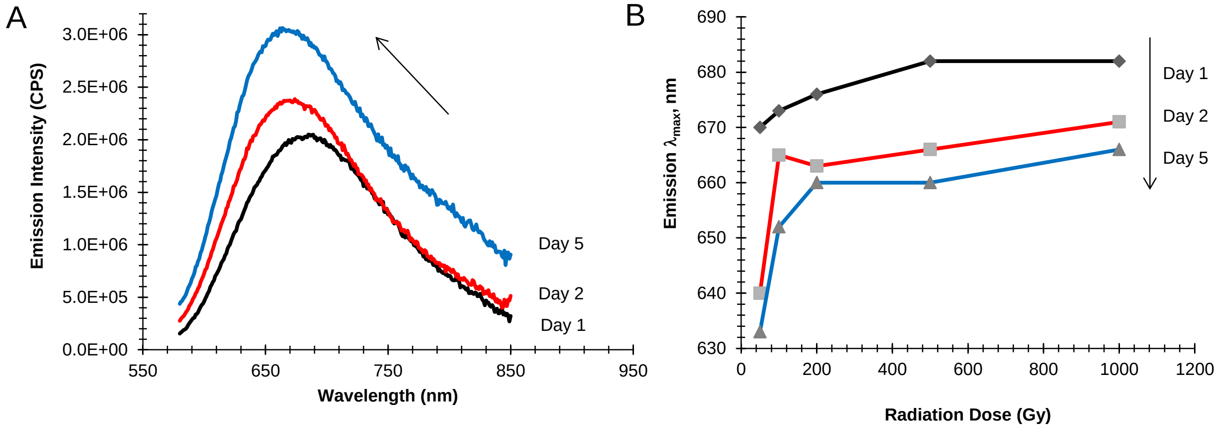

Figure S3. **A.** Emission spectra vs. time. Dose = 500 Gy. **B**. Emission λ_{max} vs dose and time.

Calculation - Theoretical Yield of Ag^0 from e^-_{aq} using Gamma-Irradiation in Aqueous Media A G-value of 2.58 e^-_{aq} electrons produced/100 eV absorbed[4,5] was used for the hydrated electron. Since 1 Gy = 6.24 x 10^{15} eV absorbed/g sample, 1 kGy results in 1.61 x 10^{17} e^-_{aq} electrons produced/mL sample. Conversion to moles gives 2.67 x 10^{-4} moles e^-_{aq} produced/L sample. This corresponds directly to the theoretical amount of Ag^+ that can undergo reduction to Ag^0 by e^-_{aq}.

Free-Radical Scavenging It is of interest that we were able to form the NPs without the addition of free-radical scavengers, in air-saturated solvents. Oxidizing radicals such as ·OH which are generated by the ionizing radiation are commonly known to oxidize metal NCs, dissolving them back to the M^+ state. A common technique to prevent this is to add free-radical scavengers such as isopropanol. The fact that such scavengers are not needed may arise because the PS-PAA or morpholine portion of the MOPS buffer salt form radical species of their own upon interaction with the gamma irradiation. These may have a radical scavenging capability of their own. Finally, solvated electrons can react with O_2 from the air to form superoxide, O_2^-. However, in our RM system there are evidently enough solvated electrons available for Ag^+ reduction. Thus it is practical for use in ambient environments.

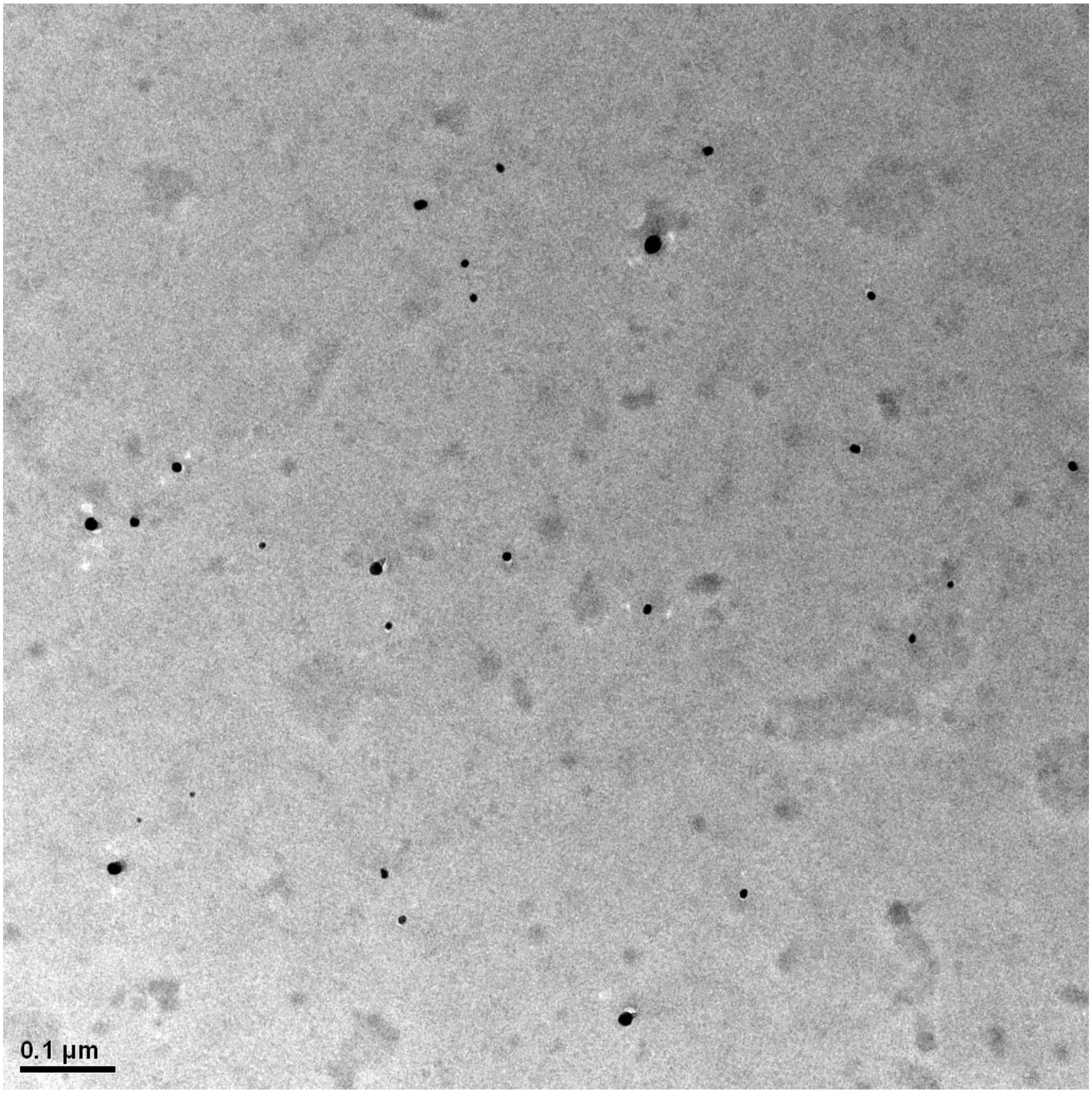

Figure S4. Additional TEM image of Ag NCs formed using PS-PAA RMs. Dose = 1000 Gy.

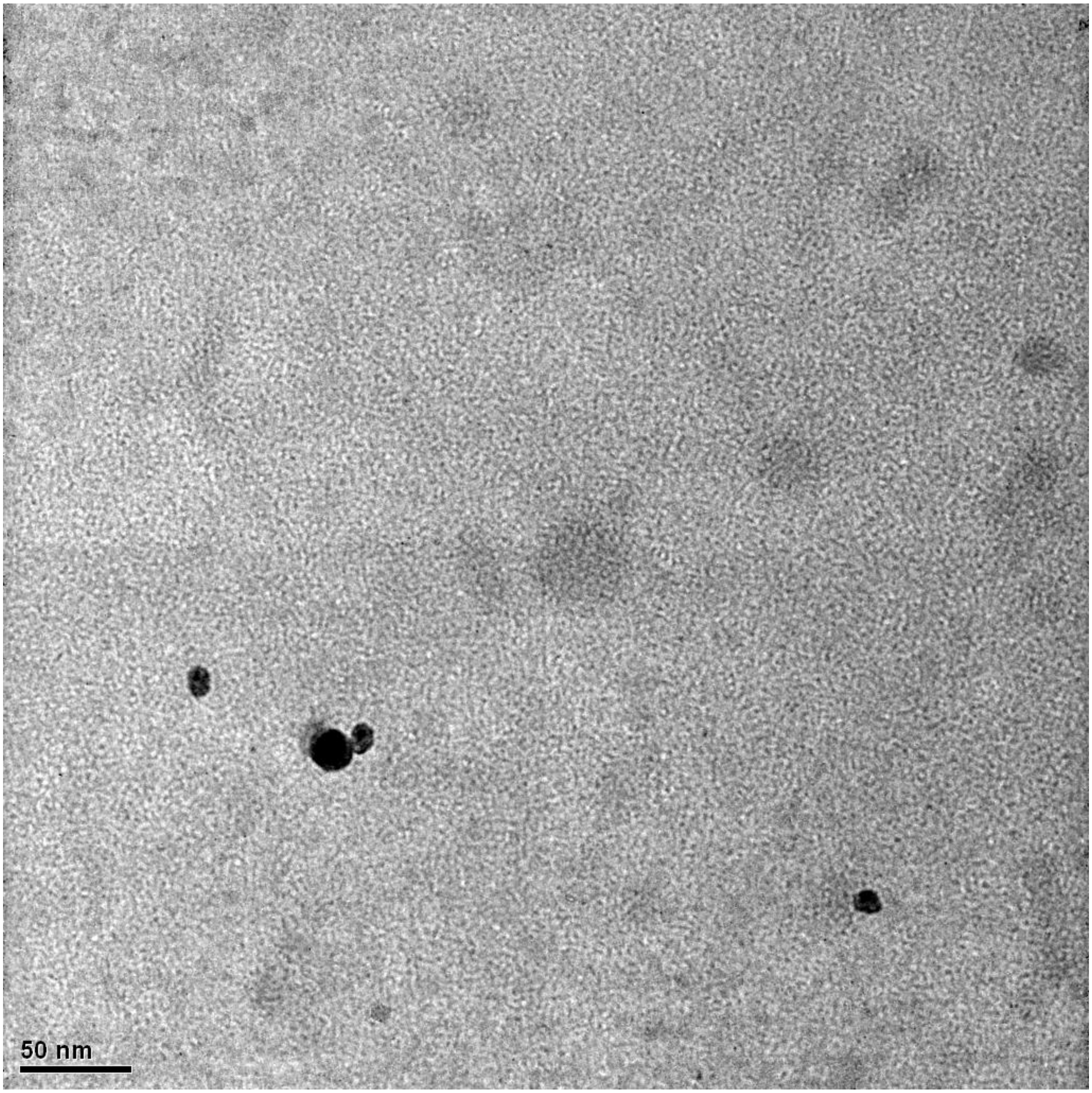

Figure S5. Additional TEM image of Ag NCs formed using PS-PAA RMs. Dose = 1000 Gy.

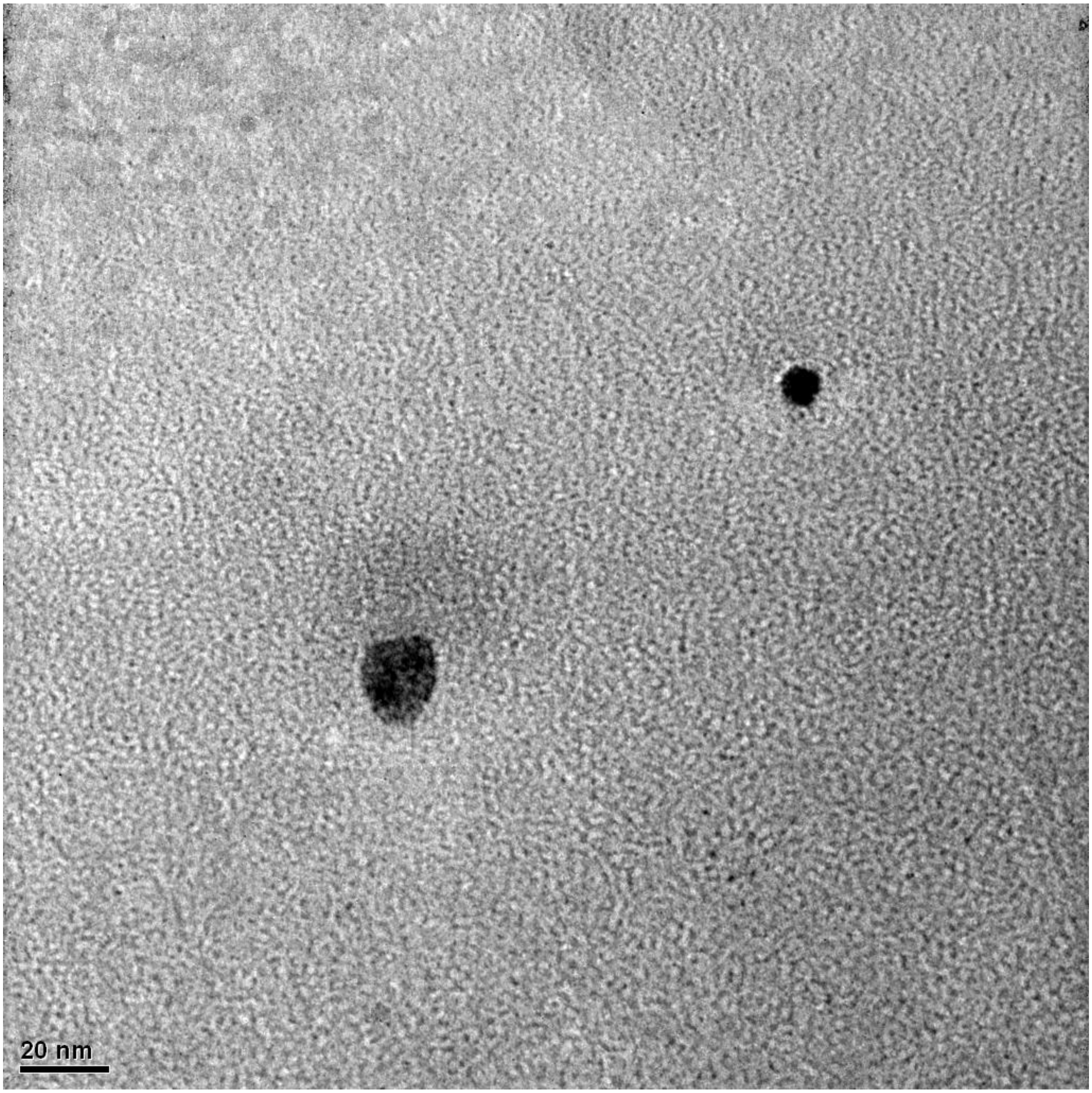

Figure S6. Additional TEM image of Ag NCs formed using PS-PAA RMs. Dose = 1000 Gy.

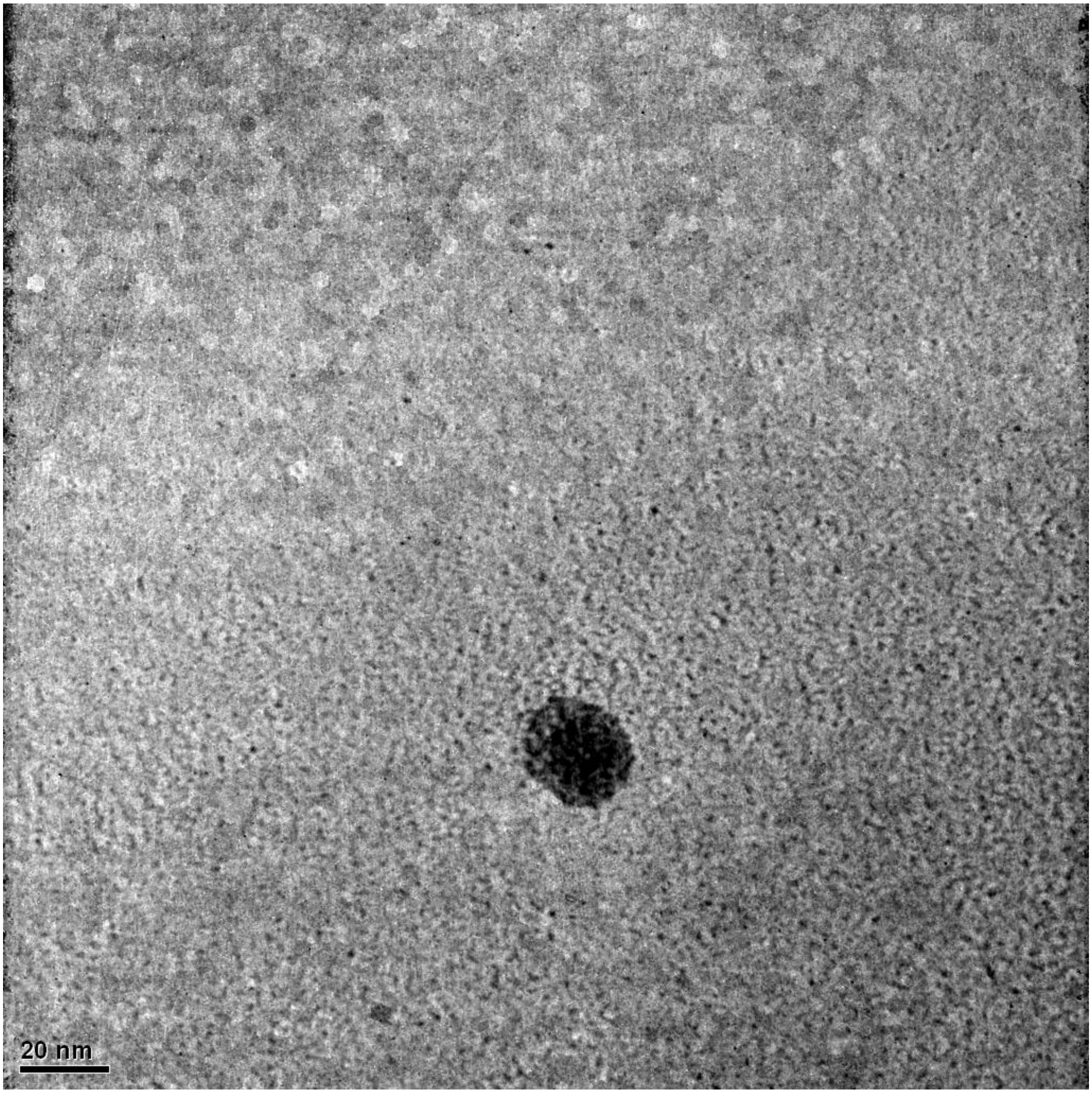

Figure S7. Additional TEM image of Ag NCs formed using PS-PAA RMs. Dose = 1000 Gy.

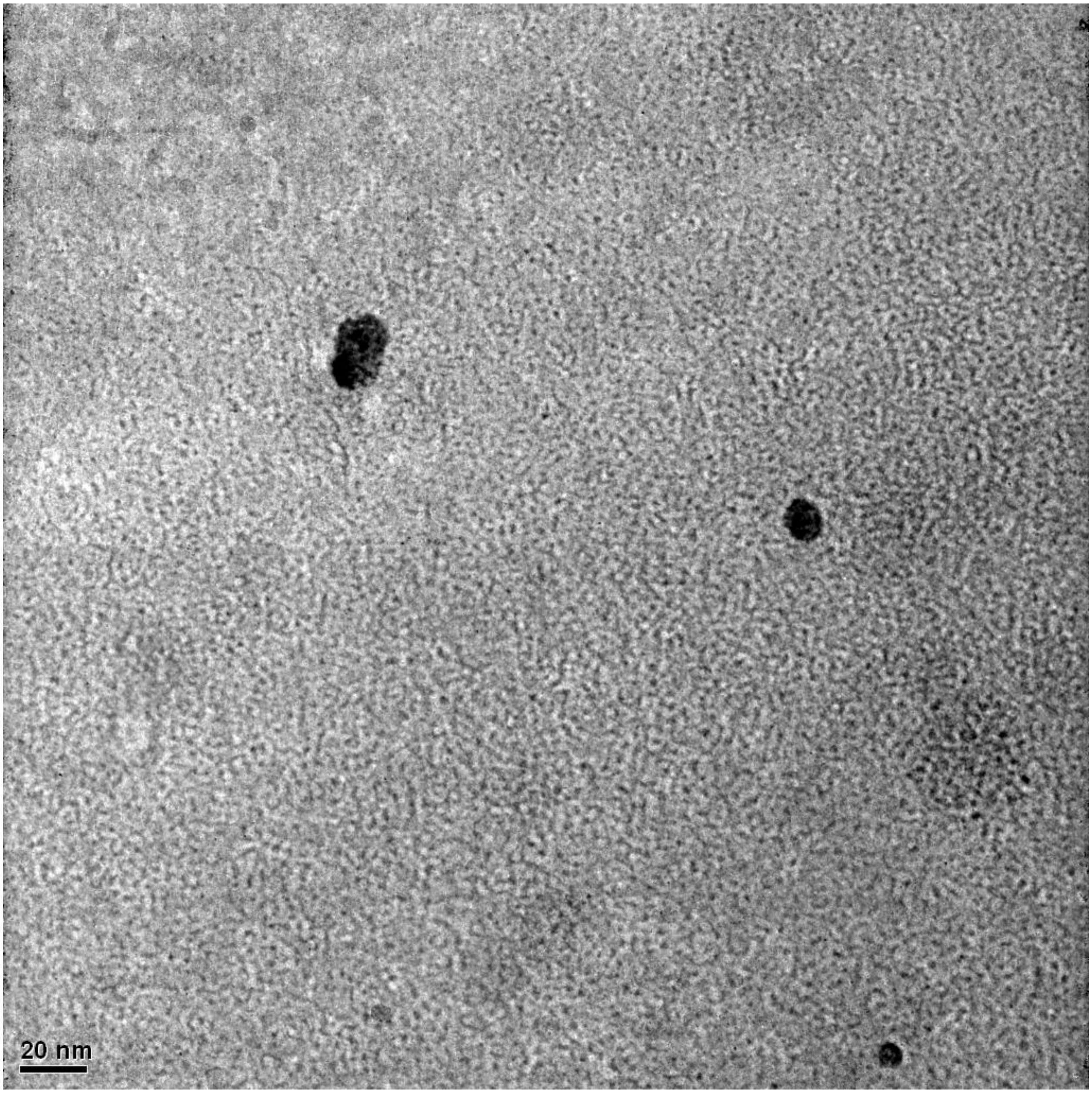

Figure S8. Additional TEM image of Ag NCs formed using PS-PAA RMs. Dose = 1000 Gy.

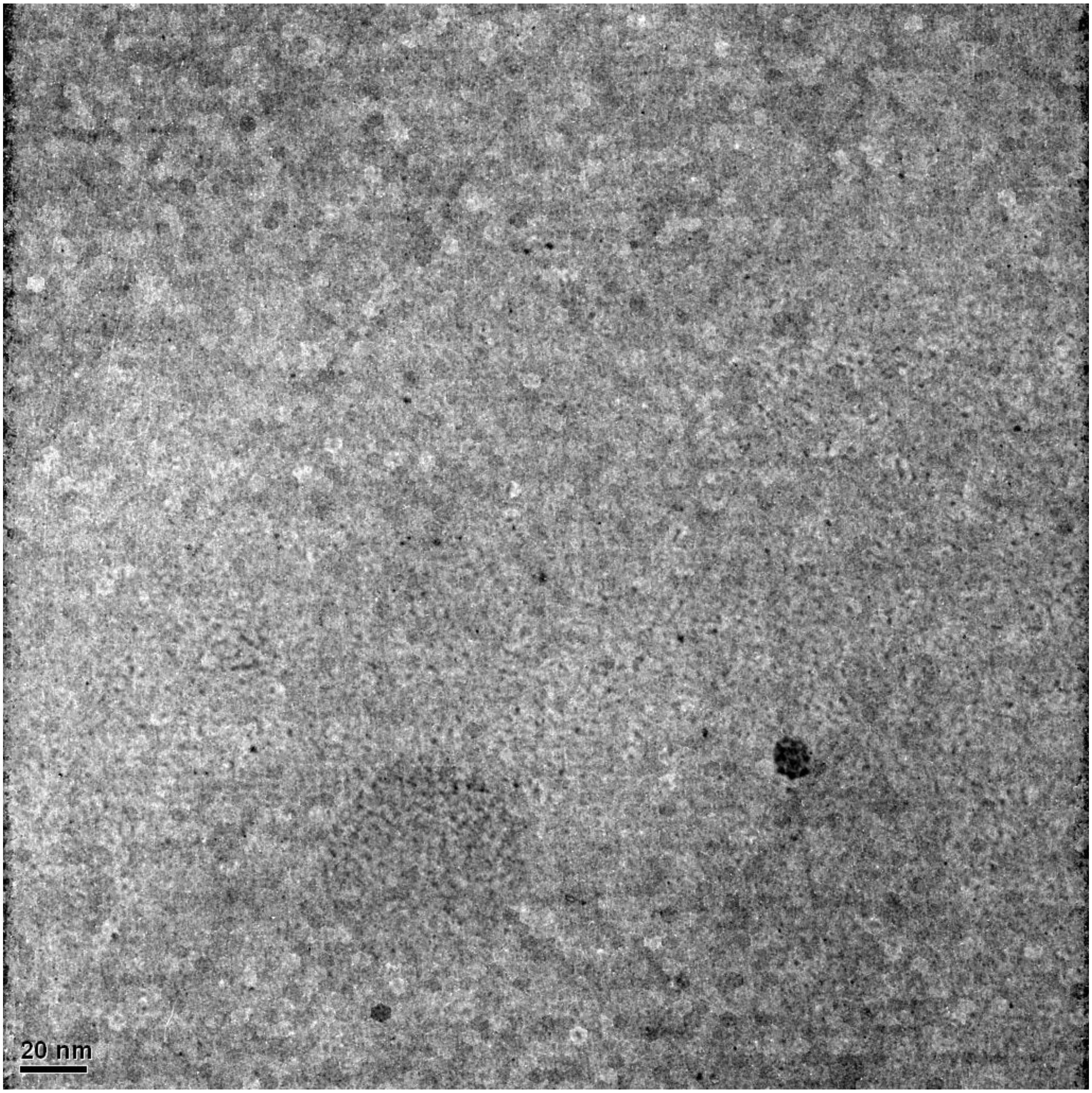

Figure S9. Additional TEM image of Ag NCs formed using PS-PAA RMs. Dose = 1000 Gy.

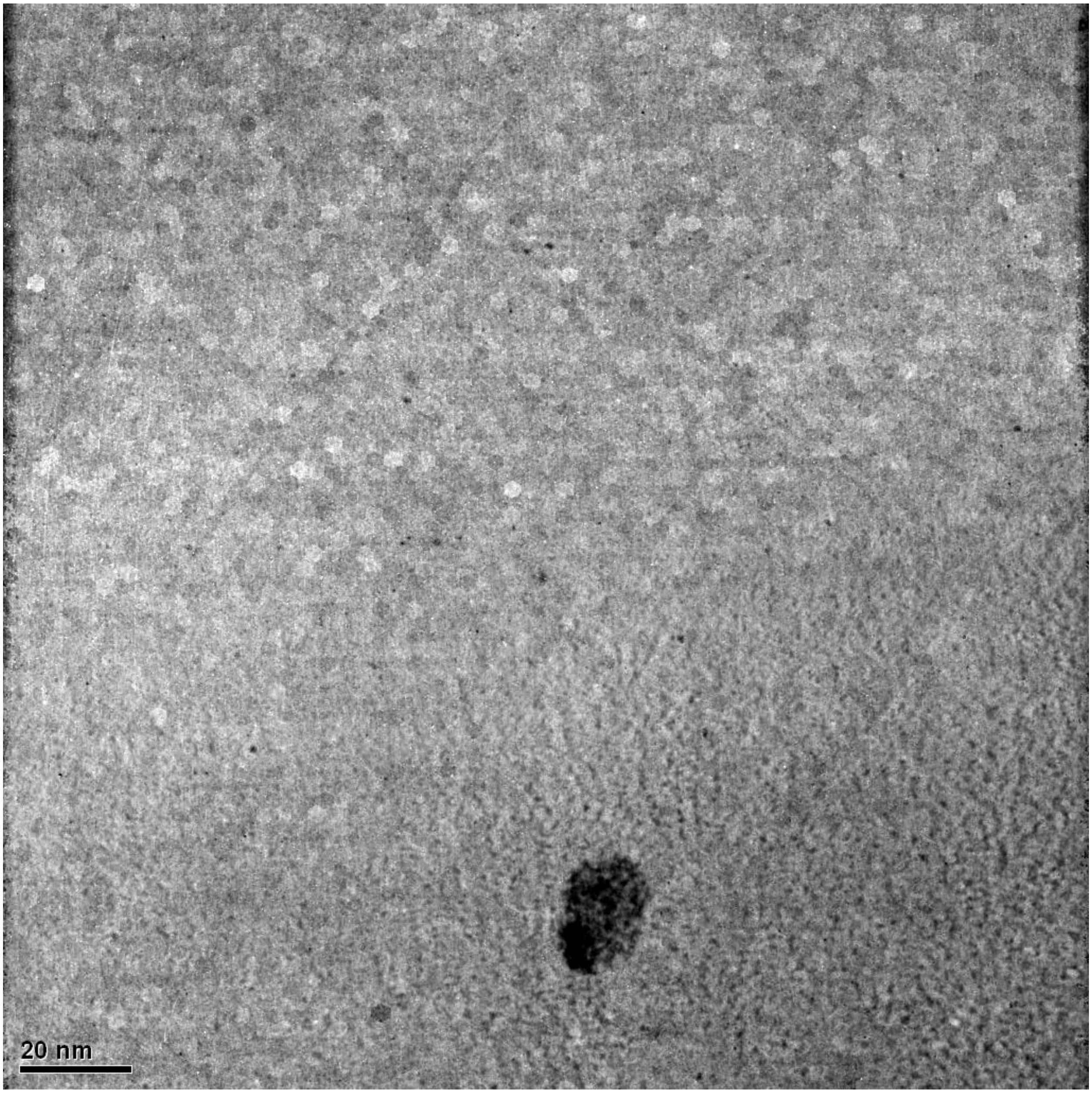

Figure S10. Additional TEM image of Ag NCs formed using PS-PAA RMs. Dose = 1000 Gy.

References

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