Plasmon-Induced Hot Electrons Trigger Polymerization Reactions on the Surface of Plasmonic Nanocrystals at Low Temperatures

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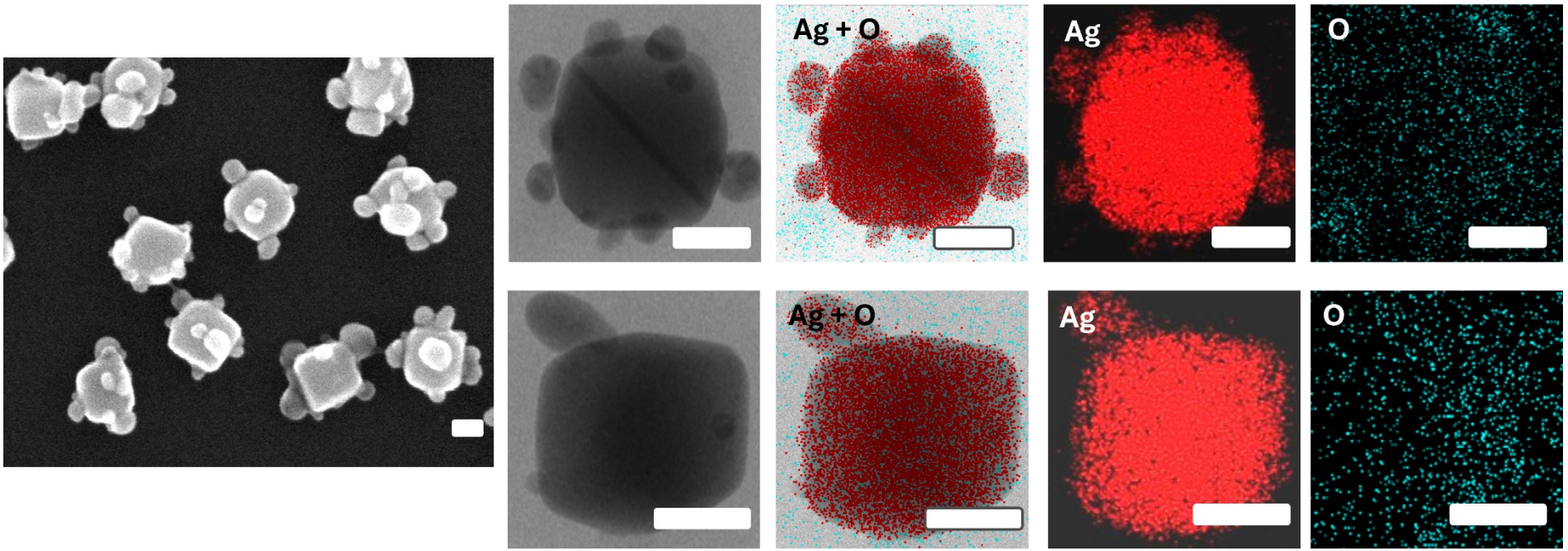

Figure S1 Characterization of lactic acid polymerization on AgNC surface at room temperature under irradiation by SEM, TEM, and EDX analysis. The results showed that in addition to the polymerization reaction, there was also oxidation of silver on AgNC surface. The scale bar was 50 nm.

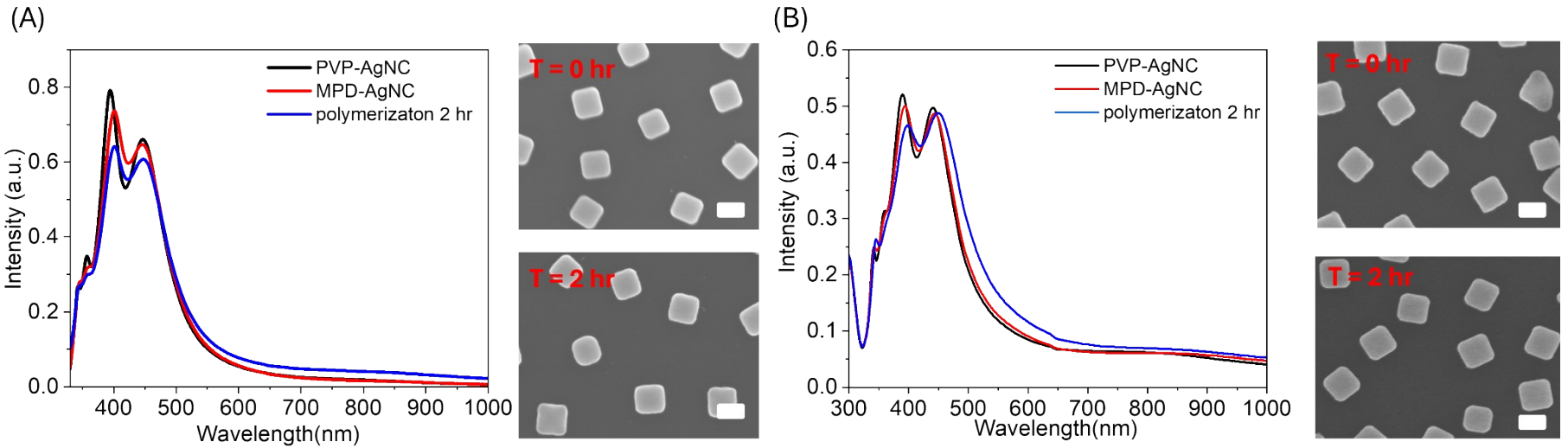

Figure S2 Changes in optical properties of AgNC during lactic acid polymerization under reference reaction conditions. (A) at room temperature without irradiation. (B) at room temperature without a monomer. Black curve: PVP coated AgNC. Red curve: MPD coated AgNC. Blue curve: AgNC after 2 hours of polymerization. And SEM images before and after 2 hours of polymerization showed that there was no lactic acid polymerization and Ag oxidation on the AgNC surface. The scale bar was 100 nm.

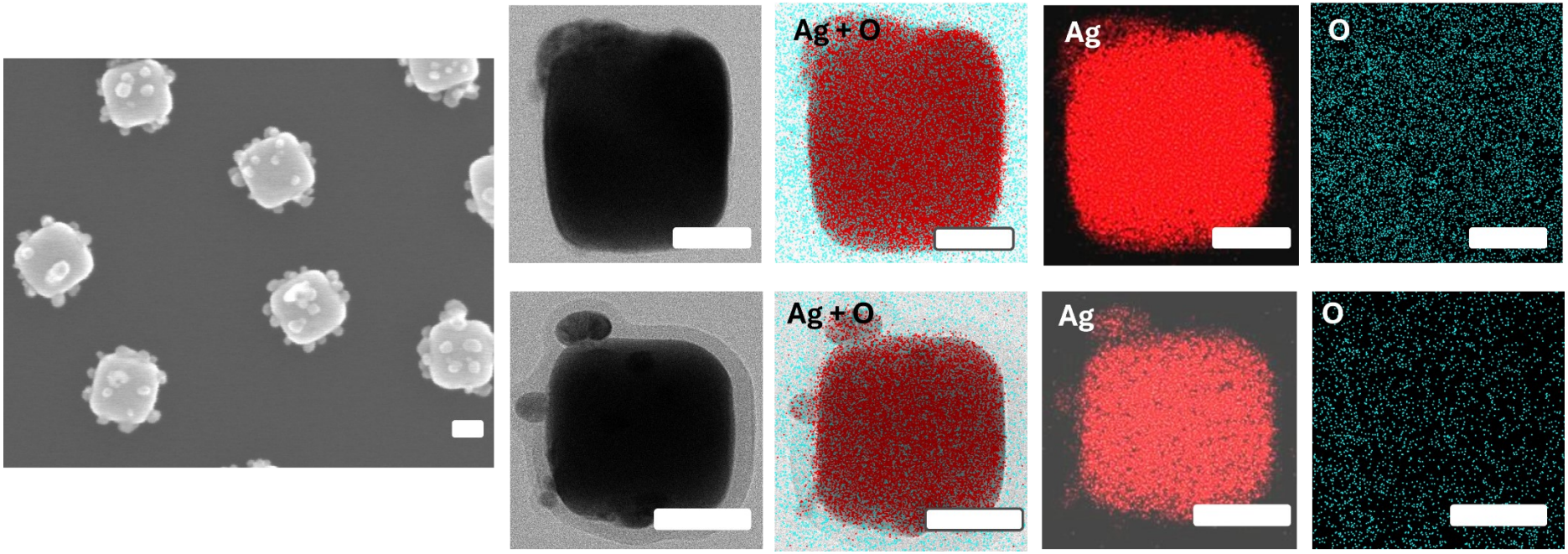

Figure S3 Characterization of lactic acid polymerization on AgNC surface at 0 °C under irradiation by SEM, TEM, and EDX analysis. The results showed that Ag oxidation on AgNC surface can be significantly inhibited compared with the reaction occurring at room temperature. The scale bar was 50 nm.

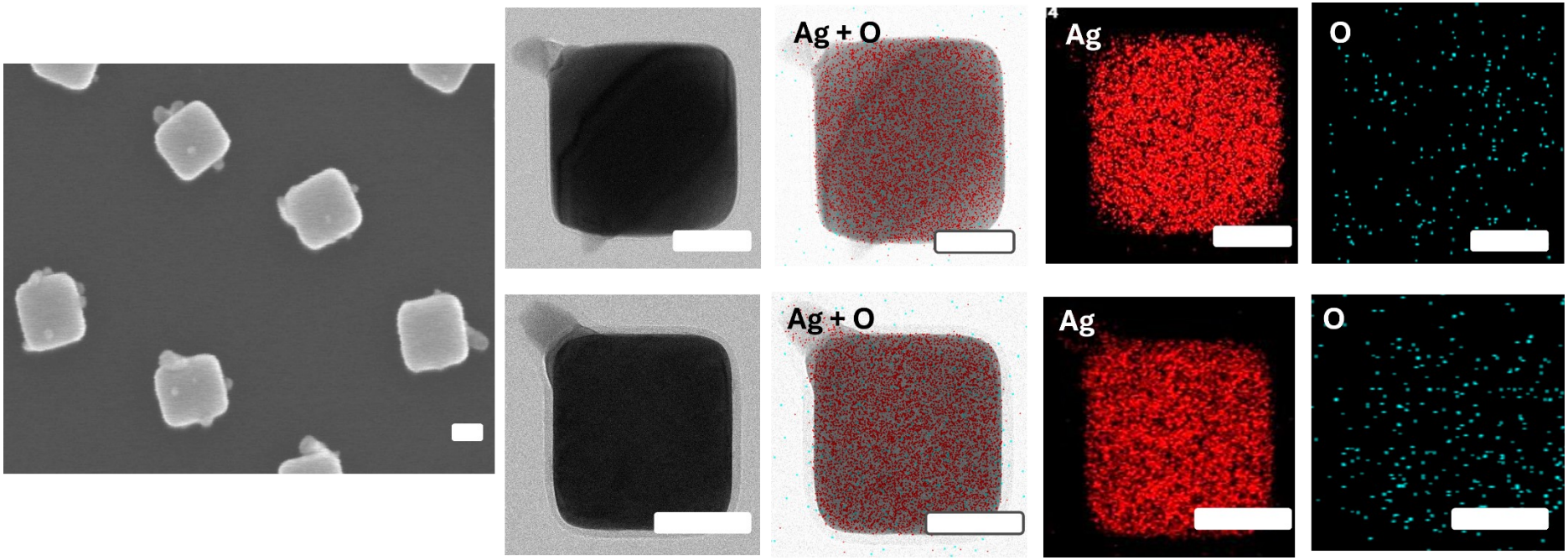

Figure S4 Characterization of lactic acid polymerization on AgNC surface at -12 °C under irradiation by SEM, TEM, and EDX analysis. The results showed that Ag oxidation on AgNC surface can be completely inhibited. The scale bar was 50 nm.

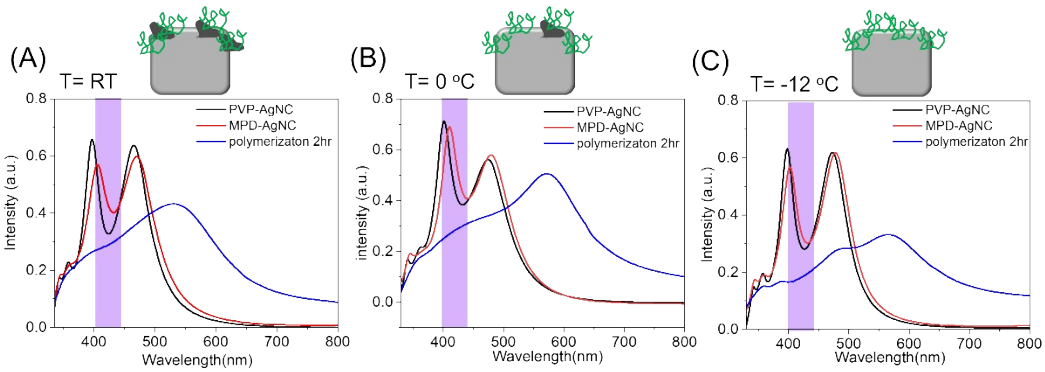

Figure S5 Changes in optical properties of AgNC during lactic acid polymerization at different temperatures under irradiation. (A) at room temperature. (B) at 0 °C. (C) at -12 °C. Black curve: PVP coated AgNC. Red curve: MPD coated AgNC. Blue curve: AgNC after 2 hours of polymerization.

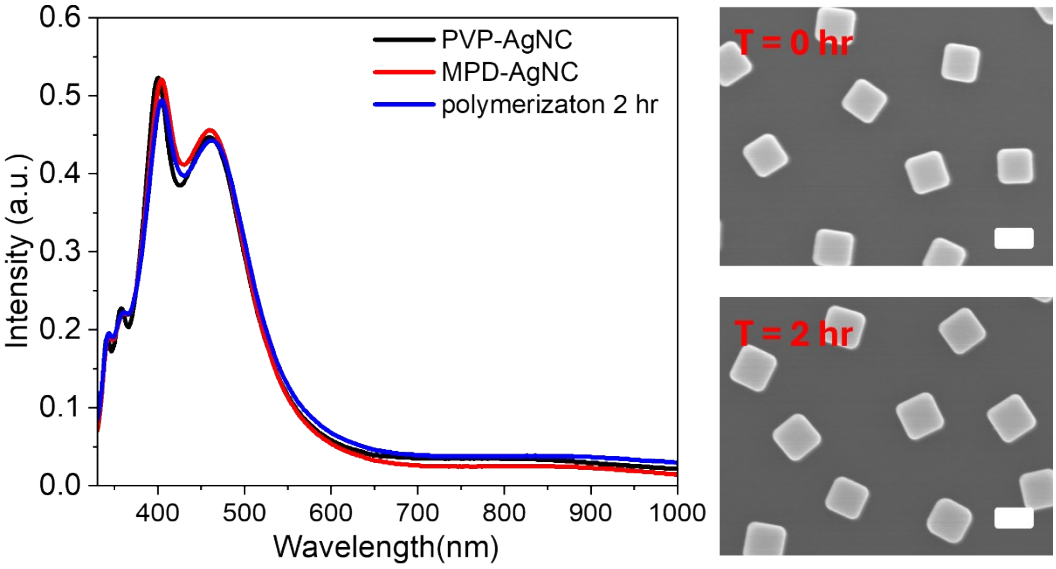

Figure S6 Changes in optical properties of AgNC during lactic acid polymerization at -12 ºC. And the light source was irradiated on the reaction solution but not on the substrate with AgNC. Black curve: PVP coated AgNC. Red curve: MPD coated AgNC. Blue curve: AgNC after 2 hours of polymerization. And SEM images before and after 2 hours of polymerization showed that there was no lactic acid polymerization and Ag oxidation on the AgNC surface. The scale bar was 100 nm.

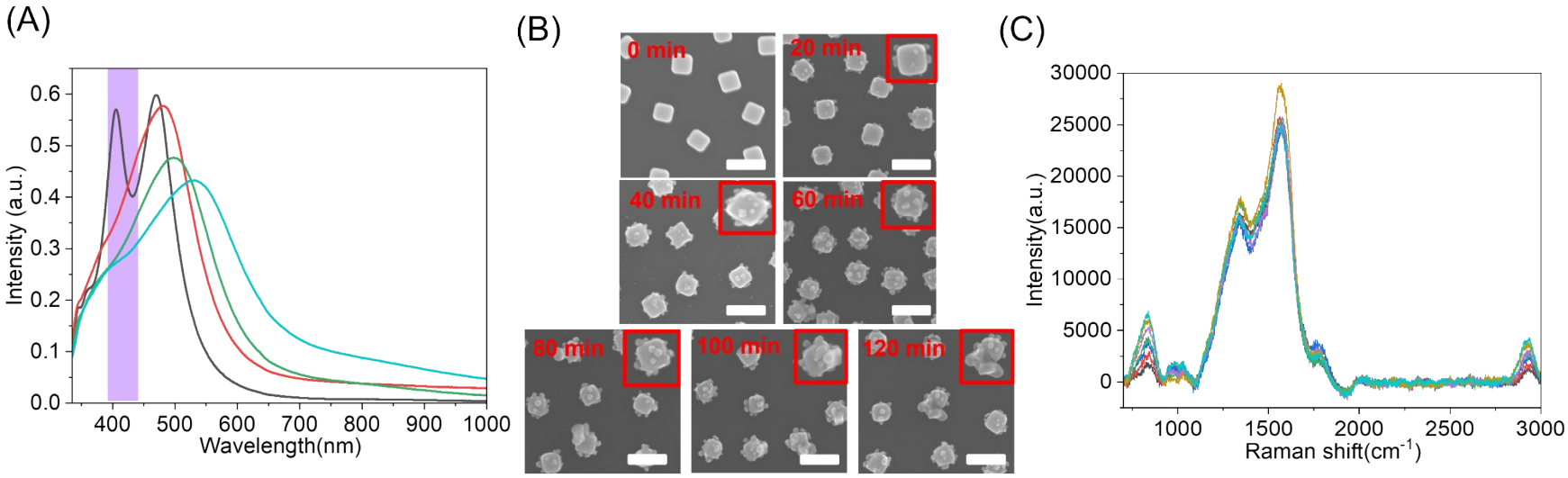

Figure S7 Lactic acid polymerization of AgNC surface under 420 ± 20 nm wavelength irradiation at room temperature. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

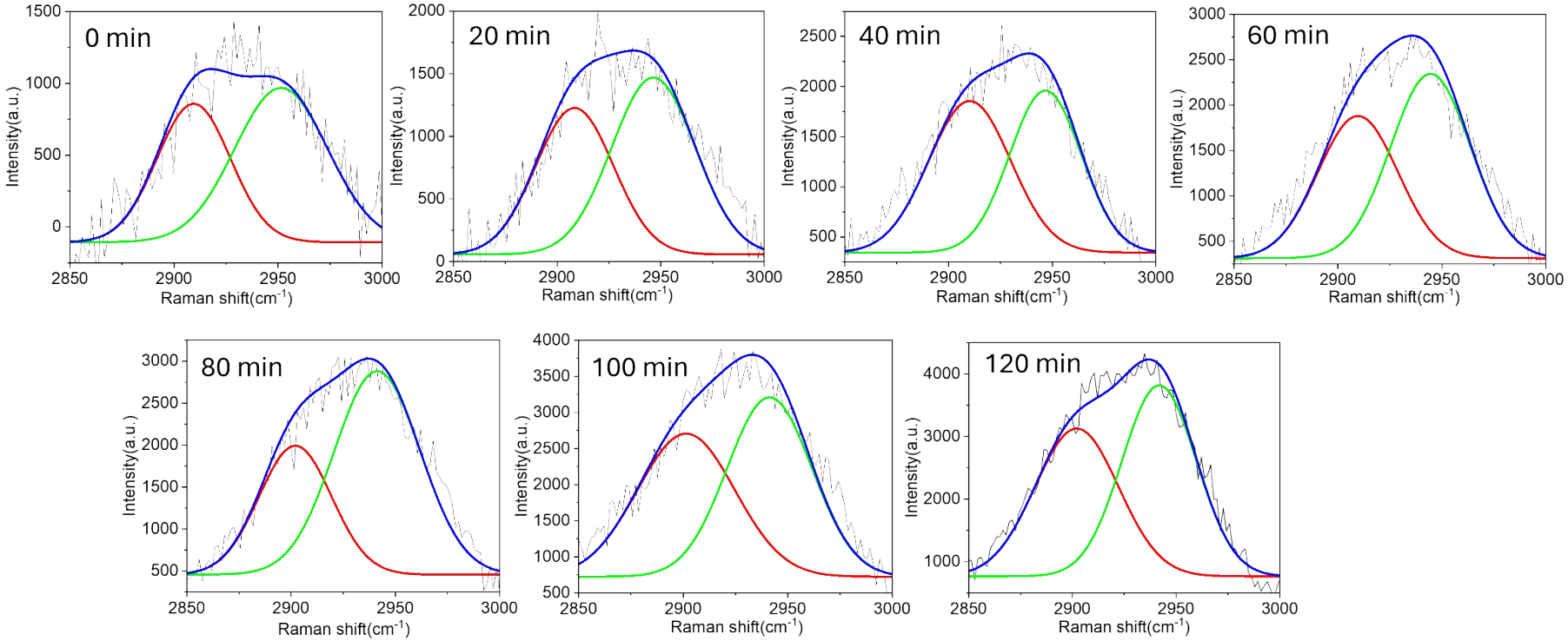

Figure S8 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on AgNC surface under 420 ± 20 nm wavelength irradiation at room temperature. The results showed the multi-curve fitting at different polymerization times.

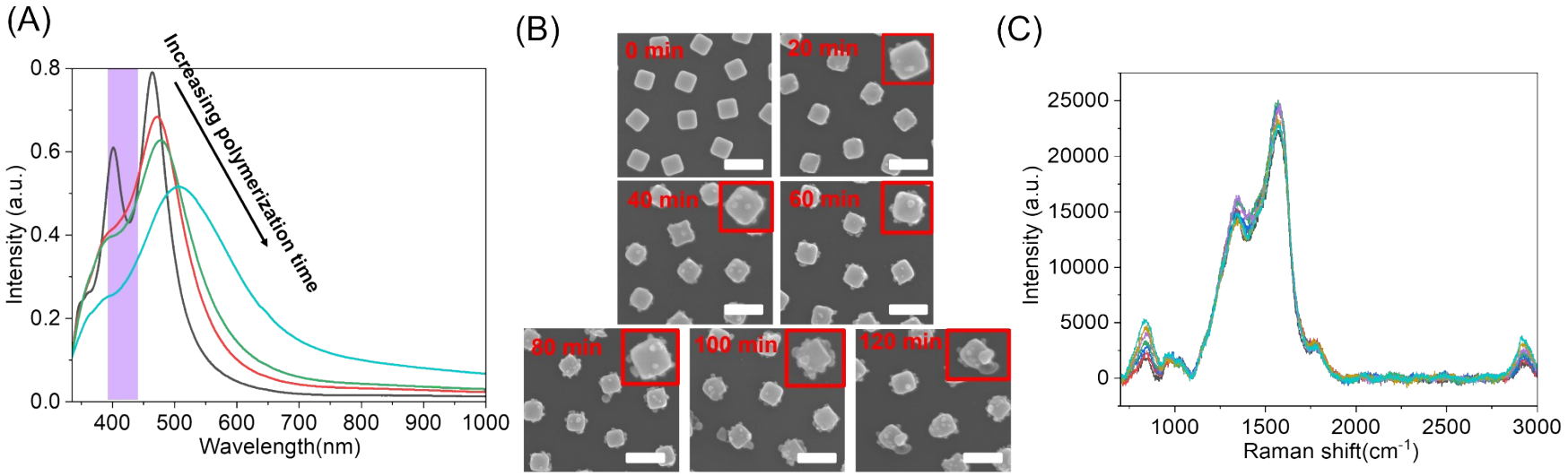

Figure S9 Lactic acid polymerization of AgNC surface under 420 ± 20 nm wavelength irradiation at 0 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

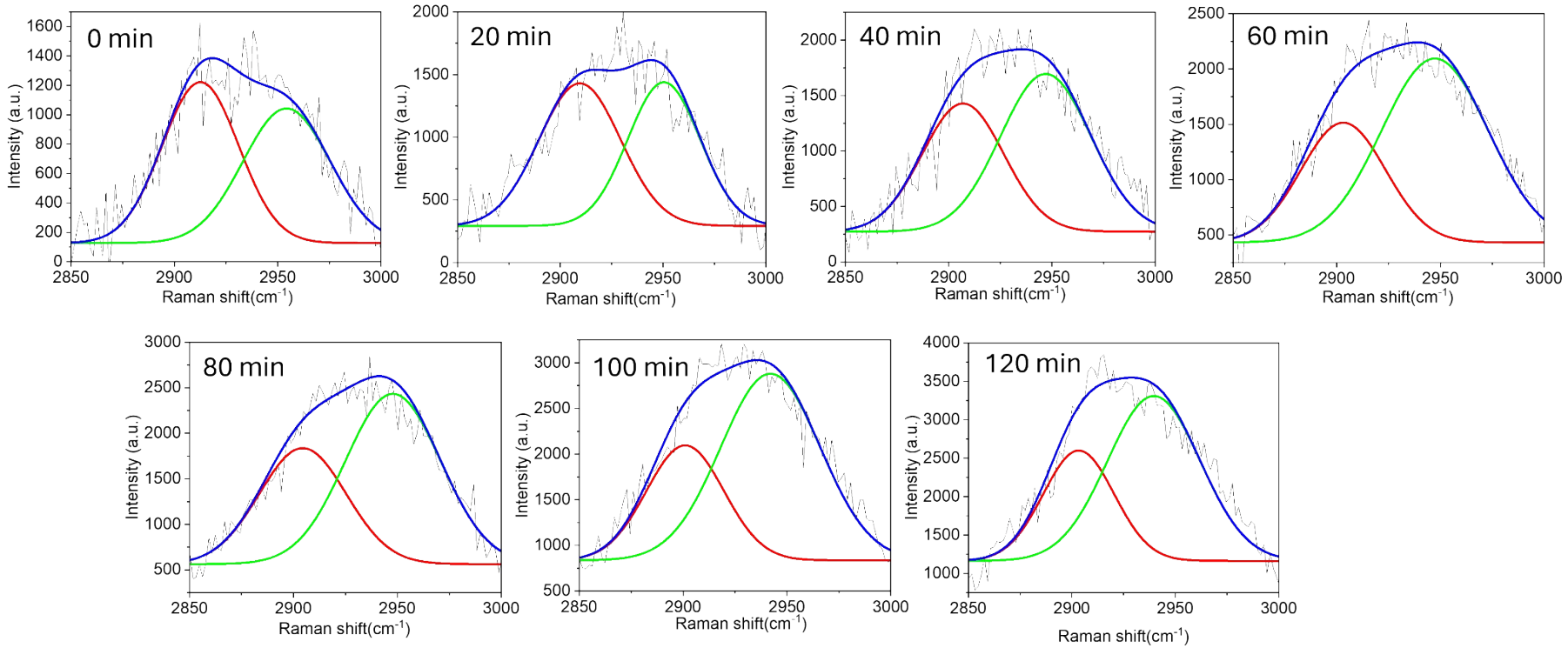

Figure S10 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on AgNC surface under 420 ± 20 nm wavelength irradiation at 0 ºC. The results showed the multi-curve fitting at different polymerization times.

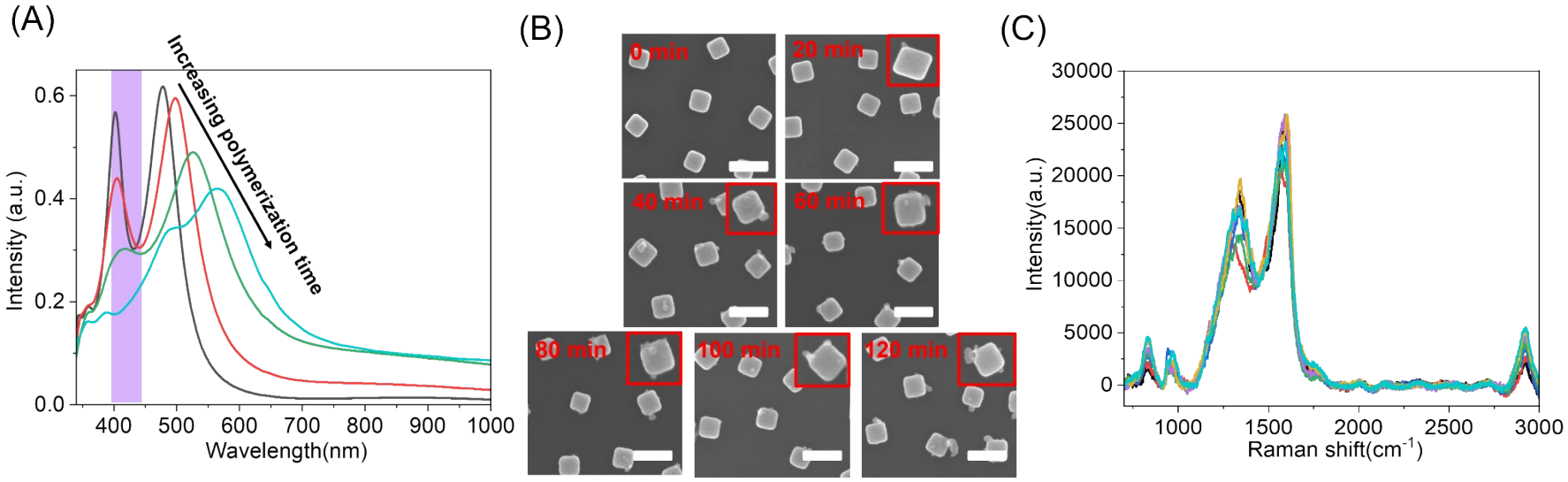

Figure S11 Lactic acid polymerization of AgNC surface under 420 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

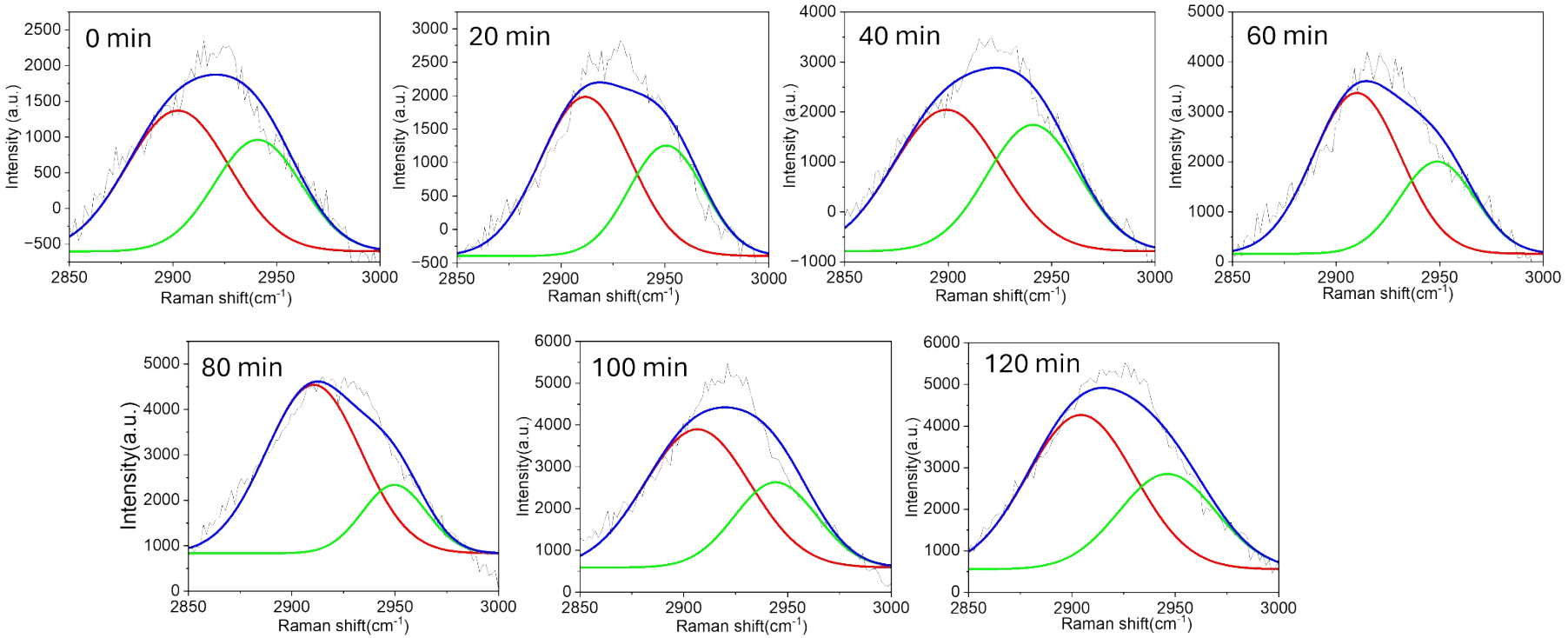

Figure S12 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on AgNC surface under 420 ± 20 nm wavelength irradiation at -12 °C. The results showed the multi-curve fitting at different polymerization times.

Table S1 Changes in Raman vibration mode intensity during polymerization process on AgNC surface under 420 ± 20 nm wavelength irradiation at different temperatures. And the Raman vibration mode intensity was adjusted by the difference in the plasmon mode intensity of AgNC at 533 nm.

Temperature	time	0min	20min	40min	60min	80min	100min	120min
RT	$I_1 = I_{849\ cm^{-1}}$	0	0.549	1.052	1.438	2.031	2.430	2.907
	$I_2 = I_{2953\ cm^{-1}}$	0	0.517	1.025	1.422	1.973	2.313	2.904
	$I_1 - I_2$	0	0.032	0.027	0.016	0.058	0.117	0.003
0°C	$I_1 = I_{849\ cm^{-1}}$	0	0.364	0.722	1.152	1.463	1.899	2.244
	$I_2 = I_{2953\ cm^{-1}}$	0	0.365	0.652	1.010	1.373	1.833	2.189
	$I_1 - I_2$	0	-0.001	0.07	0.142	0.09	0.066	0.055
-12°C	$I_1 = I_{849\ cm^{-1}}$	0	0.397	0.891	1.136	1.467	1.858	2.075
	$I_2 = I_{2953\ cm^{-1}}$	0	0.361	0.891	1.232	1.540	1.848	2.104
	$I_1 - I_2$	0	0.036	0	-0.096	-0.073	0.01	-0.029
$I_{LSPR=533\ nm\ at\ RT} = 0.421;\ I_{LSPR=533\ nm\ at\ 0°C} = 0.376;\ I_{LSPR=533\ nm\ at\ -12°C} = 0.375$ $Adjusted\ factor\ (AF),$ $AF_{RT} = \frac{I_{RT}}{I_{-12°C}} = \frac{0.421}{0.375} = 1.123;\ AF_{0°C} = \frac{I_{0°C}}{I_{-12°C}} = \frac{0.376}{0.375} = 1.002;\ AF_{-12°C} = \frac{I_{-12°C}}{I_{-12°C}} = \frac{0.375}{0.375} = 1.000$								
RT	$I_3 = I_{849\ cm^{-1}}/AF_{RT}$	0	0.489	0.937	1.280	1.808	2.164	2.589
	$I_4 = I_{2953\ cm^{-1}}/AF_{RT}$	0	0.460	0.912	1.266	1.757	2.060	2.586
	$I_3 - I_4$	0	0.029	0.025	0.014	0.051	0.104	0.003
9	$I_3 = I_{849\ cm^{-1}}/AF_{0°C}$	0	0.363	0.721	1.150	1.460	1.895	2.240
	$I_4 = I_{2953}/AF_{0°C}$	0	0.364	0.651	1.008	1.370	1.829	2.185
	$I_3 - I_4$	0	-0.001	0.070	0.142	0.090	0.066	0.055

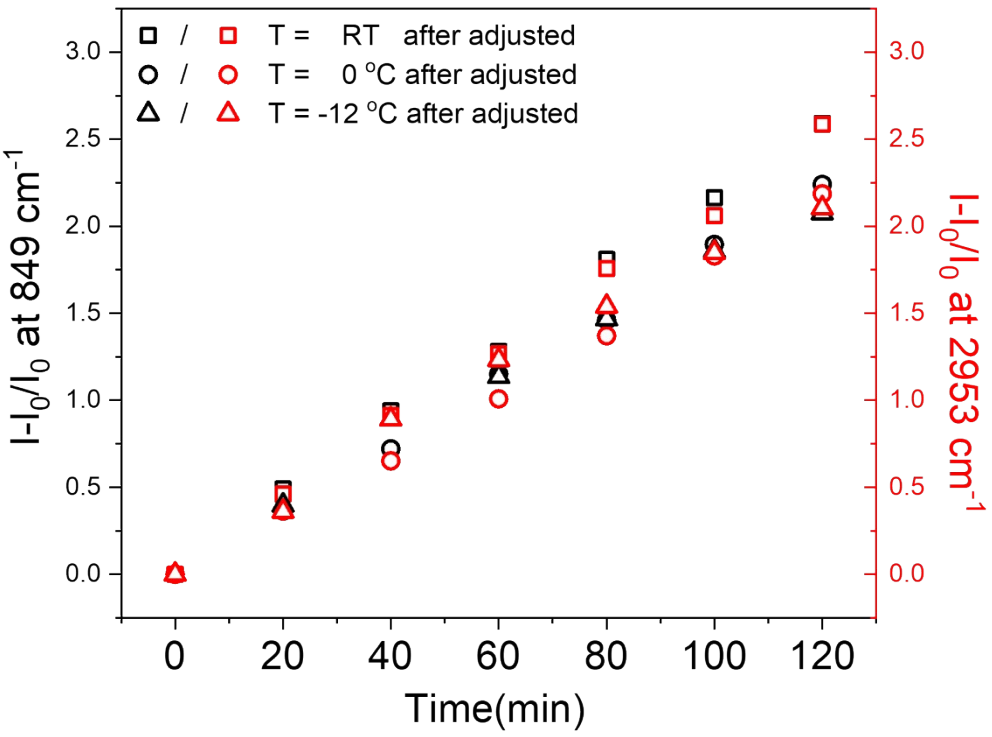

Figure S13 Changes in Raman scattering spectra during lactic acid polymerization on AgNC surface under 420 ± 20 nm wavelength irradiation at -12 °C adjusted by the difference in the plasmon mode intensity of AgNC at 533 nm.

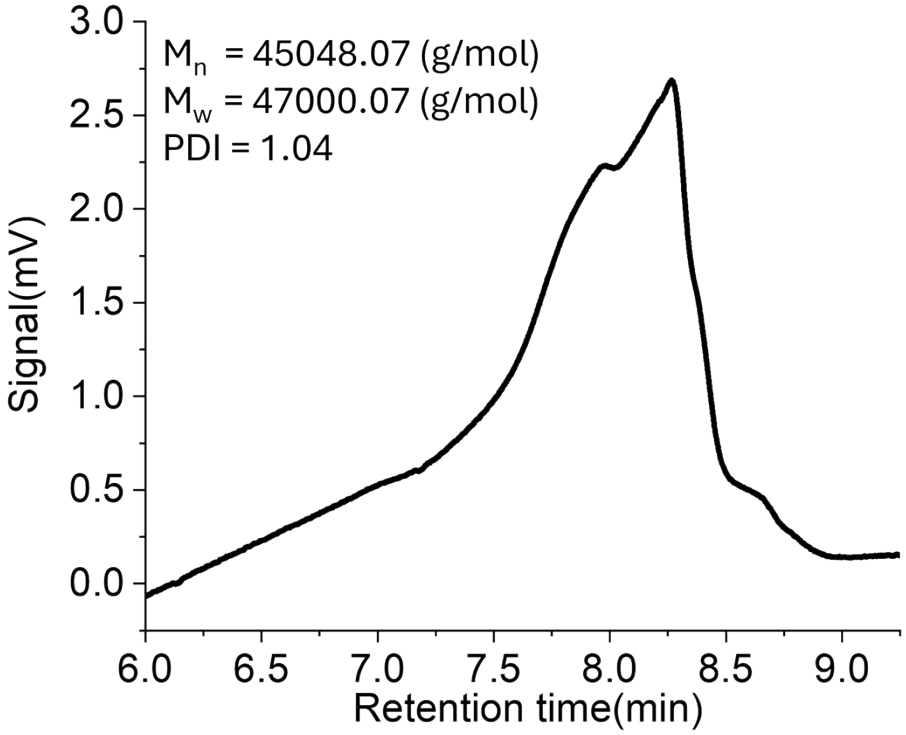

Figure S14 The gel permeation chromatography (GPC) of polylactic acid on the surface of AgNC at -12°C. Polylactic acid molecules can be removed from the surface of nanocrystals by ultrasonic treatment, and then the molecular weight of polylactic acid can be measured by gel permeation chromatography (GPC). The results showed M_n~ 45000 g/mole, M_w ~ 47000, and PDI~1.04.

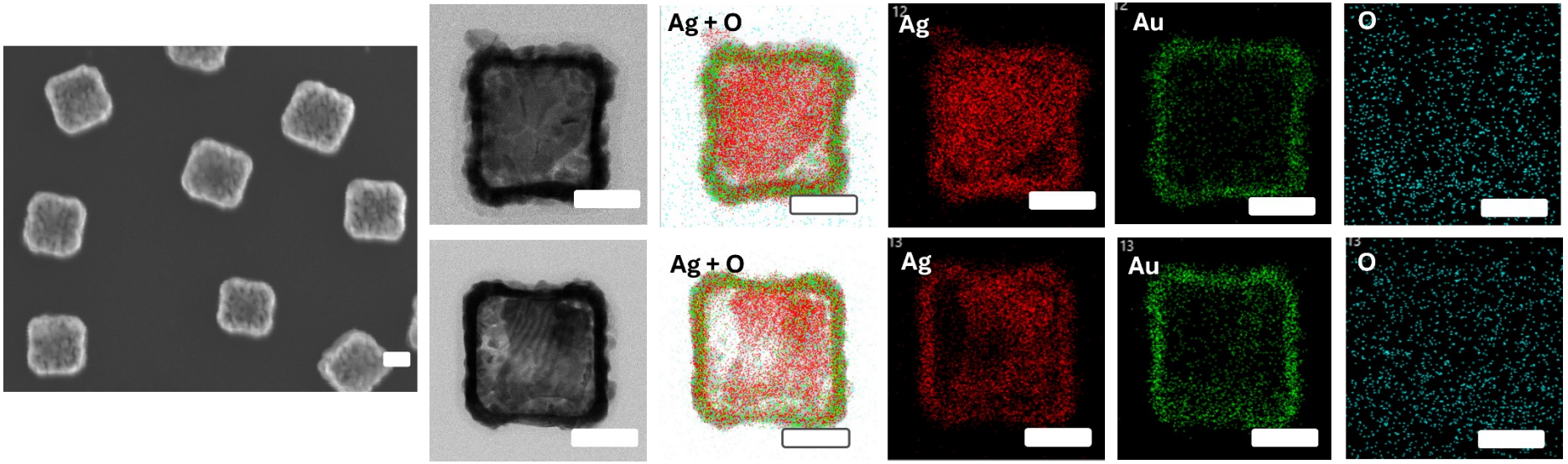

Figure S15 Characterization of lactic acid polymerization on cage-like Au-AgNC surface at -12 °C under irradiation by SEM, TEM, and EDX analysis. The results showed that Ag oxidation on cage-like Au-AgNC surface can be completely inhibited. The scale bar was 50 nm.

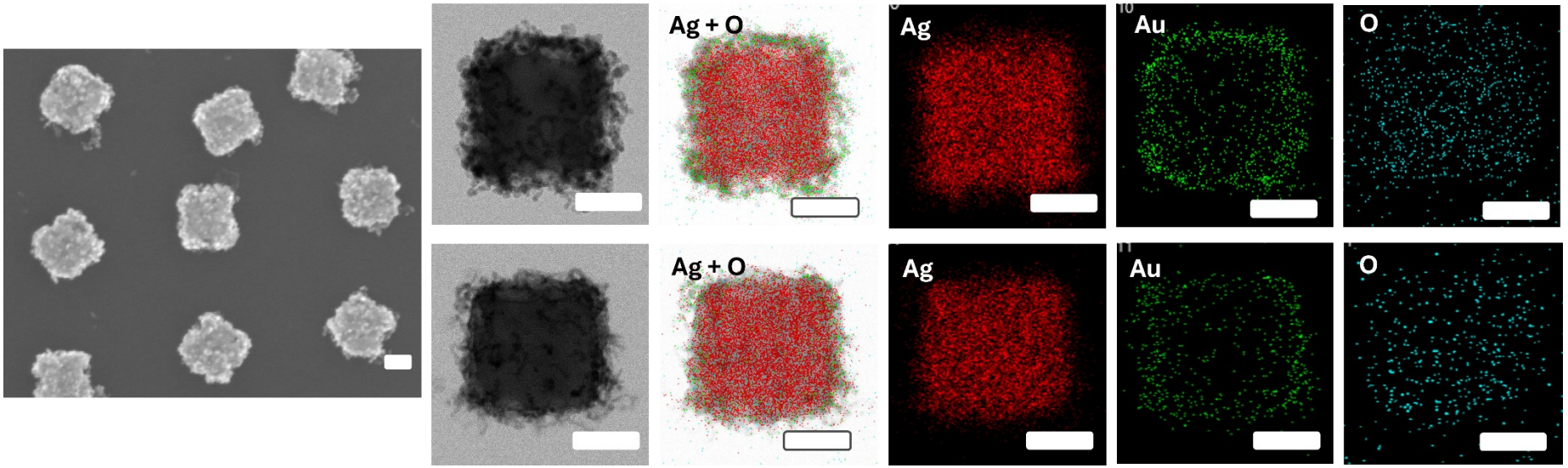

Figure S16 Characterization of lactic acid polymerization on flower like Au-AgNC surface under -12 °C under irradiation by SEM, TEM, and EDX analysis. The results showed that Ag oxidation on flower-like Au-AgNC surface can be completely inhibited. The scale bar was 50 nm.

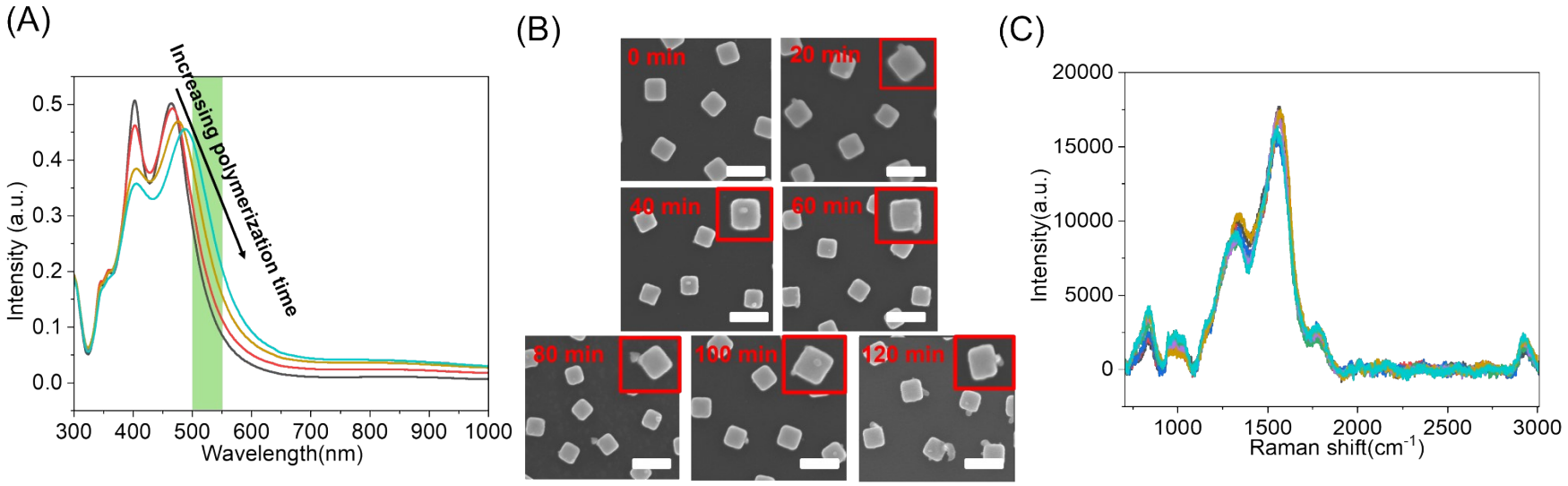

Figure S17 Lactic acid polymerization of AgNC surface under 520 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

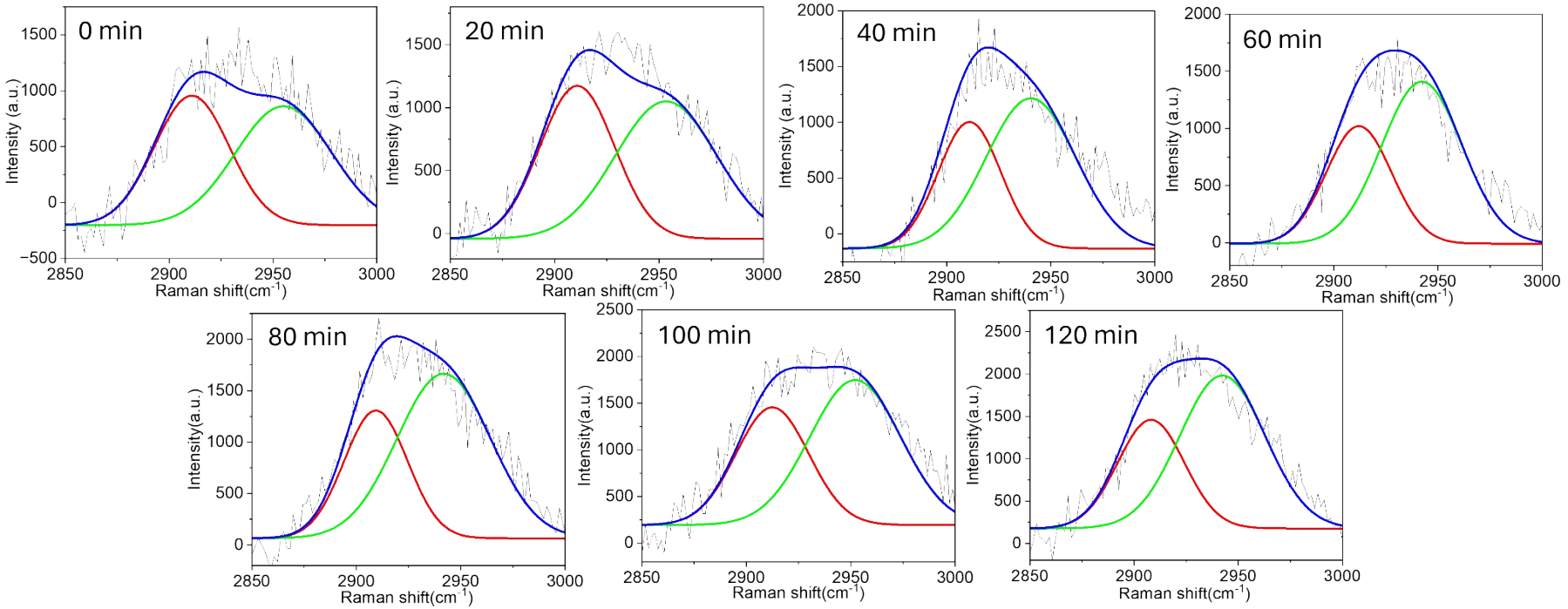

Figure S18 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on AgNC surface under 520 ± 20 nm wavelength irradiation at -12 °C. The results showed the multi-curve fitting at different polymerization times.

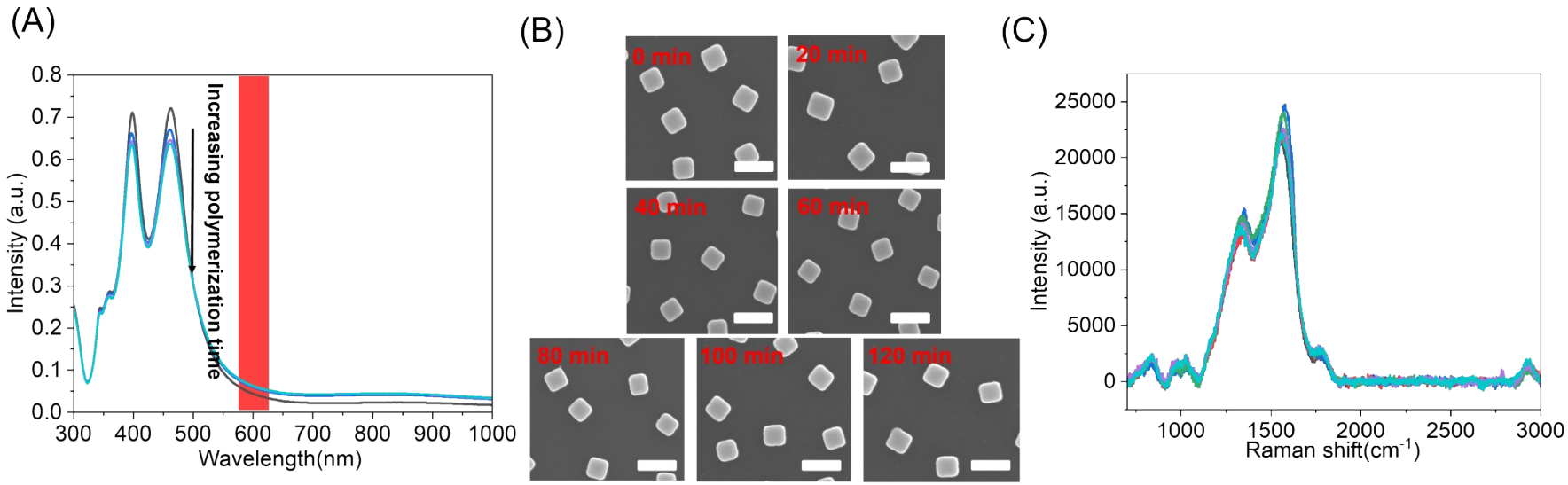

Figure S19 Lactic acid polymerization of AgNC surface under 600 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

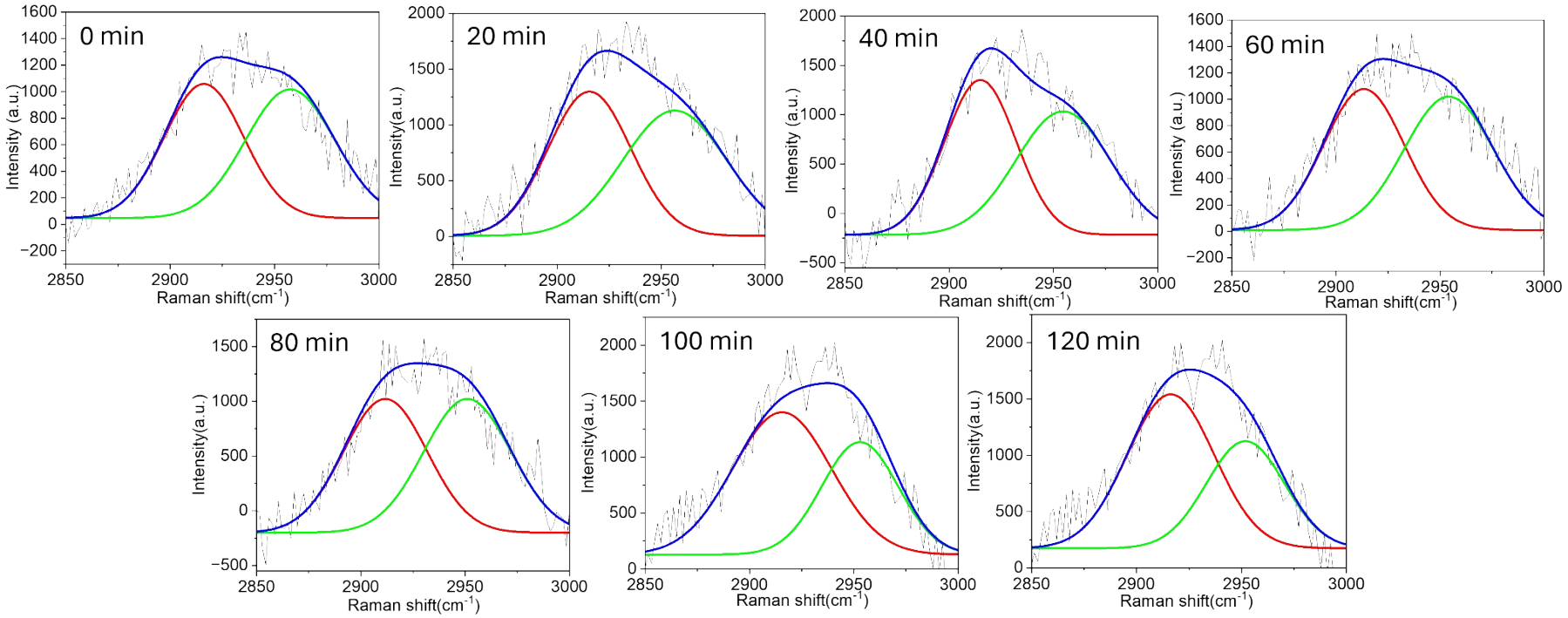

Figure S20 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on AgNC surface under 600 ± 20 nm wavelength irradiation at -12 °C. The results showed the multi-curve fitting at different polymerization times.

Table S2 Changes in Raman vibration mode intensity during polymerization process on AgNC surface under three different wavelength irradiations at -12 °C.

Irradiation wavelength	time	0min	20min	40min	60min	80min	100min	120min
420 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.397	0.891	1.136	1.467	1.858	2.075
	$I_2 = I_{2953\,cm^{-1}}$	0	0.361	0.891	1.232	1.540	1.848	2.104
	$I_1 - I_2$	0	0.036	0	-0.096	-0.073	0.01	-0.029
520 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.233	0.42	0.635	0.922	1.058	1.297
	$I_2 = I_{2953\,cm^{-1}}$	0	0.225	0.41	0.635	0.931	1.028	1.301
	$I_1 - I_2$	0	0.008	0.01	0	-0.009	0.03	-0.004
600 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.014	0.031	0.031	0.043	0.096	0.099
	$I_2 = I_{2953\,cm^{-1}}$	0	0.081	0.015	0.002	0.004	0.106	0.114
	$I_1 - I_2$	0	-0.067	0.016	0.029	0.039	-0.01	-0.015

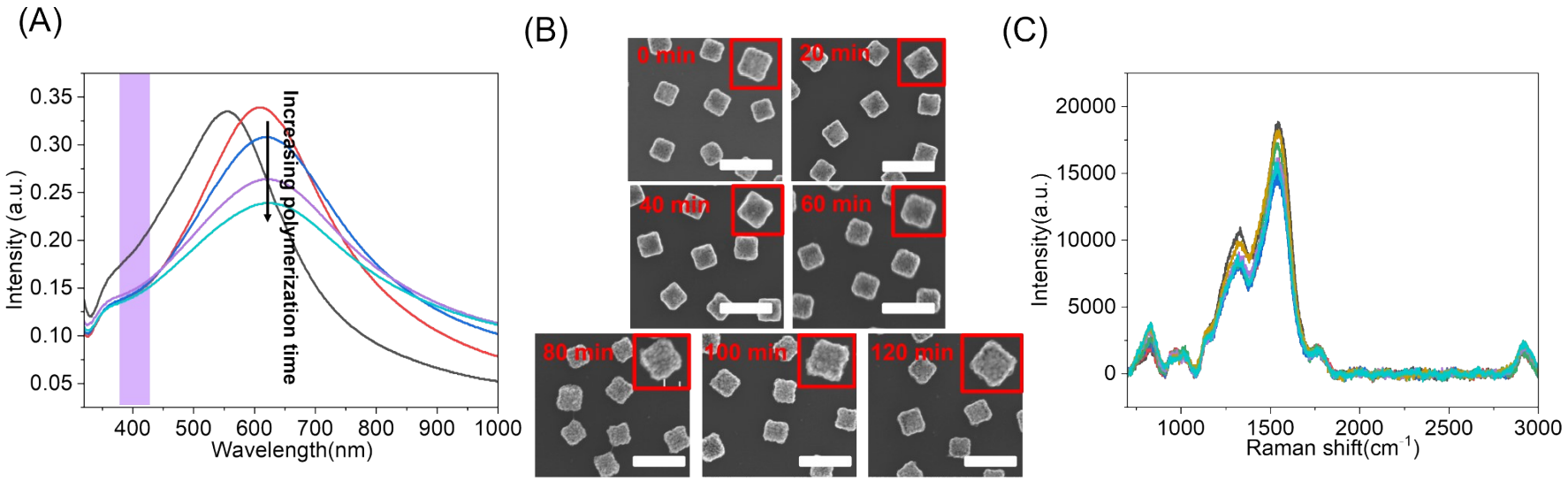

Figure S21 Lactic acid polymerization of cage-like Au-AgNC surface under 420 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

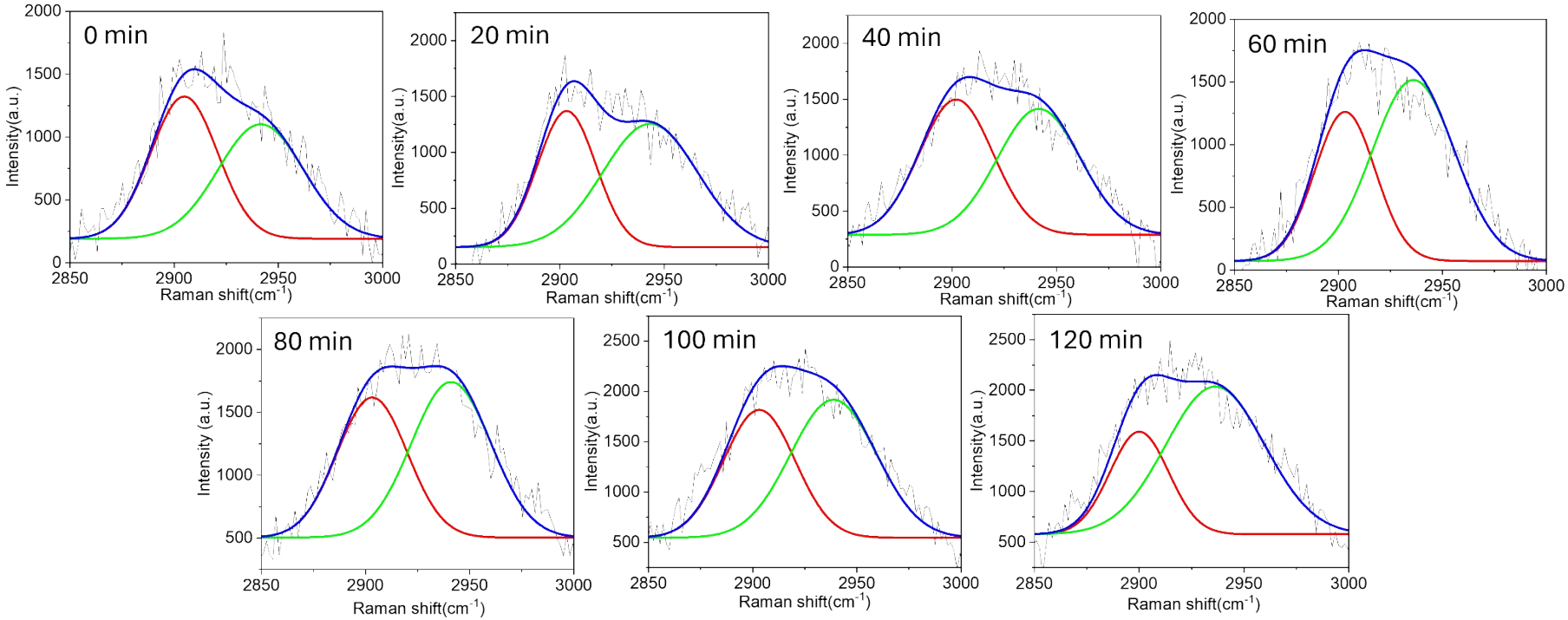

Figure S22 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on cage-like Au-AgNC surface under 420 ± 20 nm wavelength irradiation at -12 °C. The results showed the multi-curve fitting at different polymerization times.

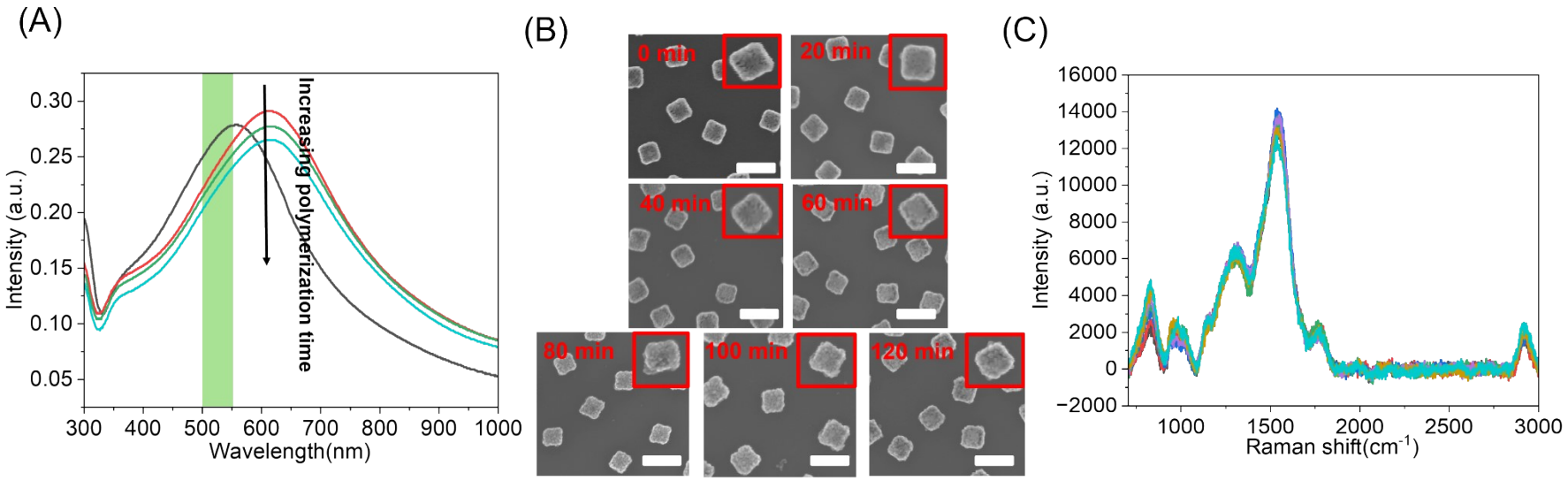

Figure S23 Lactic acid polymerization of cage-like Au-AgNC surface under 520 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

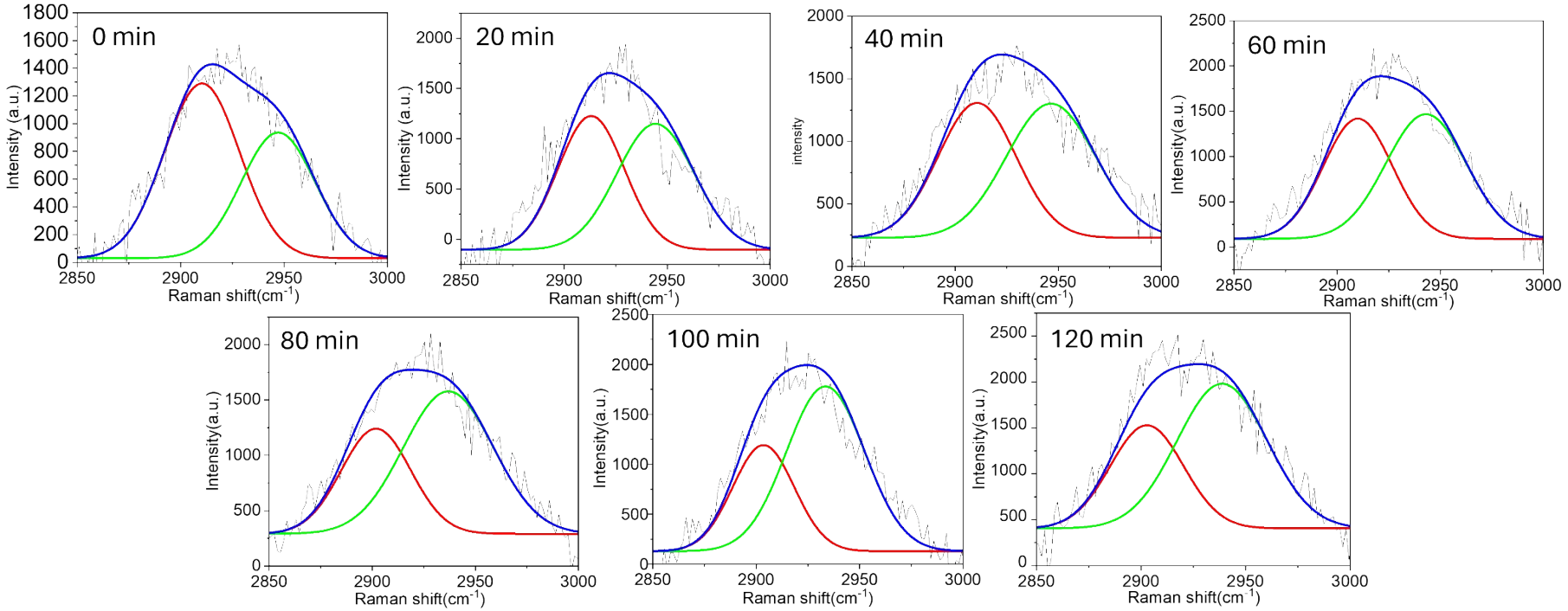

Figure S24 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on cage-like Au-AgNC surface under 520 ± 20 **nm wavelength irradiation at -12 °C.** The results showed the multi-curve fitting at different polymerization times.

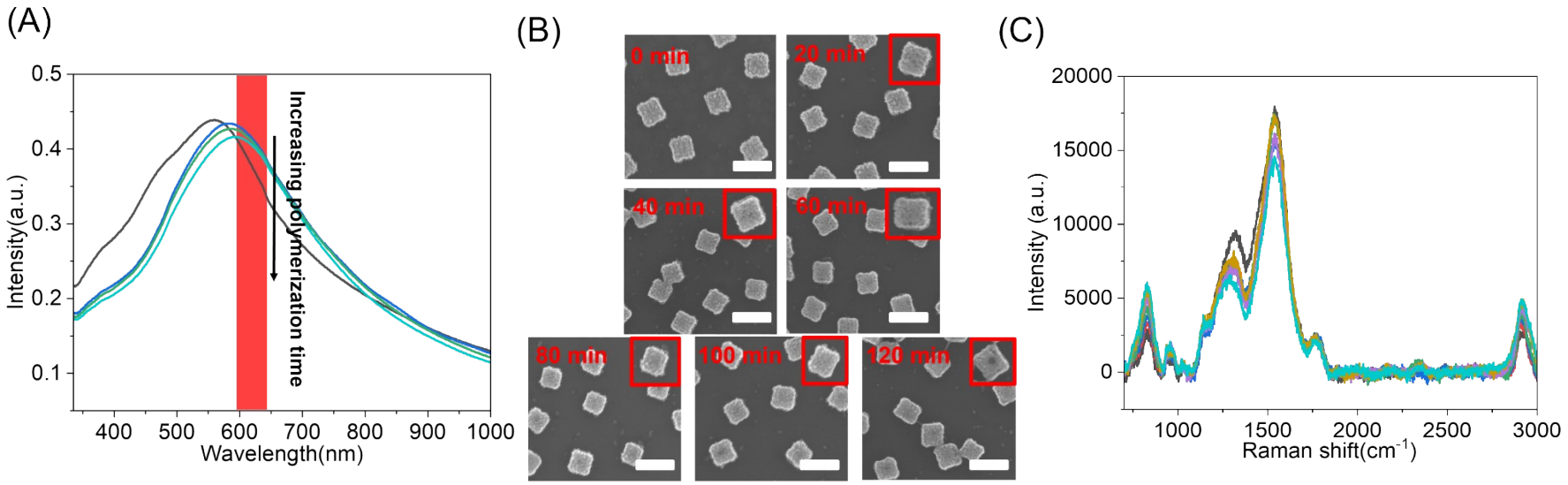

Figure S25 Lactic acid polymerization of cage-like Au-AgNC surface under 600 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

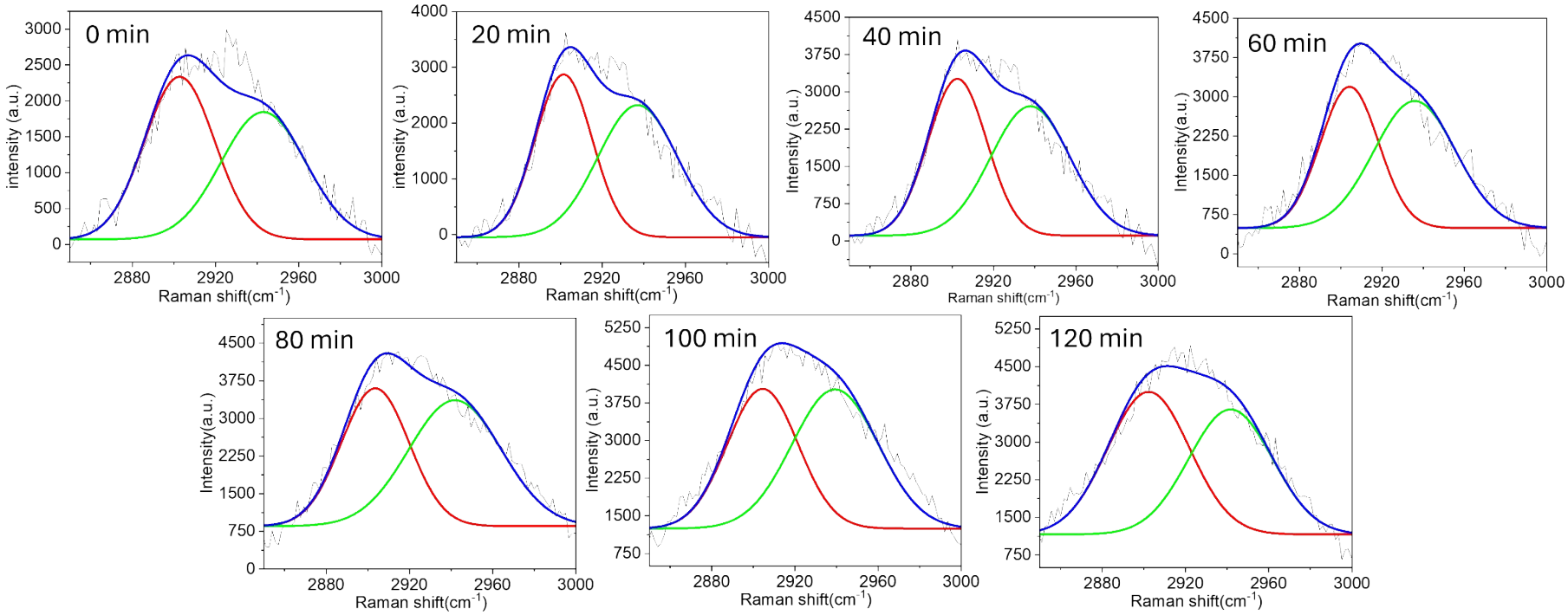

Figure S26 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on cage-like Au-AgNC surface under 600 ± 20 **nm wavelength irradiation at -12 °C.** The results showed the multi-curve fitting at different polymerization times.

Table S3 Changes in Raman vibration mode intensity during polymerization process on cage-like Au-AgNC surface under three different wavelengths irradiation at -12 °C.

Irradiation wavelength	time	0min	20min	40min	60min	80min	100min	120min
420 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.13	0.286	0.434	0.612	0.751	0.918
	$I_2 = I_{2953\,cm^{-1}}$	0	0.151	0.295	0.388	0.596	0.757	0.866
	$I_1 - I_2$	0	-0.021	-0.009	0.046	0.016	-0.006	0.052
520 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.204	0.401	0.537	0.726	0.913	1.111
	$I_2 = I_{2953\,cm^{-1}}$	0	0.214	0.388	0.564	0.687	0.902	1.111
	$I_1 - I_2$	0	-0.01	0.013	-0.027	0.039	0.011	0
600 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.273	0.433	0.626	0.884	1.042	1.254
	$I_2 = I_{2953\,cm^{-1}}$	0	0.258	0.483	0.609	0.842	0.999	1.201
	$I_1 - I_2$	0	0.015	-0.05	0.017	0.042	0.043	0.053

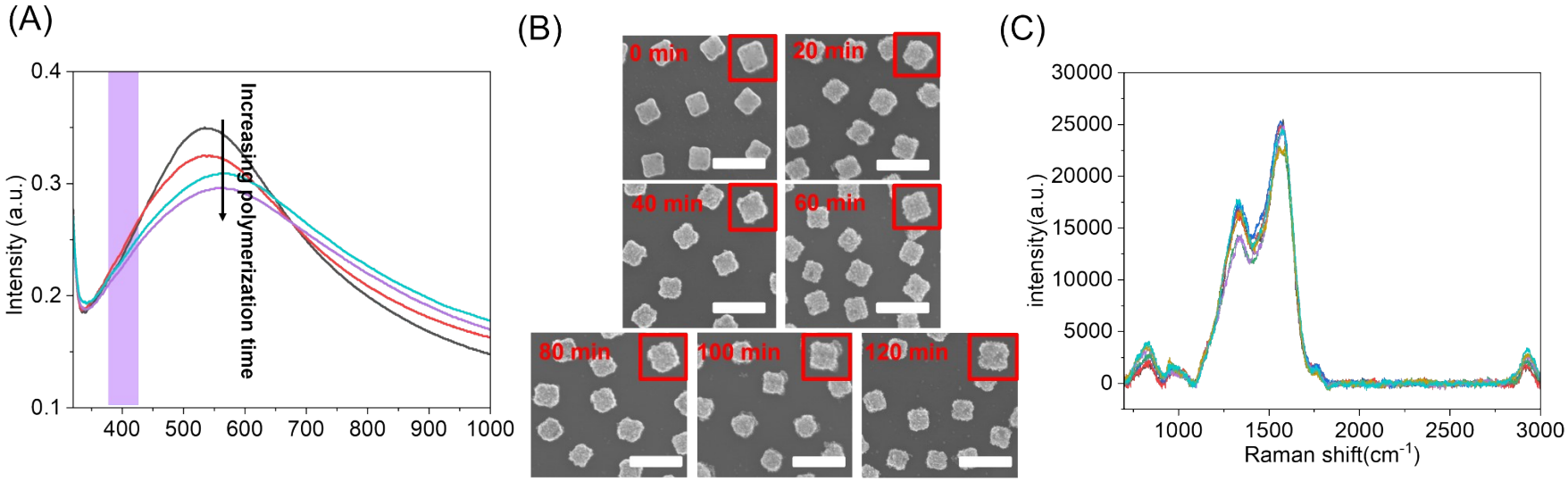

Figure S27 Lactic acid polymerization of flower-like Au-AgNC surface under 420 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

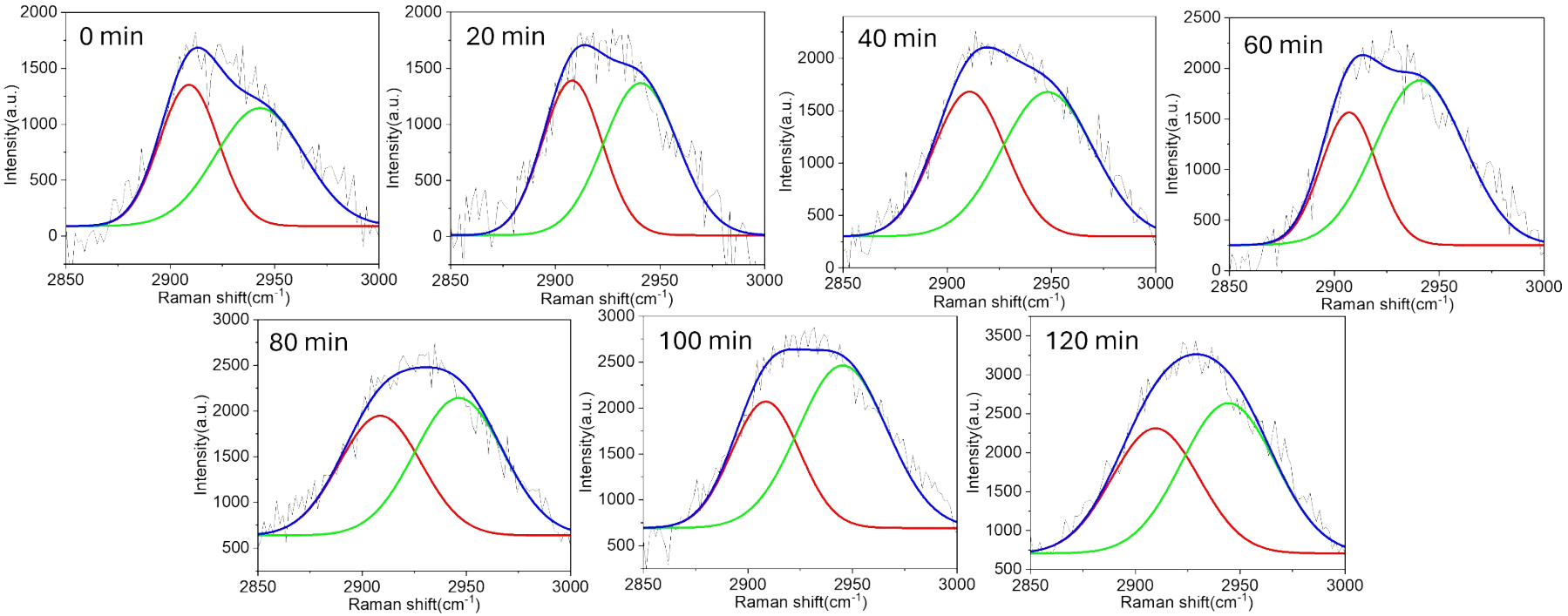

Figure S28 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on flower-like Au-AgNC surface under 420 ± 20 nm wavelength irradiation at -12 °C. The results showed the multi-curve fitting at different polymerization times.

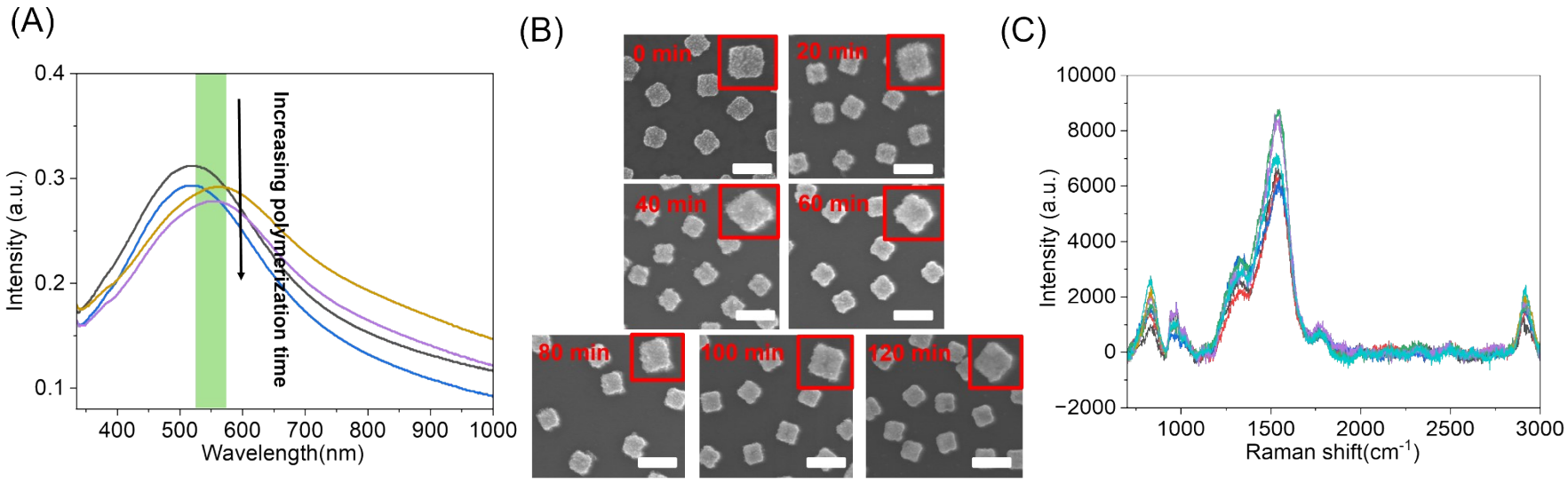

Figure S29 Lactic acid polymerization of flower-like Au-AgNC surface under 520 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

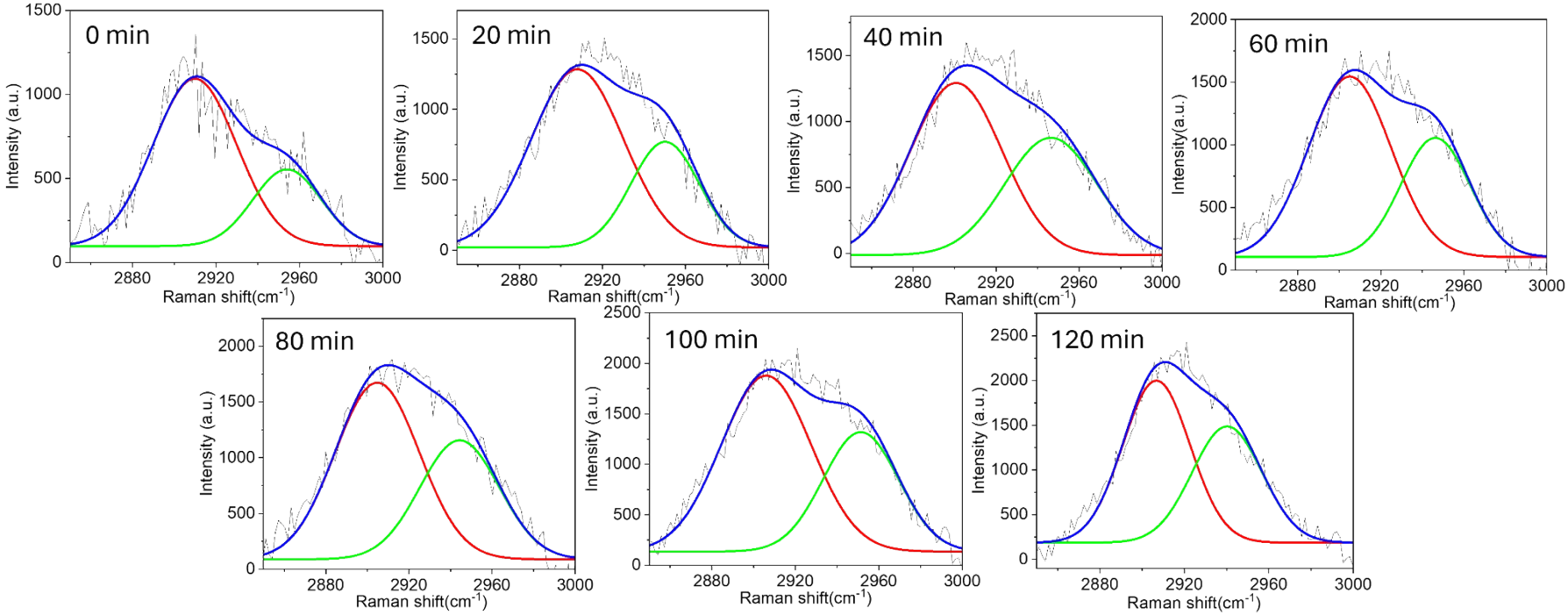

Figure S30 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on flower-like Au-AgNC surface under 520 ± 20 nm wavelength irradiation at -12 °C. The results showed the multi-curve fitting at different polymerization times.

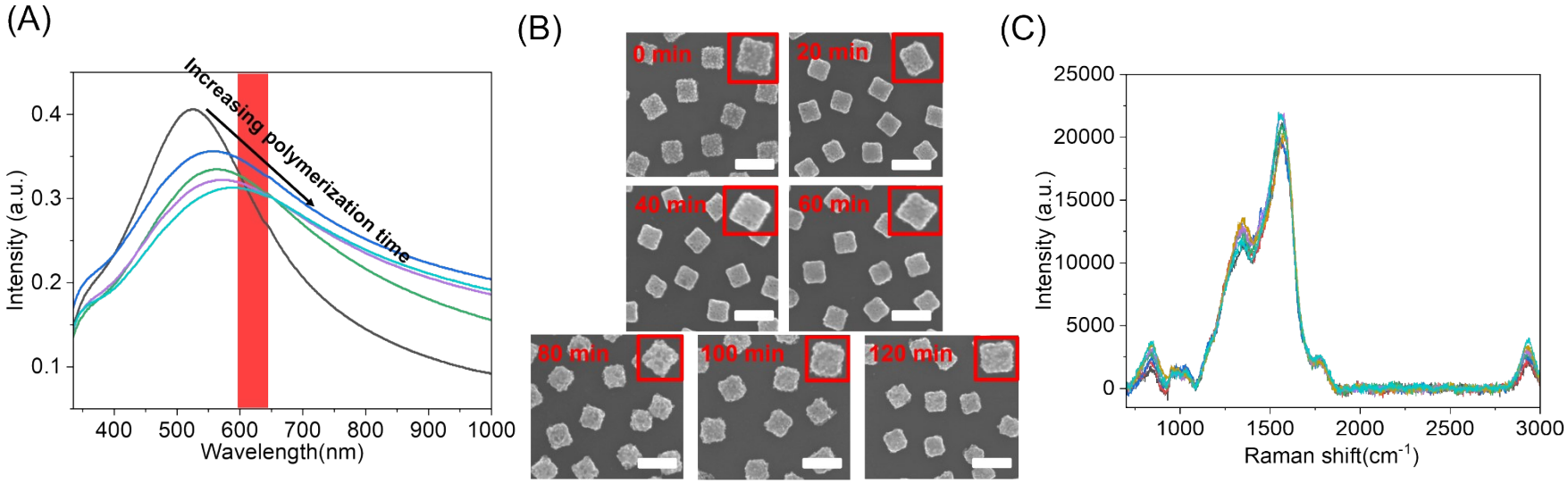

Figure S31 Lactic acid polymerization of flower-like Au-AgNC surface under 600 ± 20 nm wavelength irradiation at -12 °C. (A) changes in the extinction spectrum of AgNC during polymerization process. (B) characterization of the morphology changes of AgNC during the polymerization process through SEM images. (C) changes in Raman spectra during the polymerization process were used to characterize the amount of polylactic acid formed on AgNC surface. The scale bar was 200 nm.

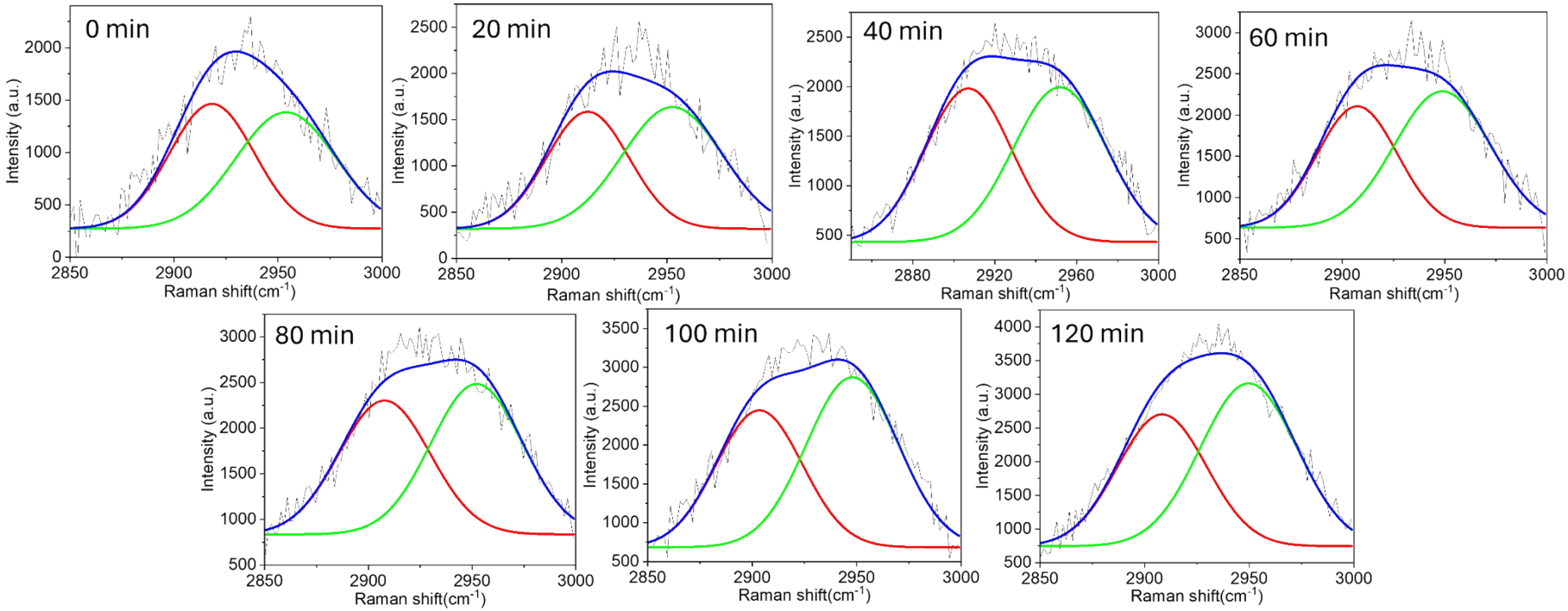

Figure S32 The multi-curve fitting results of Raman scattering spectra during lactic acid polymerization on flower-like Au-AgNC surface under 600 ± 20 nm wavelength irradiation at -12 °C. The results showed the multi-curve fitting at different polymerization times.

Table S4 Changes in Raman vibration mode intensity during polymerization process on flower-like Au-AgNC surface under three different wavelengths irradiation at -12 °C.

Irradiation wavelength	time	0min	20min	40min	60min	80min	100min	120min
420 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.206	0.464	0.643	0.895	1.145	1.336
	$I_2 = I_{2953\,cm^{-1}}$	0	0.202	0.444	0.674	0.881	1.162	1.314
	$I_1 - I_2$	0	0.004	0.02	-0.031	0.014	-0.017	0.022
520 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.415	0.691	0.926	1.215	1.417	1.727
	$I_2 = I_{2953\,cm^{-1}}$	0	0.387	0.582	0.906	1.087	1.323	1.679
	$I_1 - I_2$	0	0.028	0.109	0.02	0.128	0.094	0.048
600 nm	$I_1 = I_{849\,cm^{-1}}$	0	0.191	0.433	0.629	0.797	1.060	1.269
	$I_2 = I_{2953\,cm^{-1}}$	0	0.184	0.441	0.645	0.789	1.074	1.284
	$I_1 - I_2$	0	0.007	-0.008	-0.016	0.008	-0.014	-0.015