Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Synthesis of Fluorescent Carbon Nanoparticles by Dispersion Polymerization of Acetylene

Vijay K. Jayswal, Anna M. Ritcey and Jean-François Morin*

Département de Chimie et Centre de Recherche sur les Matériaux Avancés (CERMA),

Université Laval,

1045, Ave. de la Médecine, Quebec City, Quebec Canada G1V 0A6

*Corresponding author: jean-fancois.morin@chm.ulaval.ca

Materials and Methods

Chemicals and Materials

Chemical reagents were purchased from Sigma-Aldrich Co. Canada or Oakwood Products Inc. and were used as received, except 1,4-benzoquinone which was recrystallized in water before use. Solvents were obtained from Fisher Scientific and were used as received. 1-Propanol (1-PrOH) and triethylamine (NEt_3) used for the Pd-catalyzed homocoupling reactions were degassed 20 min before use. All anhydrous and air-sensitive reactions were performed in oven-dried glassware under positive nitrogen pressure. Acetylene cylinder, 99.6% purity, AA grade for atomic absorption was purchased from PraxAir.

Instrumentation and measurements

Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) experiments were recorded using a JEOL apparatus, model JEM-1230. The images for repetition experiments and scale-up experiments were recorded with a *Tecnai* 12 transmission electron microscope (100 kV; Philips Electronic) equipped with an integrated Mega-View II digital camera (SIS, Germany). The samples were prepared from a dispersion of particles dropped onto a nickel grid (hexagonal, 200 mesh) precoated with amorphous carbon. The substrate was dried in the air prior to analysis. The analyses of nanoparticles were performed with ImageJ and the average nanoparticle size and size histogram were created with the size data of a minimum of 100 nanoparticles. The size of aggregation of nanoparticles was measured by measuring between both ends of visible nanoparticle shapes.

Dynamic light scattering (DLS) measurements were performed on a Malvern apparatus, model Zetasizer Nano ZS. The analyses were performed with the solution placed in disposable cuvettes with propanol as a dispersant.

FT-IR spectra were recorded in ATR mode using a Thermo-Nicolet Magna 850 infrared spectrometer equipped with Golden Gate with the CNPs dispersed in solvents (methanol,1-propanol, acetonitrile) and letting it air dry after dropping on the detector.

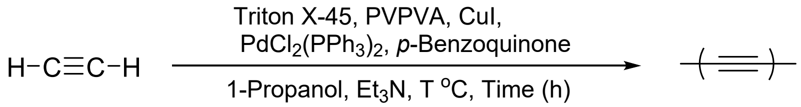
Raman spectra were recorded with an inVia Raman spectrometer from Renishaw, coupled to a Leica DM2700 microscope. For measurements, CNPs were deposited on a silicon wafer by drop-casting, and a 633nm laser was used at 10mW power with an acquisition time of 36s (6s x 6) at the grating of 1800 lines/mm.

UV−visible absorption spectroscopy was performed using a Varian diode-array spectrophotometer (model Cary 500) using 10 mm path length quartz cells. Solution phase fluorescence spectroscopy was performed using a Cary Eclipse fluorescence spectrophotometer.

A PHI 5600-ci spectrometer (Physical Electronics U.S.A.) was used to perform XPS analysis of CNPs. A standard aluminum X-ray source (1486.6 eV) was used for survey spectra (1400−0 eV). High-resolution spectra of C 1s were obtained using a standard magnesium X-ray source (1253.6 eV). XAES measurements were taken with a monochromated aluminum Kα source (1486.6 eV). Charge neutralization was not applied in either analysis. Detection was performed at 45° relative to the surface normal of a 0.5 mm^2 area. The spectrometer work function was adjusted to give 284.8 eV for the main C 1s peak. Data processing and analysis were performed with MultiPak and later processed with Origin for graphing. Curve fittings for high-resolution peaks were determined utilizing the least-squares minimization procedure employing Gaussian−Lorentzian functions and a Shirley-type background. The XAES data were smoothened with a 25-point Savitzky-Golay filter 15 times before applying the first derivative. The D-parameter was calculated as the distance between the maximum and minimum points found in the derivative spectra. For each sample analyzed, measurements were acquired at two different points on the sample.

Photochemical reactions were performed in a CCP-ICH2 Luzchem® photochemical reactor. Photochemical reactions were conducted in a 15 mL quartz tubes bought from Chemglass®.

Synthesis



Scheme 1

To a round-bottom flask charged with a stir bar, Triton X-45 (3.5 mmol, 1.60 g), and poly (1-vinylpyrrolidone-co-vinyl acetate) (PVPVA) (1.44 g) were dissolved in 13 mL of 1-PrOH and degassed for 15 min by bubbling with nitrogen. Then, acetylene was bubbled, and the reaction was kept at room temperature (25 °C) or heated to 50 °C and 70 °C depending on the reaction with an oil bath before adding $PdCl_2(PPh_3)_2$ (3 mg, 0.004 mmol), CuI (6 mg, 0.03 mmol), and *p*-benzoquinone (10 mg, 0.09 mmol). The system was purged with nitrogen and stirred for 5 min to dissolve the catalyst and reagents. A degassed solution of NEt_3 (3.5 mL, 15% in 1-PrOH) was injected at once to start the polymerization process. The reaction mixture turned turbid and was left to completion for the time of reaction. The resulting CNPs were purified by centrifugation and exchange of the supernatant three times with methanol. The CNPs were stored by dispersion in 1-propanol.

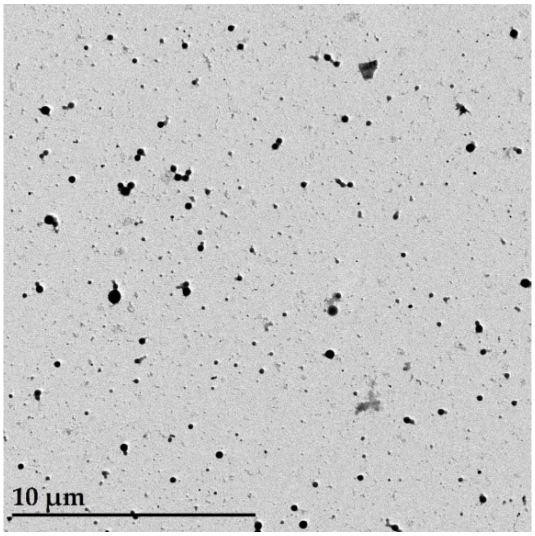
Photochemical reaction

$$\mathrm{CNP} \xrightarrow[\substack{\text{Acetonitrile} \\ \text{Time=12h, 24h, 48h, 72h, 96h}}]{\text{UV-254nm}} \mathrm{CNP}_{\text{graphitized}}$$

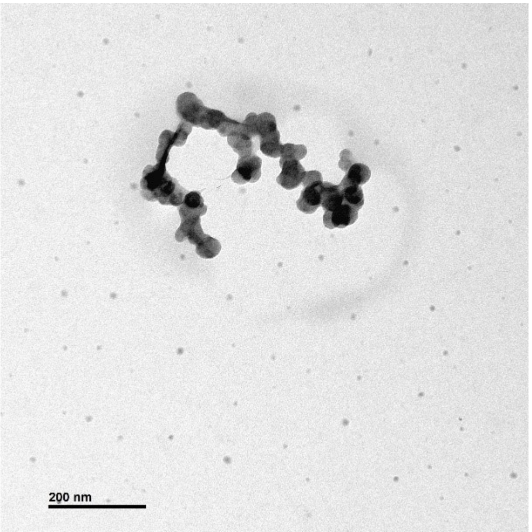
Scheme-2

The CNPs prepared in the previous step were dispersed in acetonitrile in quartz tubes for UV-irradiation. The sample was stirred throughout the reaction. The samples were placed in a specially designed UV-photoreactor for the time of reaction and samples were collected at time intervals to monitor the change in absorption and emission properties.

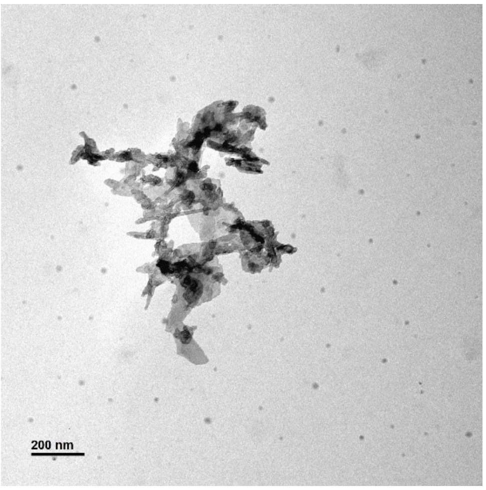
TEM images



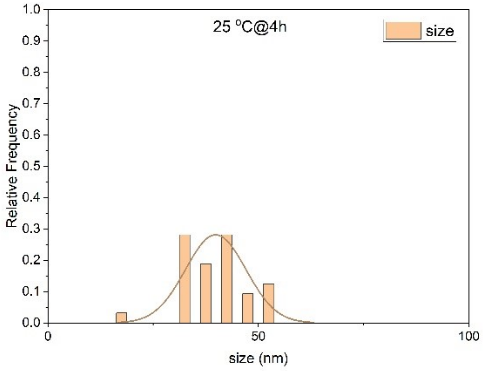
a)



b)



c)



d)

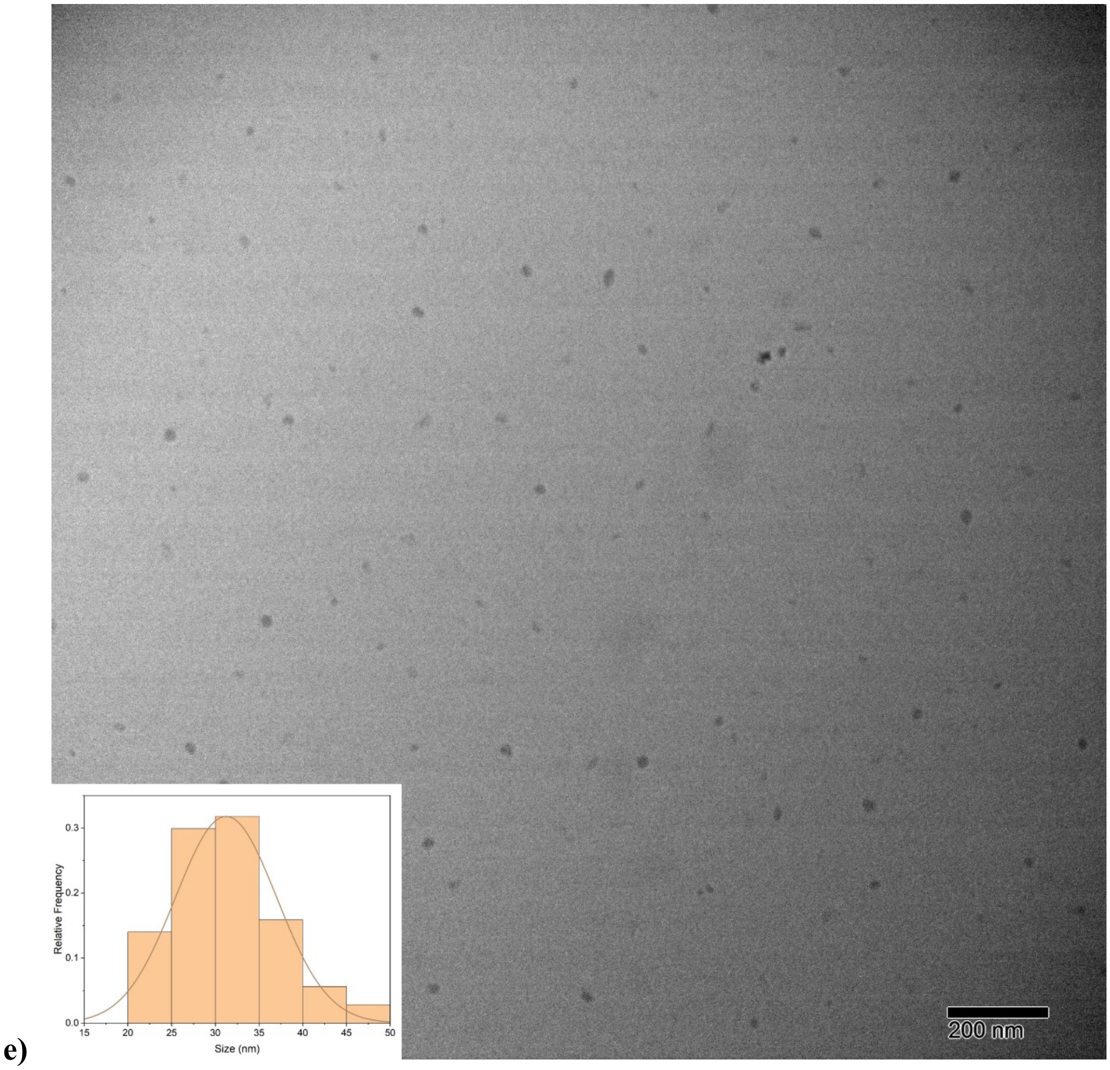
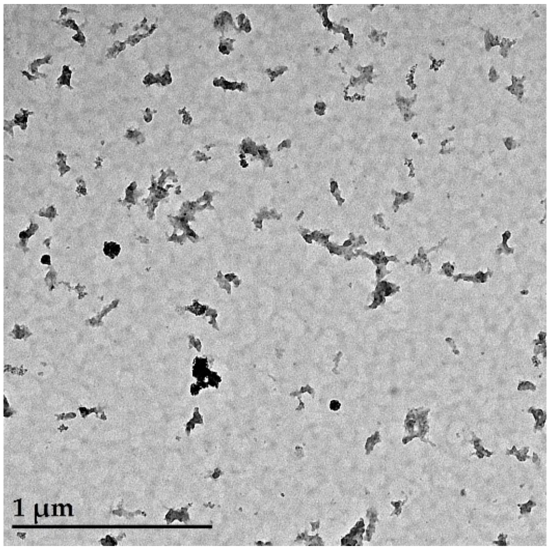
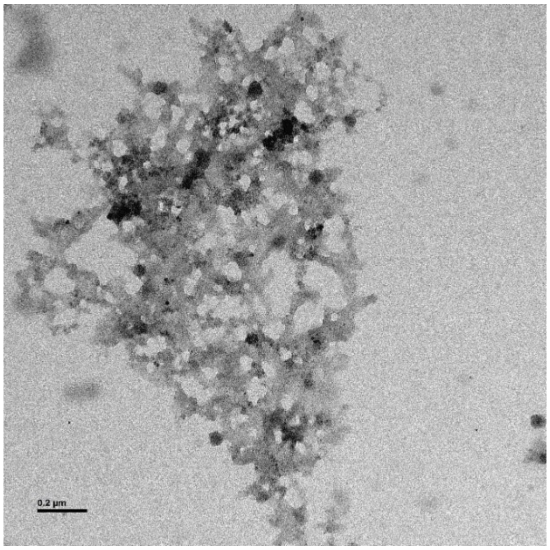


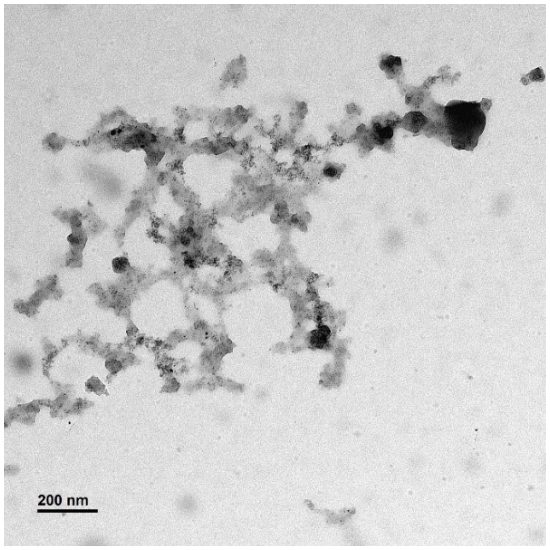
Figure S1: CNPs synthesized at 2;5 °C for 4 hours, TEM images: **a, b, c**; histogram: **d**, TEM image and histogram (inset, average size: 31±6 nm) of repetition experiment: **e**.


1 µm

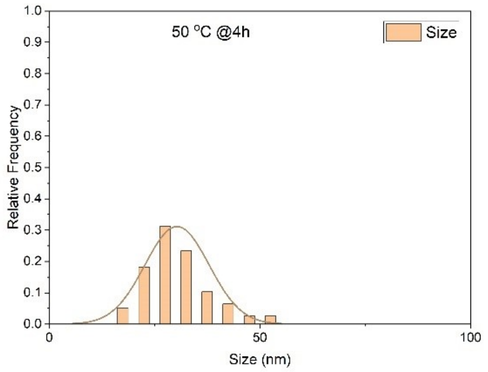
a)


0.2 µm

b)


200 nm

c)


50 °C @4h
Size
Relative Frequency
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
50
100
Size (nm)

d)

e)

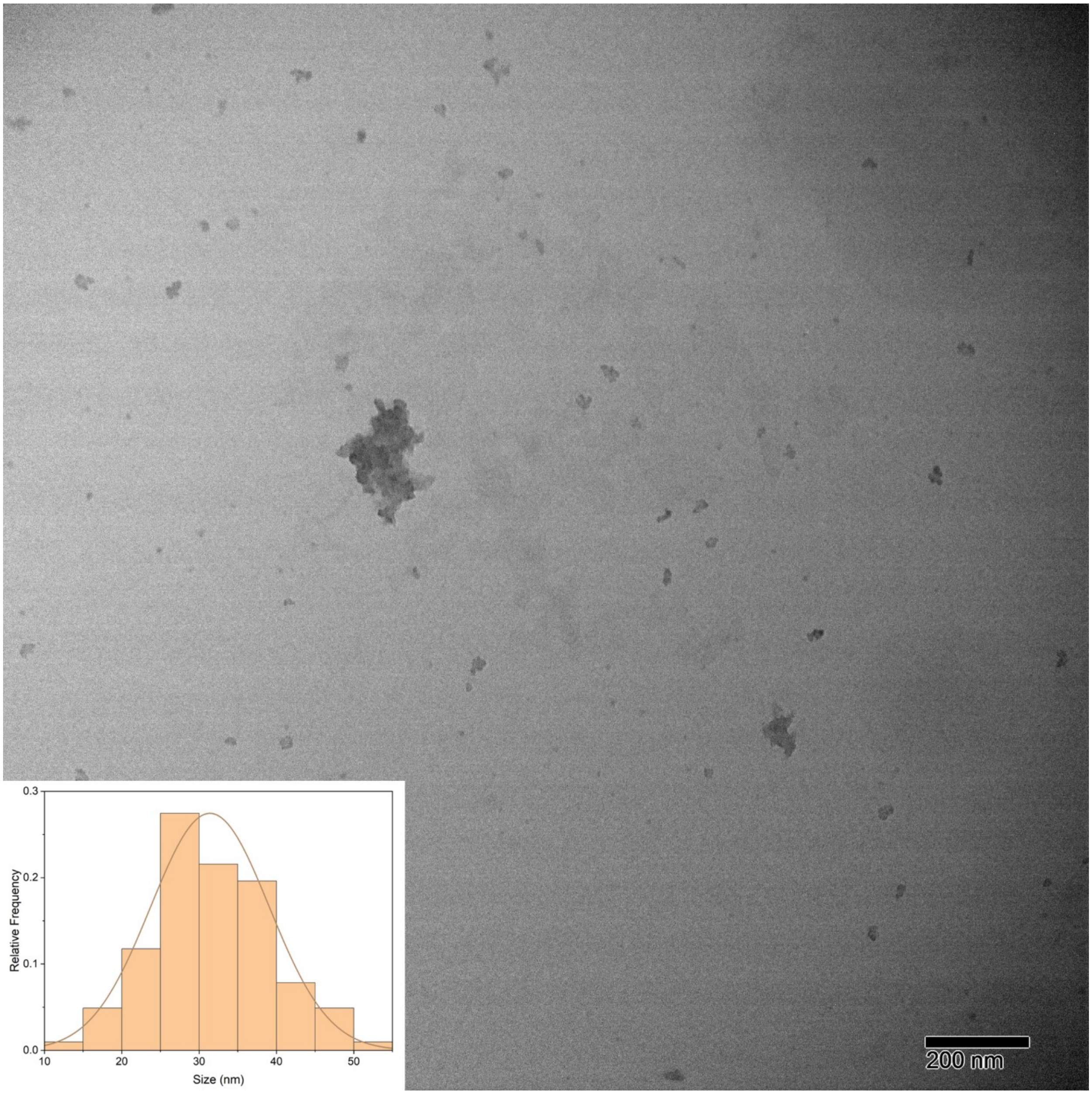


Figure S2: CNPs synthesized at 50 °C for 4 hours; TEM images**: a, b, c**; histogram: **d**, TEM image and histogram (inset, average size: 31±8 nm) of repetition experiment: **e**.

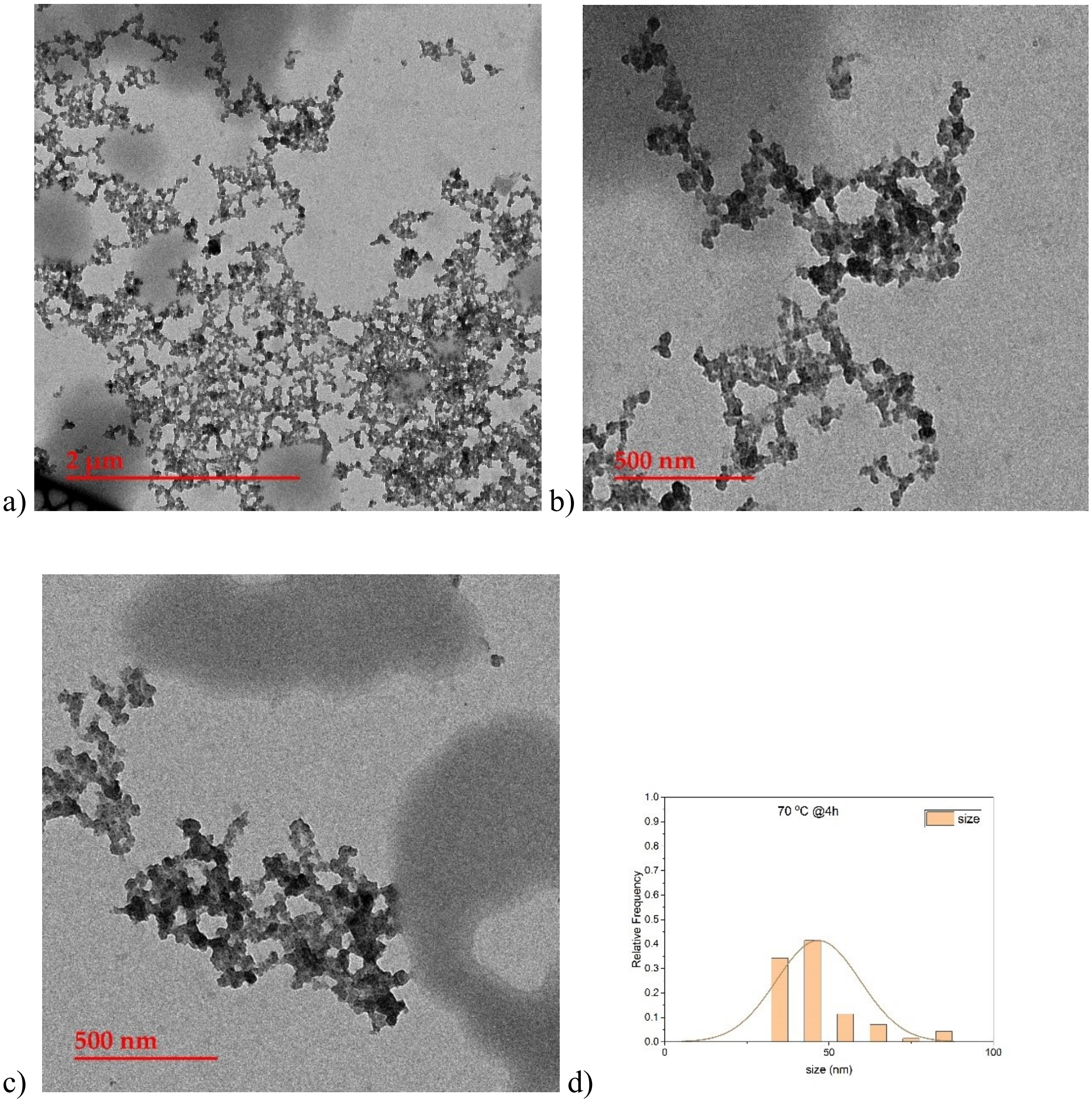
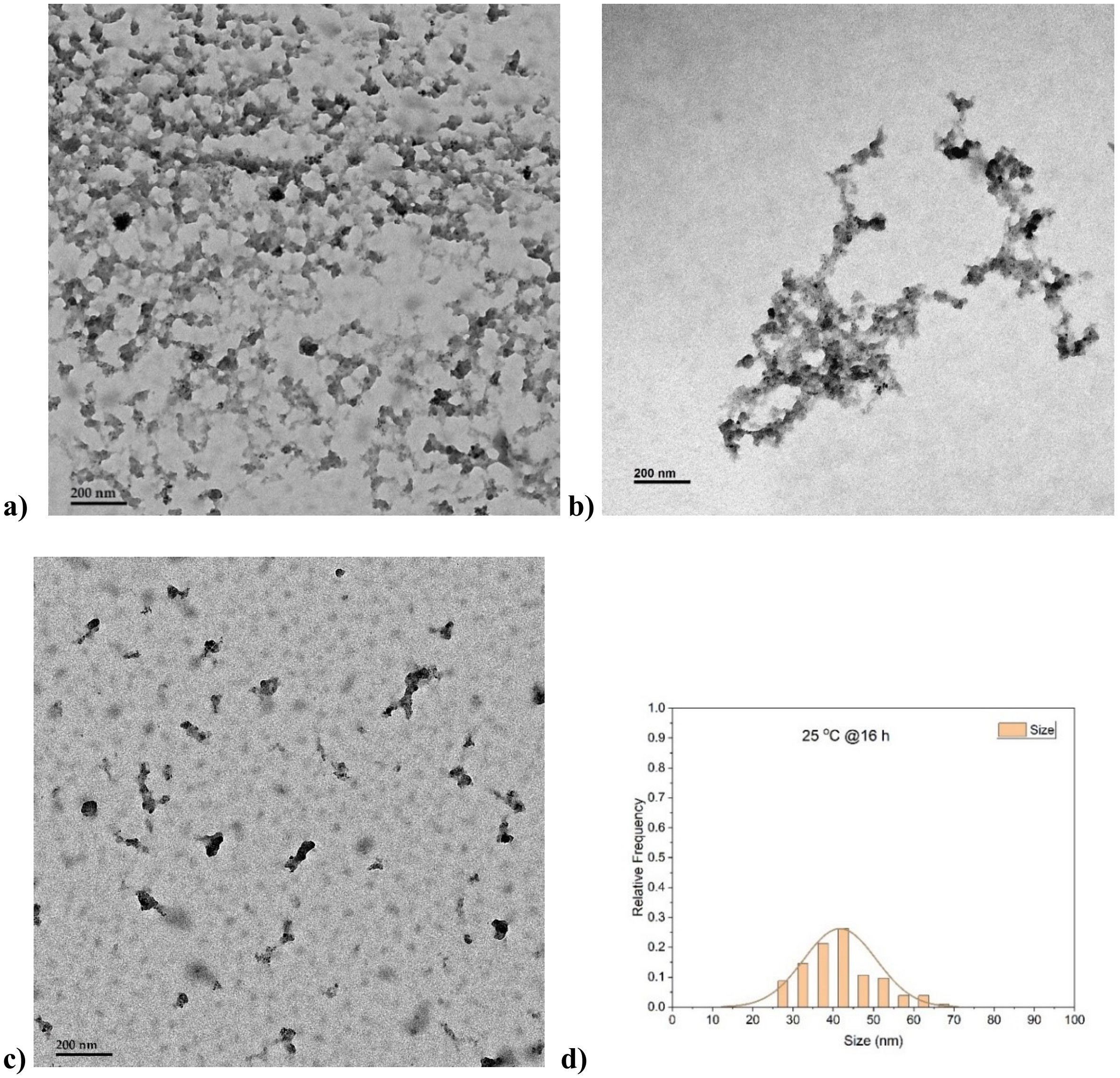


Figure S3: CNPs synthesized at 70 °C for 4 hours; TEM images: **a, b, c**; histogram: **d**.


a)
200 nm
b)
200 nm
c)
200 nm
d)
25 °C @16 h
Size
Relative Frequency
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
10
20
30
40
50
60
70
80
90
100
Size (nm)

e)

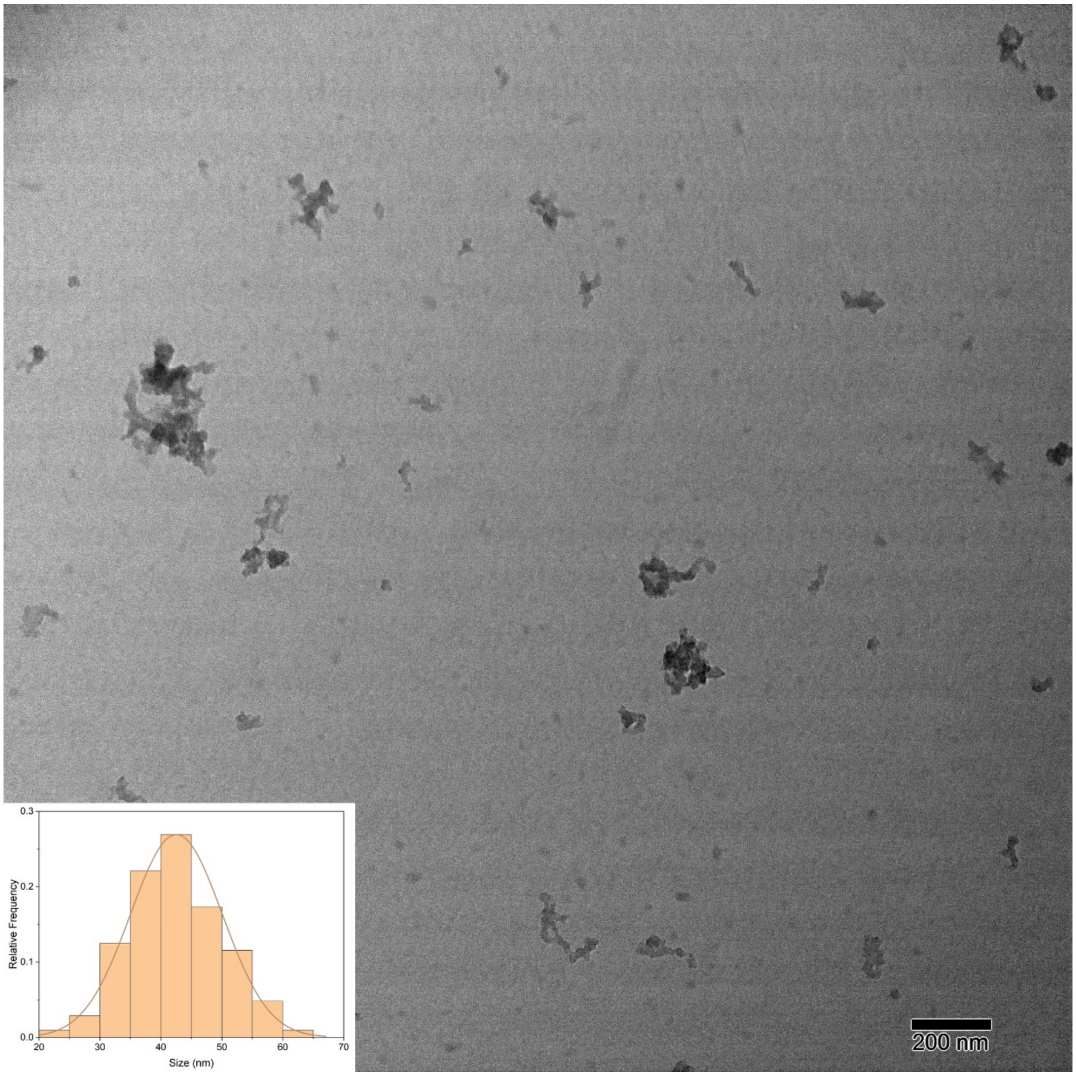


Figure S4: CNPs synthesized at 25 °C for 16 hours; TEM images: **a, b, c**; histogram: **d**, TEM image and histogram (inset, average size: 42±7nm) of repetition experiment: **e**.

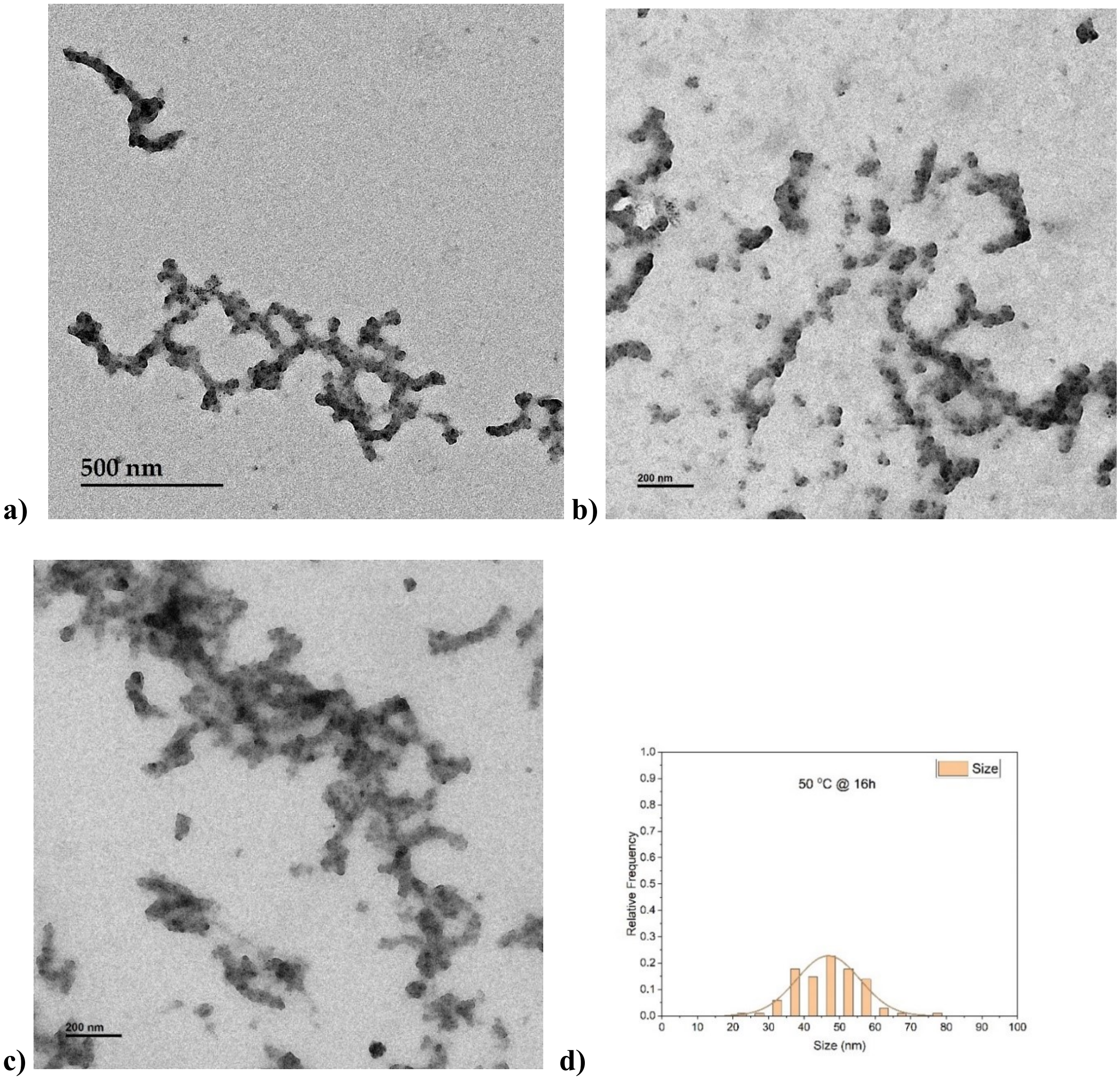


Figure S5: CNPs synthesized at 50 °C for 16 hours; TEM images: **a, b, c**; histogram: **d**.

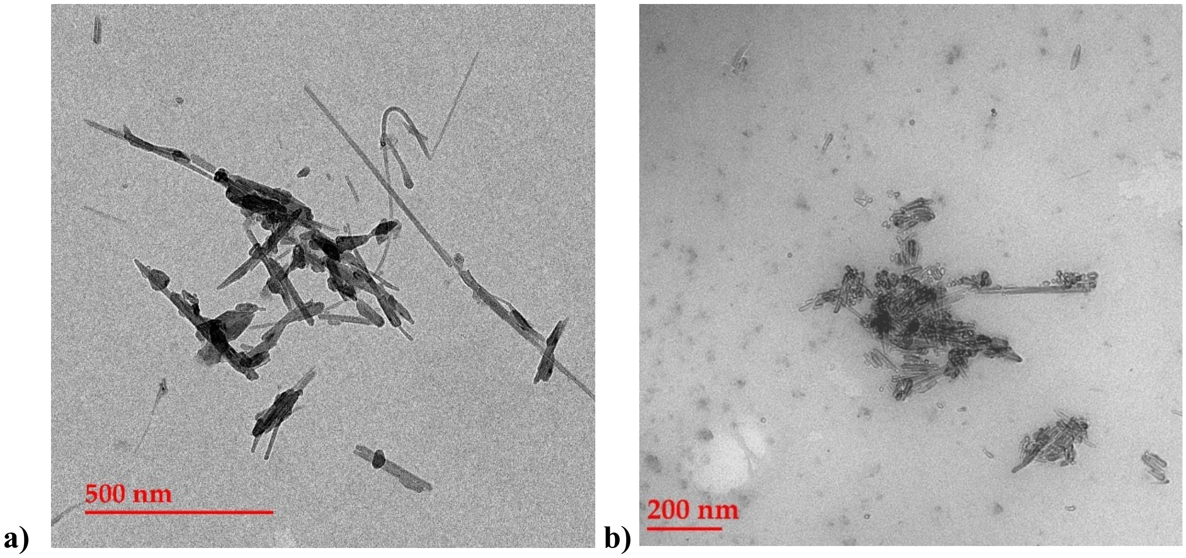
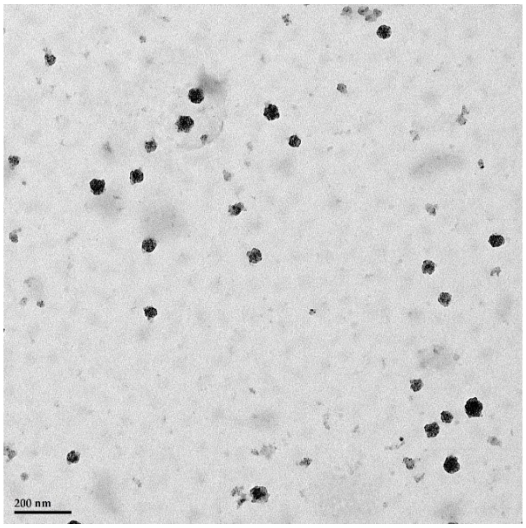
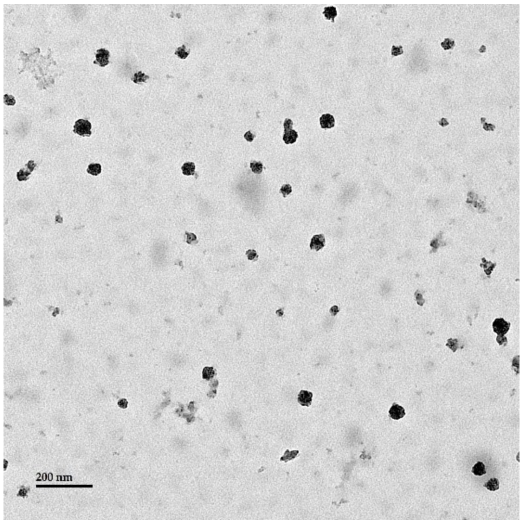


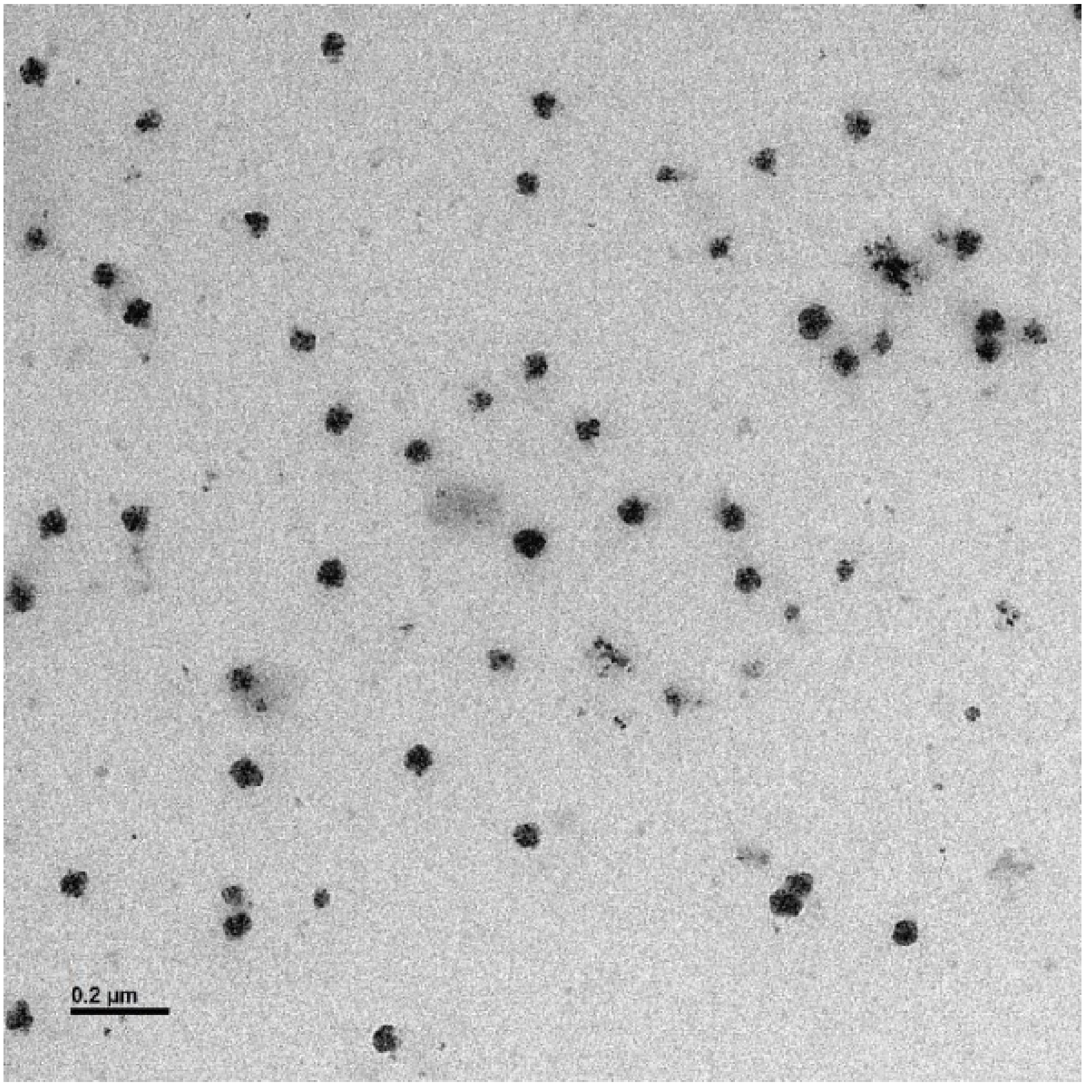
Figure S6: CNPs synthesized at 50 °C for 16 hours; TEM images: **a, b**.



a)

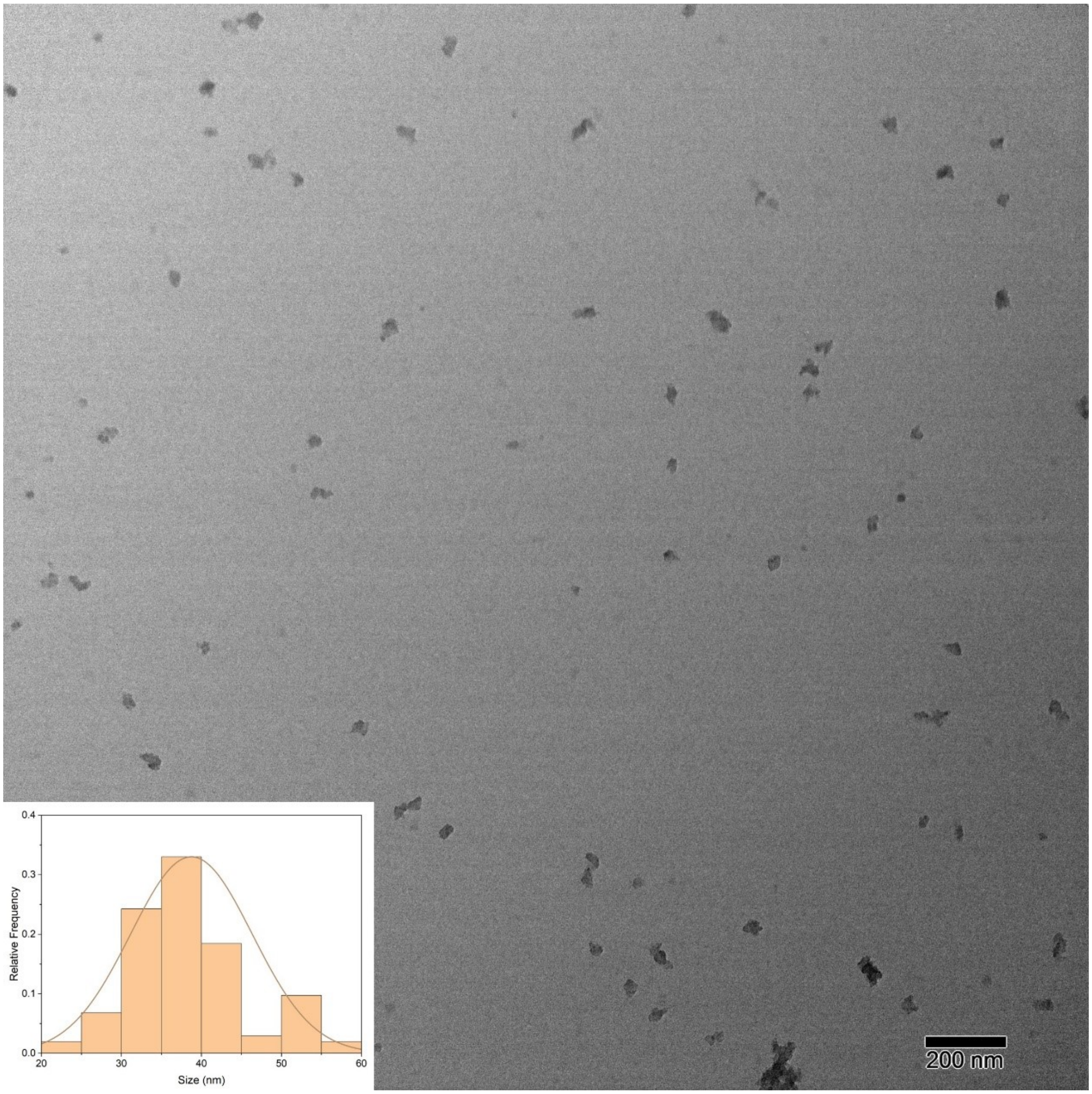


b)

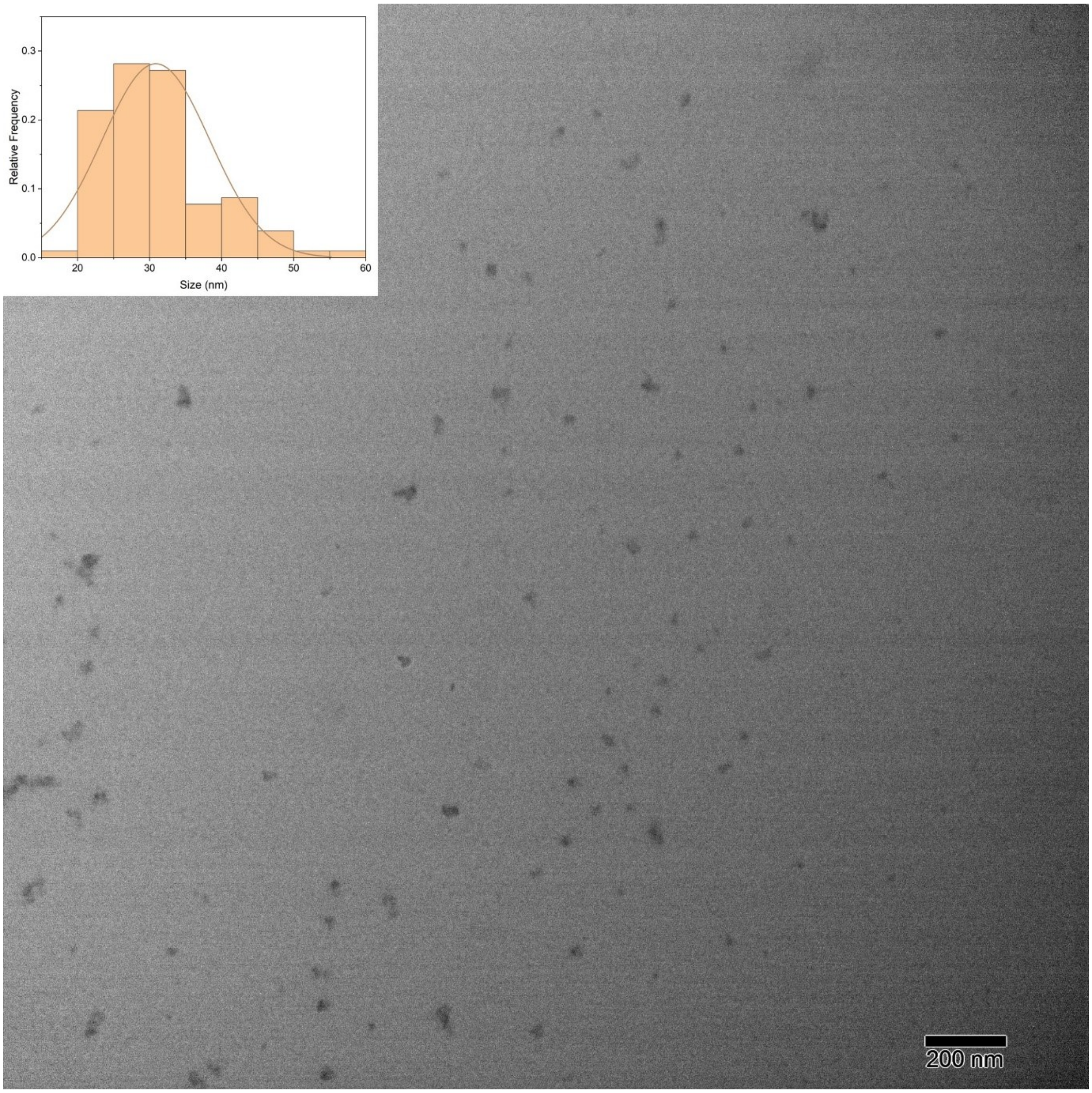


c)

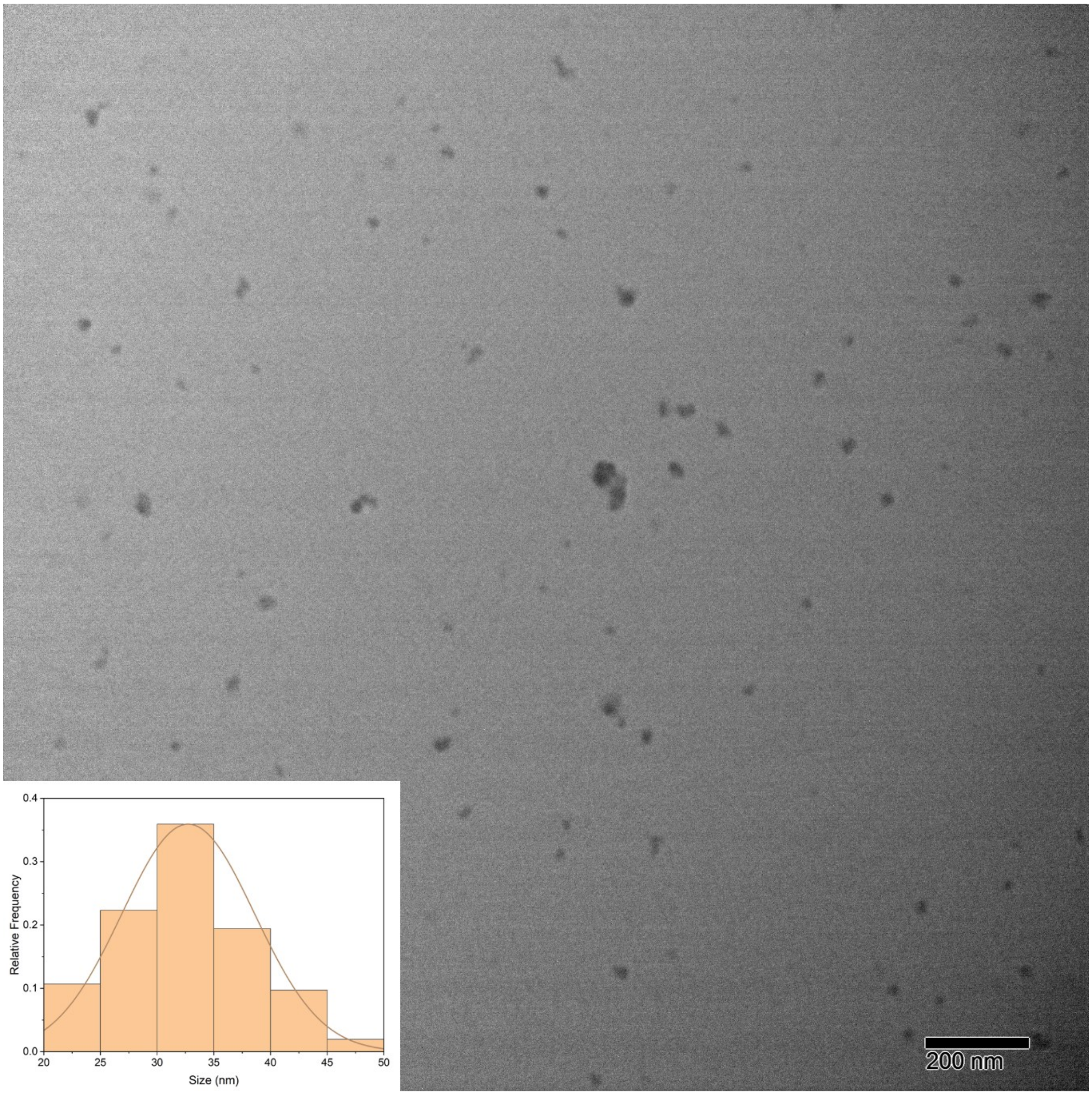
d)



e)



f)


200 nm
Relative Frequency
0.0
0.1
0.2
0.3
0.4
Size (nm)
20
25
30
35
40
45
50

g)

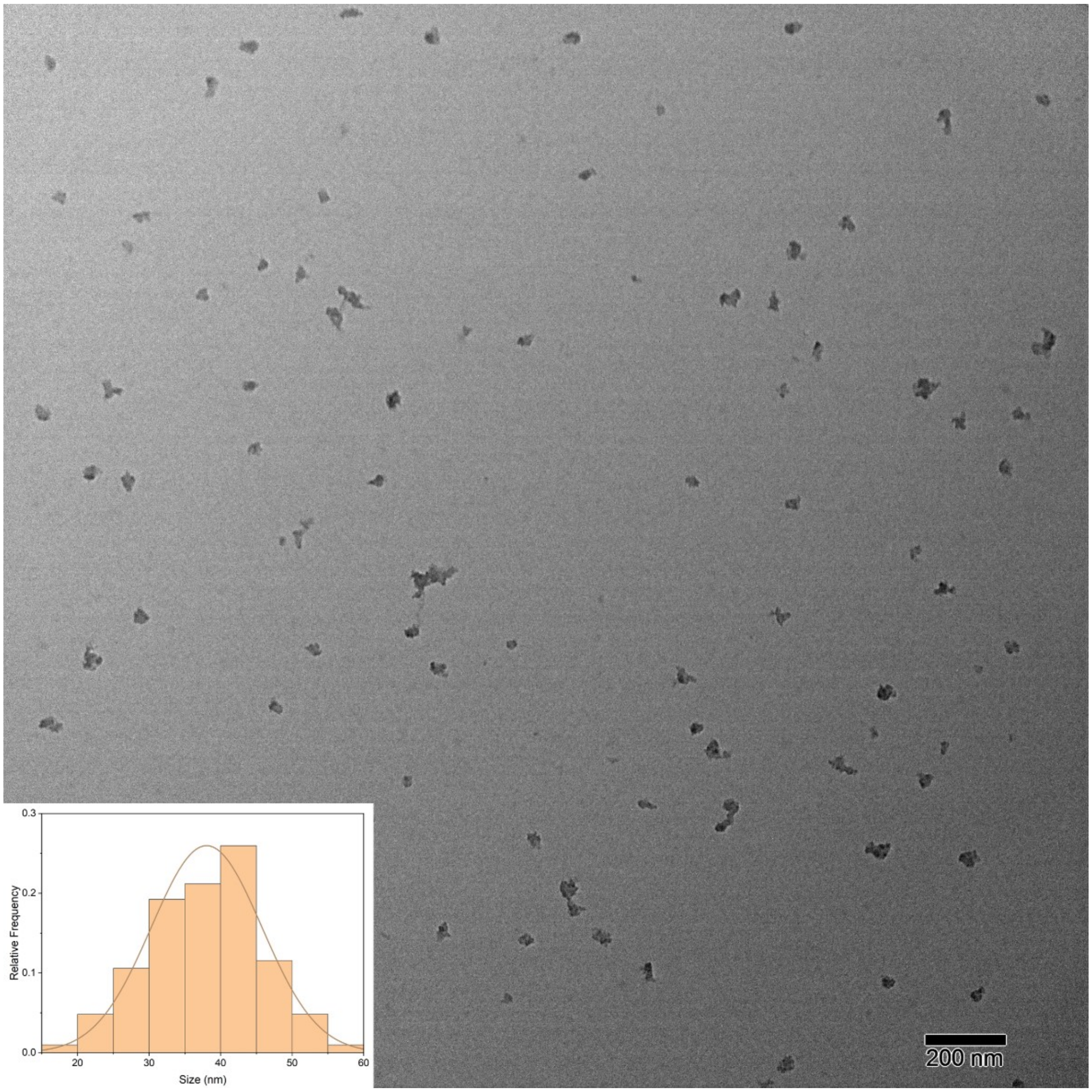


Figure S7: CNPs synthesized at 70 °C for 16 hours; TEM images: **a, b, c**; TEM image and histogram (inset) of repetition experiment: **d** (average size: 39±8 nm), **e** (average size: 31±8 nm), **f** (average size: 33±6 nm); TEM images and histogram (inset, average size: 38±8 nm) of the scale-up synthesis at 10 times scale: **g**.

Dynamic light scattering (DLS)

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	423.0	Peak 1:	403.3	97.1	143.6
PdI:	0.320	Peak 2:	5387	2.9	318.4
Intercept:	0.691	Peak 3:	0.000	0.0	0.000
Result quality :	Refer to quality report				

Figure S8: DLS Size distribution spectrum for CNPs synthesized at 25 °C for 4 hours.

Z-Average (d.nm): 52.36

PdI: 0.173

Intercept: 0.907

Result quality : Good

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Peak 1:	64.25	98.6	27.20
Peak 2:	11.71	1.4	2.171
Peak 3:	0.000	0.0	0.000

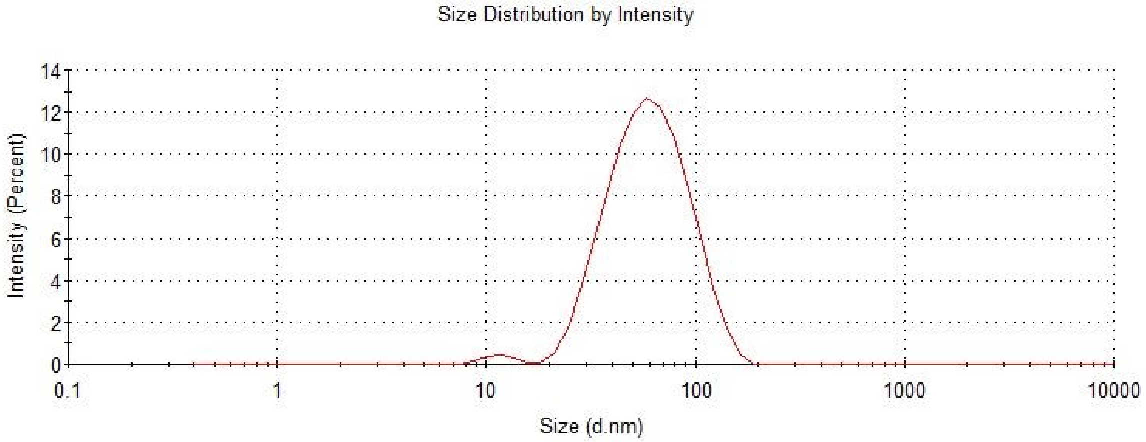


Figure S9: DLS size distribution spectrum for CNPs synthesized at 50 °C for 4 hours.

Z-Average (d.nm): 50.42

PdI: 0.136

Intercept: 0.922

Result quality : Good

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Peak 1:	58.81	100.0	23.50
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

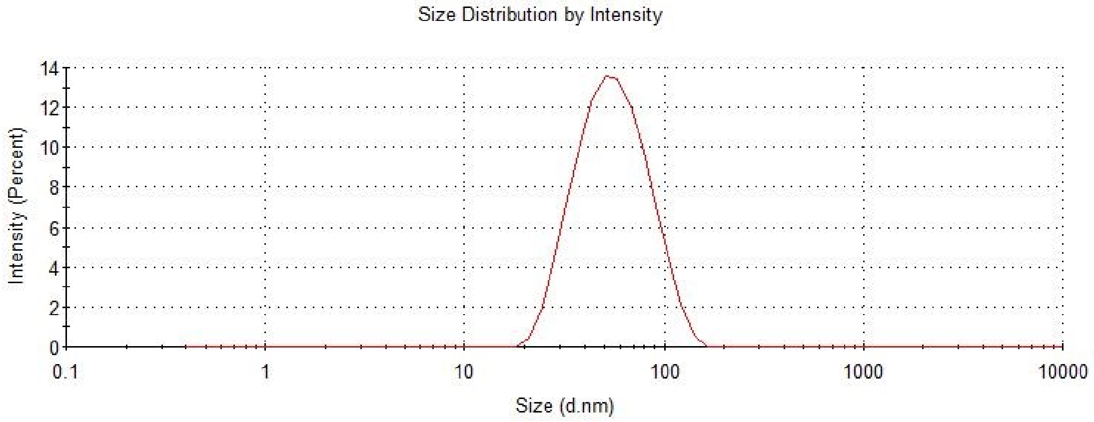


Figure S10: DLS size distribution spectrum for CNPs synthesized at 70 °C for 4 hours.

Temperature (°C):	25.0	**Duration Used (s):**	60
Count Rate (kcps):	546.4	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	10

			Size (d.nm):	**% Intensity:**	**St Dev (d.nm):**
Z-Average (d.nm):	89.17	**Peak 1:**	35.28	100.0	10.01
PdI:	0.379	**Peak 2:**	0.000	0.0	0.000
Intercept:	0.958	**Peak 3:**	0.000	0.0	0.000
Result quality :	Refer to quality report				

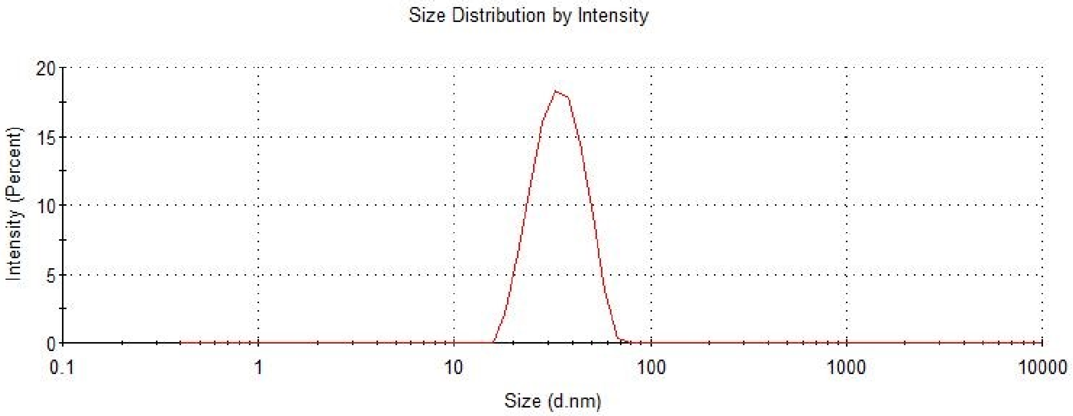


Figure S11: DLS size distribution spectrum for CNPs synthesized at 25 °C for 16 hours.

			Size (d.nm):	**% Intensity:**	**St Dev (d.nm):**
Z-Average (d.nm):	49.76	**Peak 1:**	54.50	100.0	17.12
PdI:	0.091	**Peak 2:**	0.000	0.0	0.000
Intercept:	0.922	**Peak 3:**	0.000	0.0	0.000
Result quality :	Good				

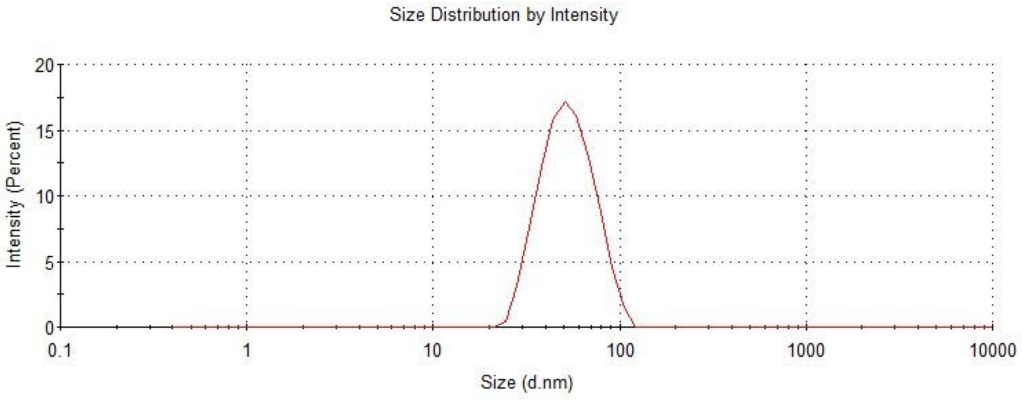


Figure S12: DLS size distribution spectrum for CNPs synthesized at 50 °C for 16 hours.

			Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm):	35.78	Peak 1:	38.34	94.7	15.28
PdI:	0.235	Peak 2:	4221	5.3	997.2
Intercept:	0.914	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

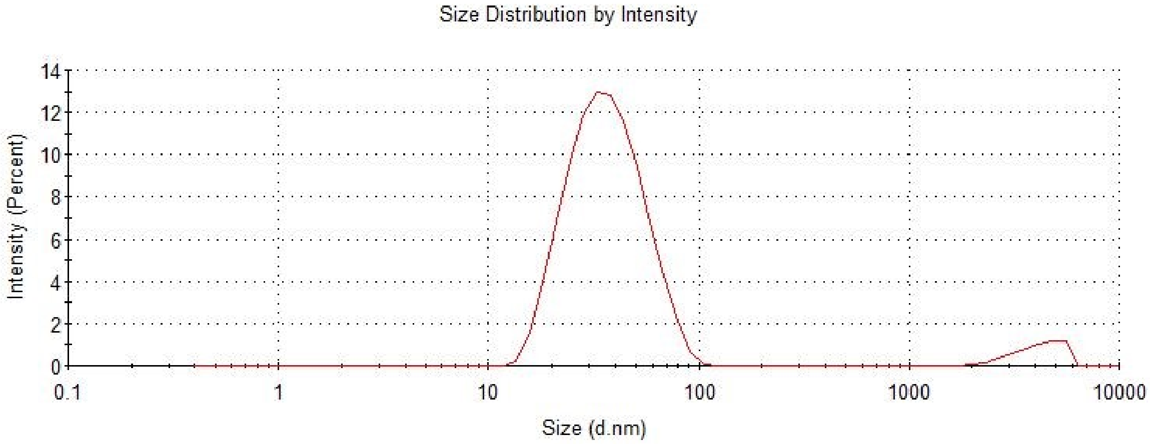


Figure S13: DLS size distribution spectrum for CNPs synthesized at 70 °C for 16 hours.

Table S1: Polydispersity Index(PDI) values of CNPs calculated by DLS

Reaction Temperature	*Reaction Time*	*Polydispersity Index (PDI)*
25 °C	4 h	0.32
50 °C	4 h	0.17
70 °C	4 h	0.14
25 °C	16 h	0.38
50 °C	16 h	0.09
70 °C	16 h	0.24

SEAD images

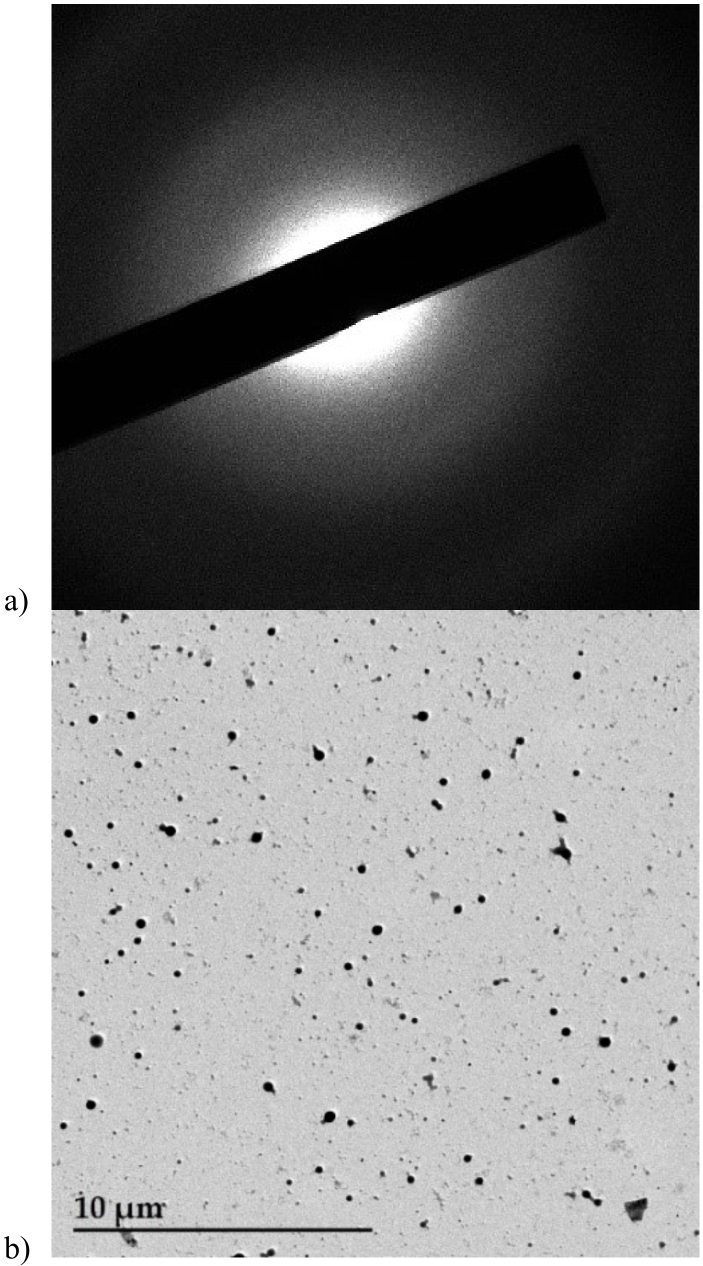


Figure S14: a) SAED image and b) the corresponding TEM image of CNPs synthesized at 25 °C for 4 hours.

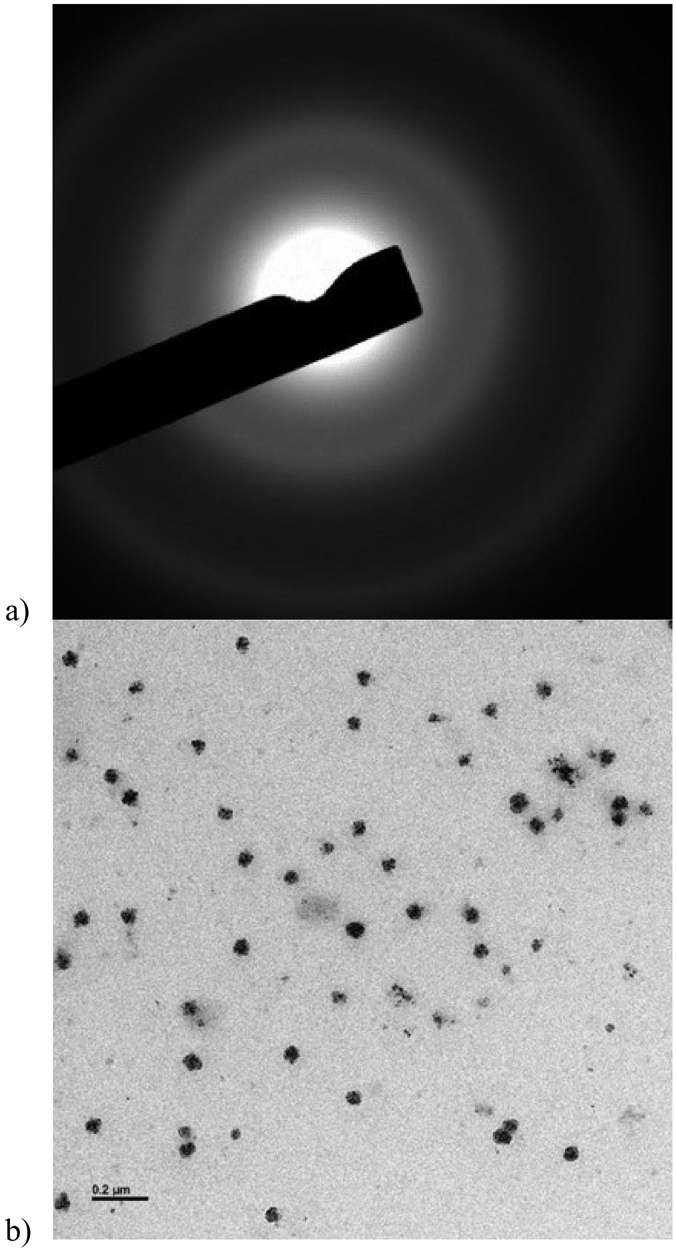
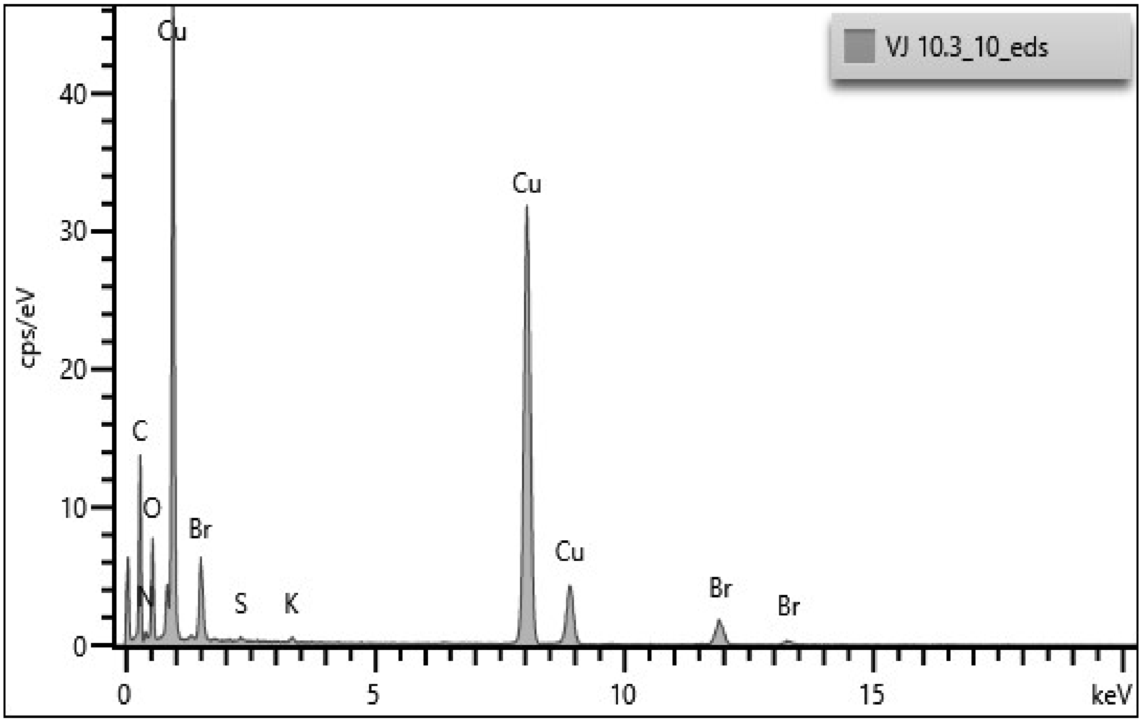


Figure S15: a) SAED image and b) corresponding TEM image of CNPs synthesized at 70 °C for 16 hours.

EDS spectroscopy

a)



b)

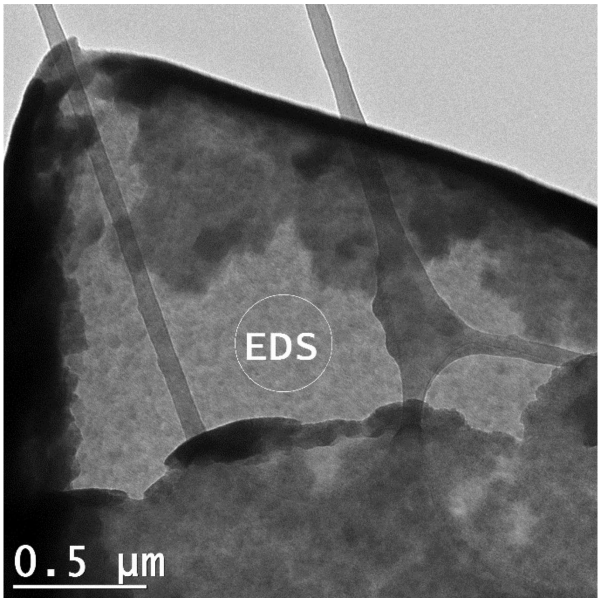


Figure S16: a) EDS spectrum and b) corresponding TEM image of CNP synthesized at 70 °C, for 16 hours.

XPS survey spectra

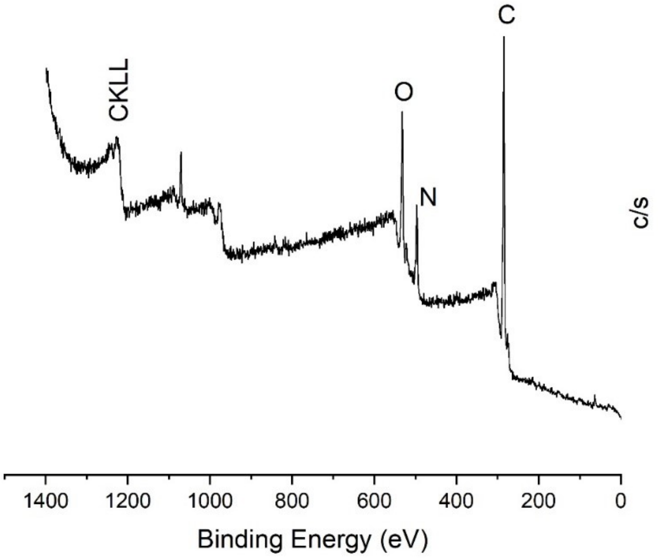


Figure S17: XPS survey spectrum for CNPs synthesized at 25 °C for 4 hours.

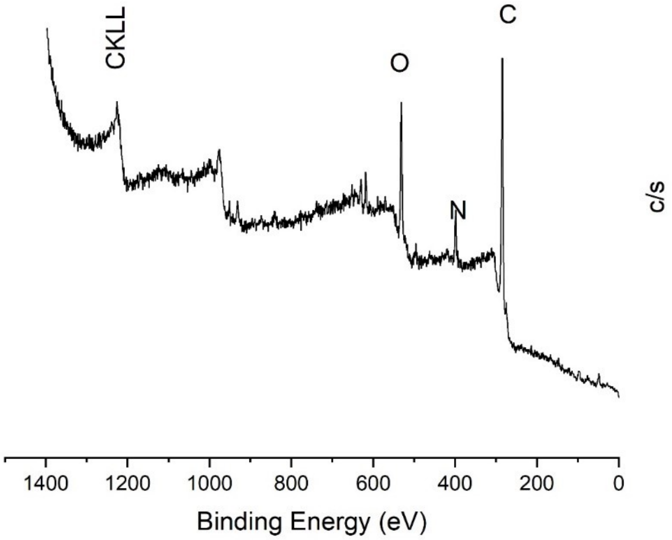


Figure S18: XPS survey spectrum for CNPs synthesized at 50 °C for 4 hours.

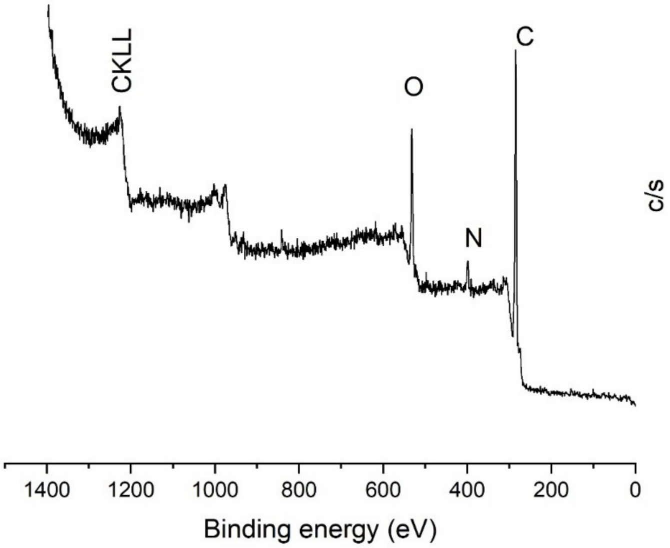


Figure S19: XPS survey spectrum for CNPs synthesized at 70 °C for 4 hours.

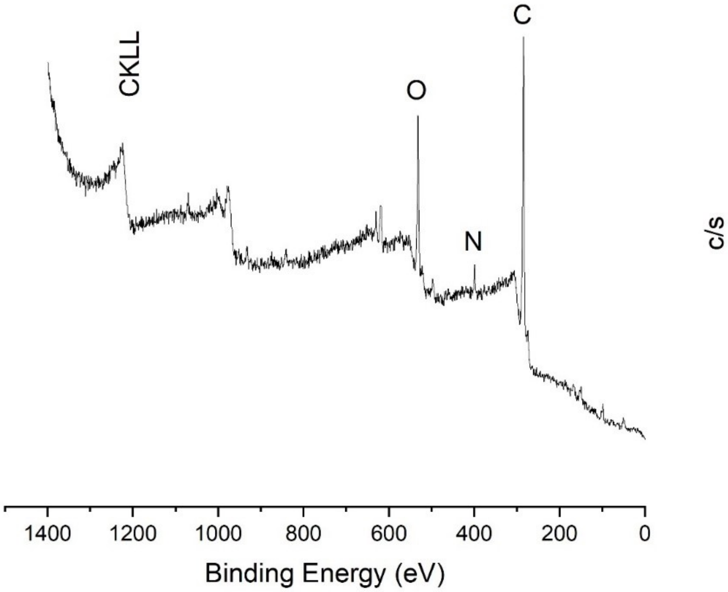


Figure S20: XPS survey spectrum for CNPs synthesized at 25 °C for 16 hours.

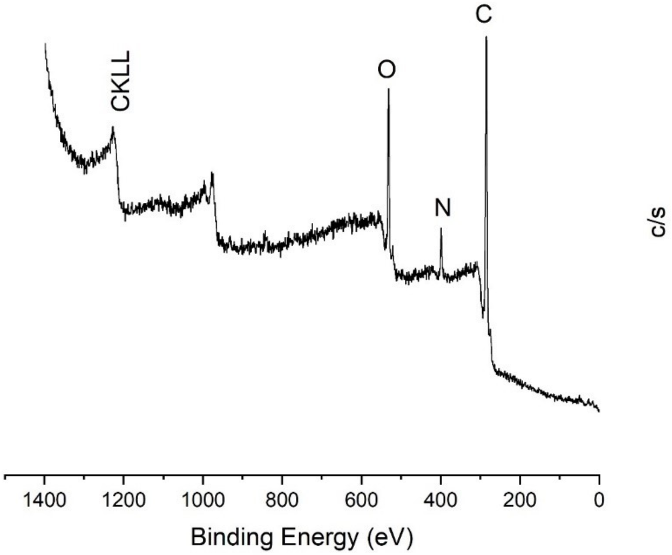


Figure S21: XPS survey spectrum for CNPs synthesized at 50 °C for 16 hours.

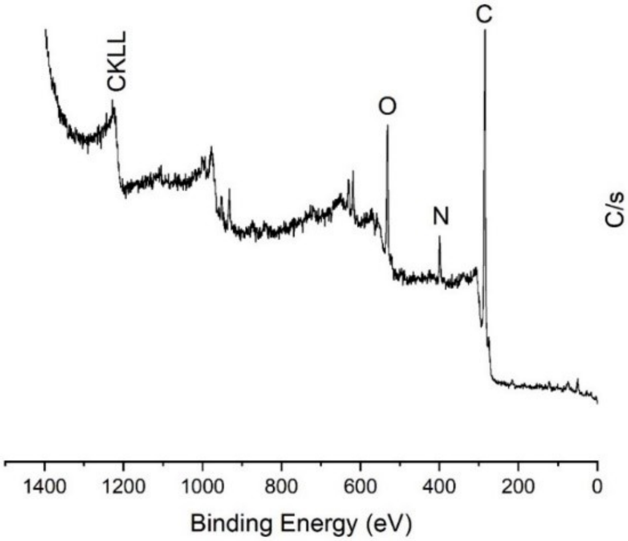


Figure S22: XPS survey spectrum for CNPs synthesized at 70 °C for 16 hours.

Table S2: Summary of atomic % values of elements (C, O, N) in CNPs from XPS survey spectra

Reaction Temperature	*Reaction Time*	*C*	*O*	*N*	*O/C*
25 °C	4 h	78.5	19.5	2	0.25
50 °C	4 h	78.6	16	5.5	0.20
70 °C	4 h	74.3	17.2	8.4	0.23
25 °C	16 h	76.5	17.9	5.6	0.23
50 °C	16 h	74.9	19.1	6	0.26
70 °C	16 h	83.4	14.2	2.4	0.17

X-Ray Induced Auger Electron Spectroscopy (XAES)

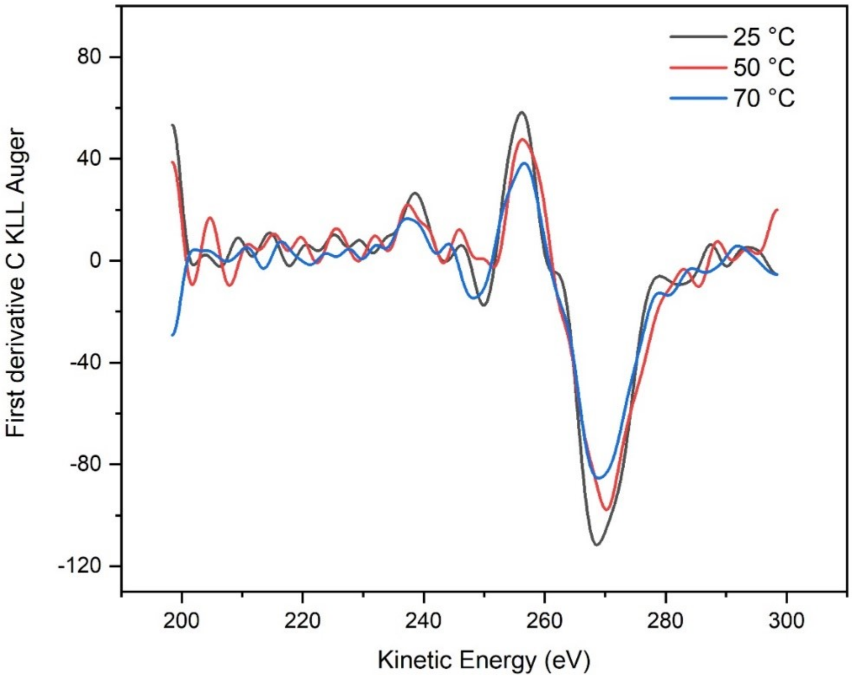


Figure S23: First derivative CKLL XAES spectrum recorded for CNPs synthesized at 4 hours with variations in temperature.

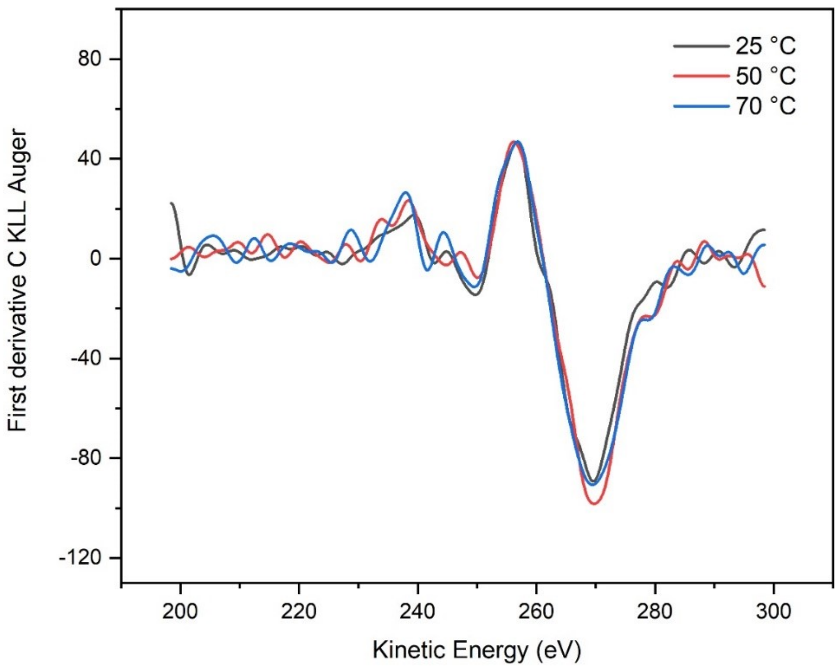


Figure S24: First derivative CKLL XAES spectrum recorded for CNPs synthesized at 16 hours with temperature variations.

Table S3: D-parameter values calculated from first derivative CKLL XAES spectra for CNPs

Reaction Temperature	*Reaction Time*	*D-Parameter (eV)*
25 °C	4 h	12.2
50 °C	4 h	12.7
70 °C	4 h	13.5
25 °C	16 h	12.9
50 °C	16 h	13.6
70 °C	16 h	11.5
Graphite		15.5

FT-IR Spectroscopy

To characterize the functional groups, CNPs were characterized with Fourier transform infrared spectroscopy (FT-IR), shown in Figures S26 and S27. The peaks at 830 cm^{-1} and 950 cm^{-1} are due to sp^2 C-H bending; several peaks between 1000-1350 cm^{-1} could be attributed to C-O vibrations, peaks at 1330-1410 cm^{-1} are from sp^3 C-H vibrations, several weak peaks between 1500 to 1625 cm^{-1} are due to C=C stretching, the several small peaks could be arising from the presence of C=C alkene and aromatic C=C stretching of carbon. C=O stretch can be observed between 1625-1750 cm^{-1}. Peaks between 2800-300cm^{-1} are from the C-H stretch and peaks between 3000-3600cm^{-1} are from O-H stretch of alcohols.

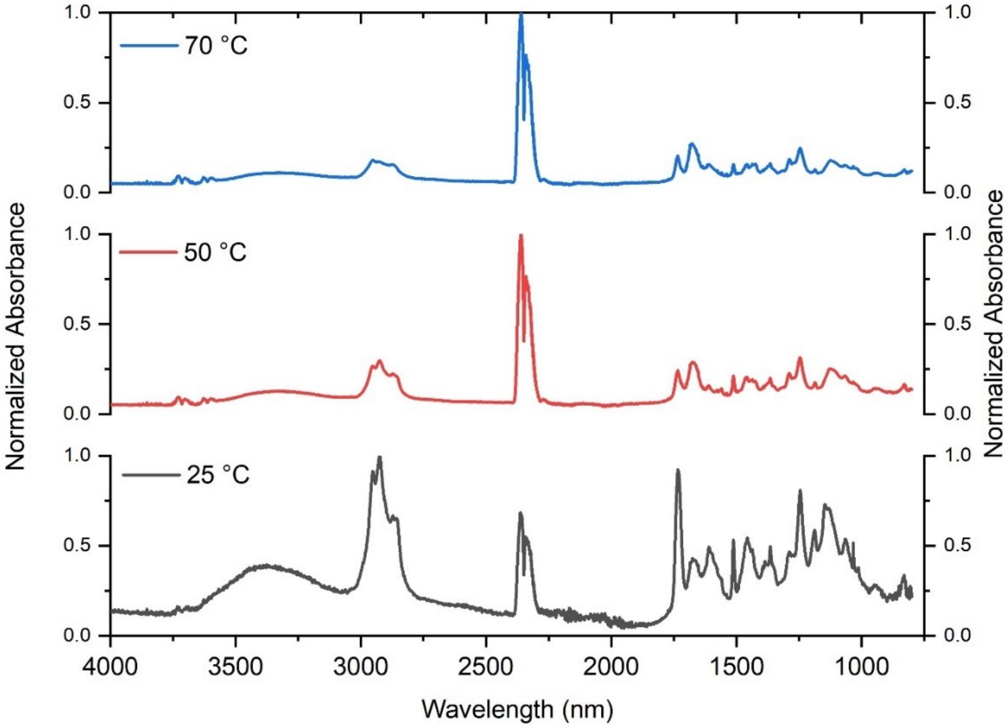


Figure S25: FT-IR spectrum recorded in ATR mode for CNPs synthesized at 4 hours with variations in temperature.

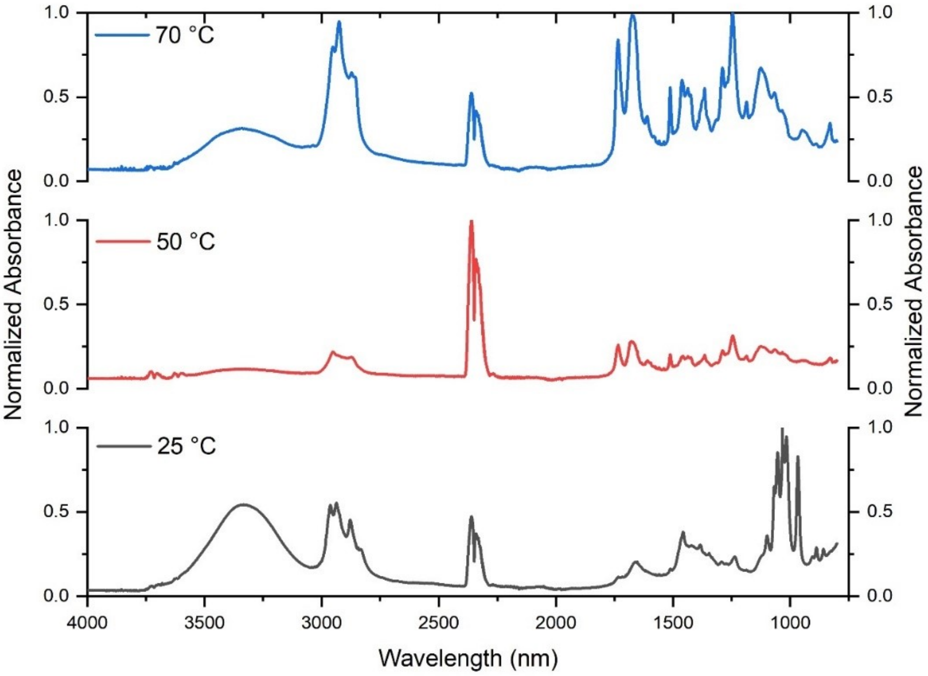


Figure 26: FT-IR spectrum recorded in ATR mode for CNPs synthesized at 16 hours with variations in temperature.

High-Resolution XPS C1s Spectra

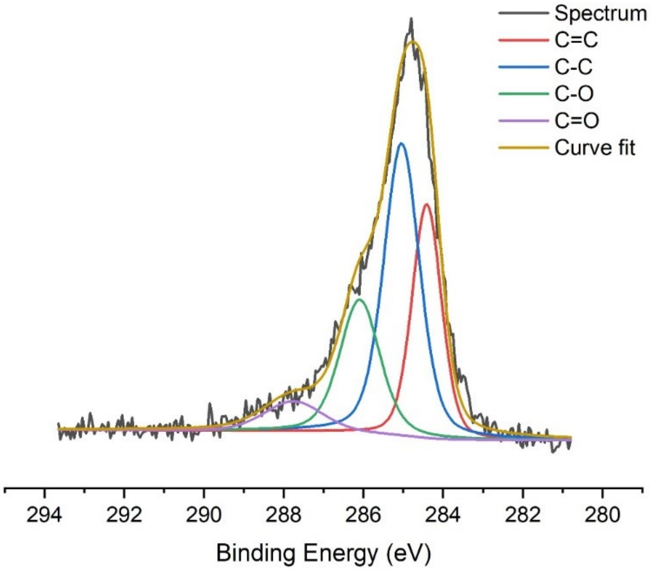


Figure S27: Curve fit spectra of high-resolution XPS C1s spectra for CNPs synthesized at 25 °C for 4 hours.

Table S4: Summary of the curve-fit data for Figure S27

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.45	0	372	0.95	70	429	33.1	1.62
C-C	285.06	0.61	486	0.96	70	569	43.88	
C-O	286.15	1.7	160	0.95	70	185	14.24	
C=O	287.89	3.44	55	1.78	80	114	8.78	

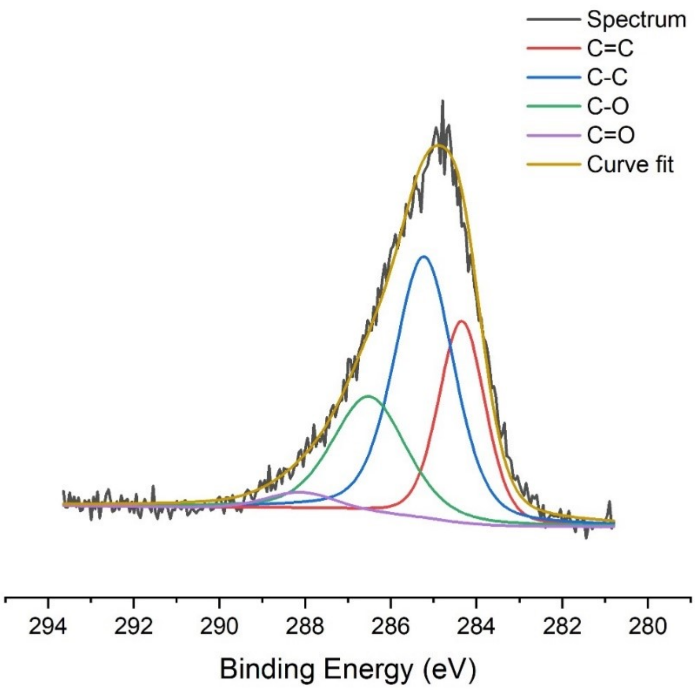


Figure S28: Curve fit spectra of high-resolution XPS C1s spectra for CNPs synthesized at 50 °C for 4 hours.

Table S5: Summary of the curve-fit data for Figure S28

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.18	0	152	1.53	75	278	25.68	1.72
C-C	284.86	0.68	258	1.59	75	488	45.15	
C-O	286	1.82	107	2.1	75	268	24.81	
C=O	288.04	3.86	20	2.04	85	47	4.35	

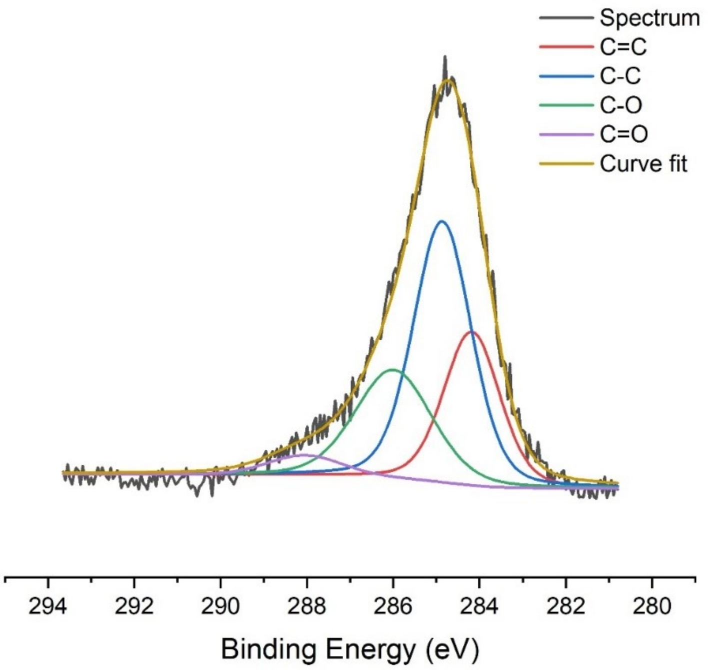


Figure S29: Curve fit spectra of high-resolution XPS C1s spectra for CNPs synthesized at 70 °C for 4 hours.

Table S6: Summary of the curve-fit data for Figure S29

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.34	0	237	1.28	75	361	26.26	1.51
C-C	285.22	0.88	307	1.65	65	629	45.81	
C-O	286.51	2.17	136	2.02	65	342	24.89	
C=O	288.1	3.76	20	1.86	85	42	3.05	

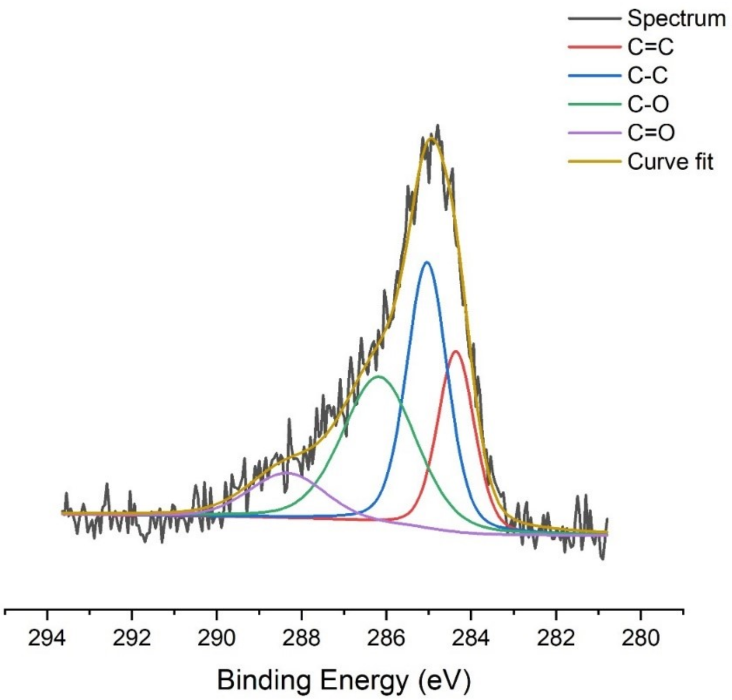


Figure S30: Curve fit spectra of high-resolution XPS C1s spectra for CNPs synthesized at 25 °C for 16 hours.

Table S7: Summary of the curve-fit data for Figure S30

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.29	0	230	1.46	75	401	31.98	1.64
C-C	285.15	0.85	339	1.47	75	594	47.35	
C-O	286.4	2.11	124	1.41	75	210	16.72	
C=O	288.14	3.14	33	1.32	85	50	3.95	

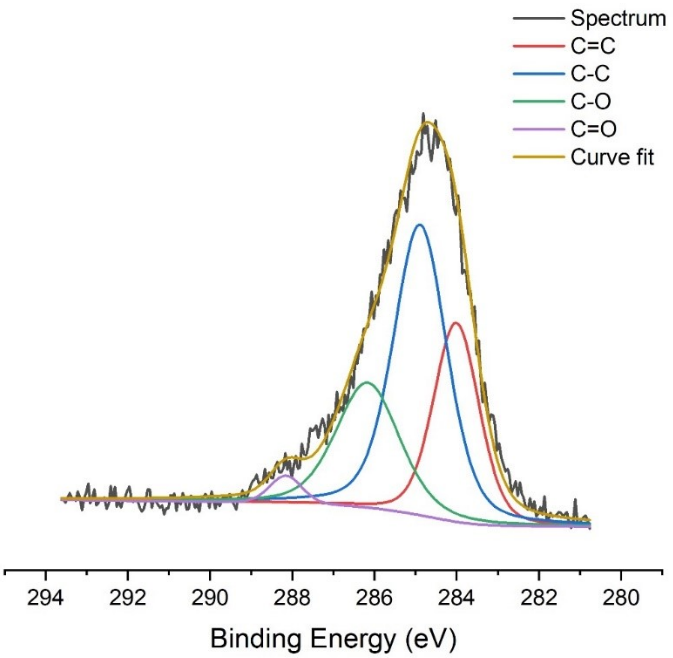


Figure S31: Curve fit spectra of high-resolution XPS C1s spectra for CNPs synthesized at 50 °C for 16 hours.

Table S8: Summary of the curve-fit data for Figure S31

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	283.98	0	196	1.7	75	397	27.77	1.5
C-C	284.78	0.79	329	1.59	75	623	43.56	
C-O	286.11	2.12	160	1.69	65	336	23.49	
C=O	287.93	3.95	37	1.76	85	85	5.18	

Table S9: Summary of functional groups extracted from curve-fit data of C1s spectra of CNPs in Figure 2

	Peak (eV)	**Delta**	**Height**	**FWHM**	**% Gauss**	**Area**	**% of total area**	**Chi Square**
C=C	284.21	0	237	1.07	75	301	21.6	1.88
C-C	285.01	0.80	446	1.12	65	620	44.6	
C-O	286.04	1.84	202	1.65	65	414	29.8	
C=O	287.78	3.57	32	1.48	80	56	4.0	

Table S10: Summary of functional groups extracted from curve-fit data of C1s spectra of CNPs

Reaction Temperature	*Reaction Time*	*C=C (%)*	*C-C (%)*	*C-O (%)*	*C=O (%)*	*CO/CC*
25 °C	4 h	33.1	43.88	14.24	8.78	**0.30**
50 °C	4 h	25.68	45.15	24.81	4.35	**0.41**
70 °C	4 h	26.26	45.81	24.89	3.05	**0.39**
25 °C	16 h	31.98	47.35	16.72	3.95	**0.26**
50 °C	16 h	27.77	43.56	23.49	5.18	**0.40**
70 °C	16 h	21.63	44.59	29.76	4.02	**0.51**

UV-Visible Absorption Spectroscopy

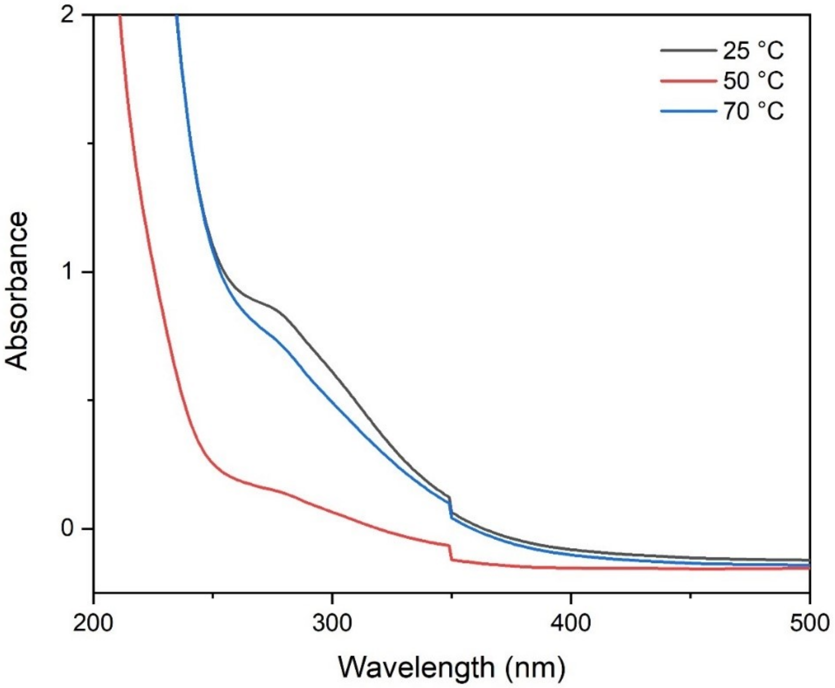
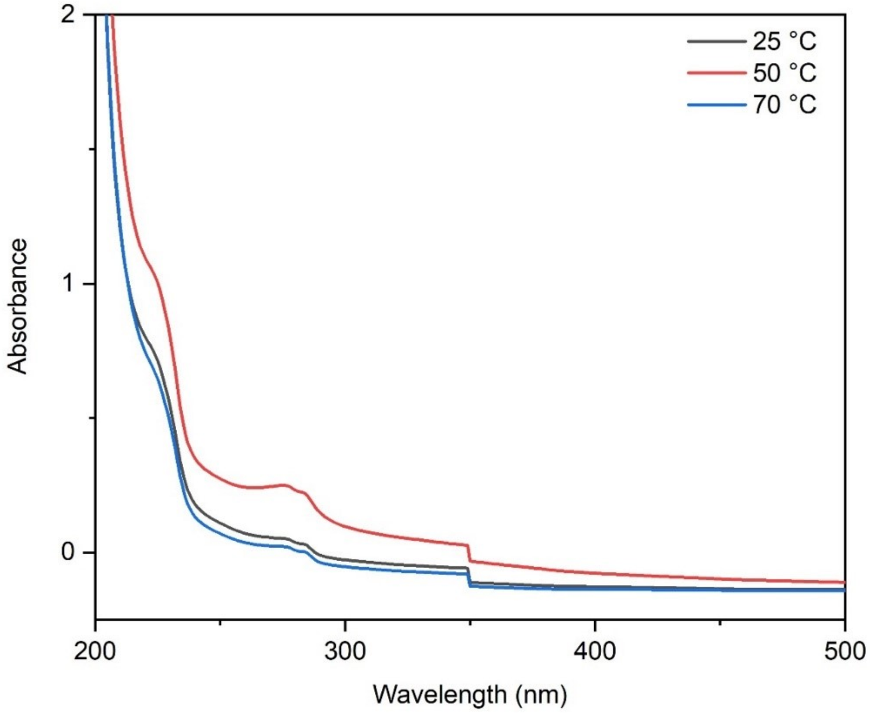


Figure S32: UV-vis. absorption spectra recorded in methanol as a dispersant for CNPs synthesized at various temperatures (reaction time = 4 hours).



FigureS33: UV-vis. absorption spectra recorded in methanol as a dispersant for CNPs synthesized at various temperatures (reaction time = 16 hours).

Photoluminescence Spectroscopy

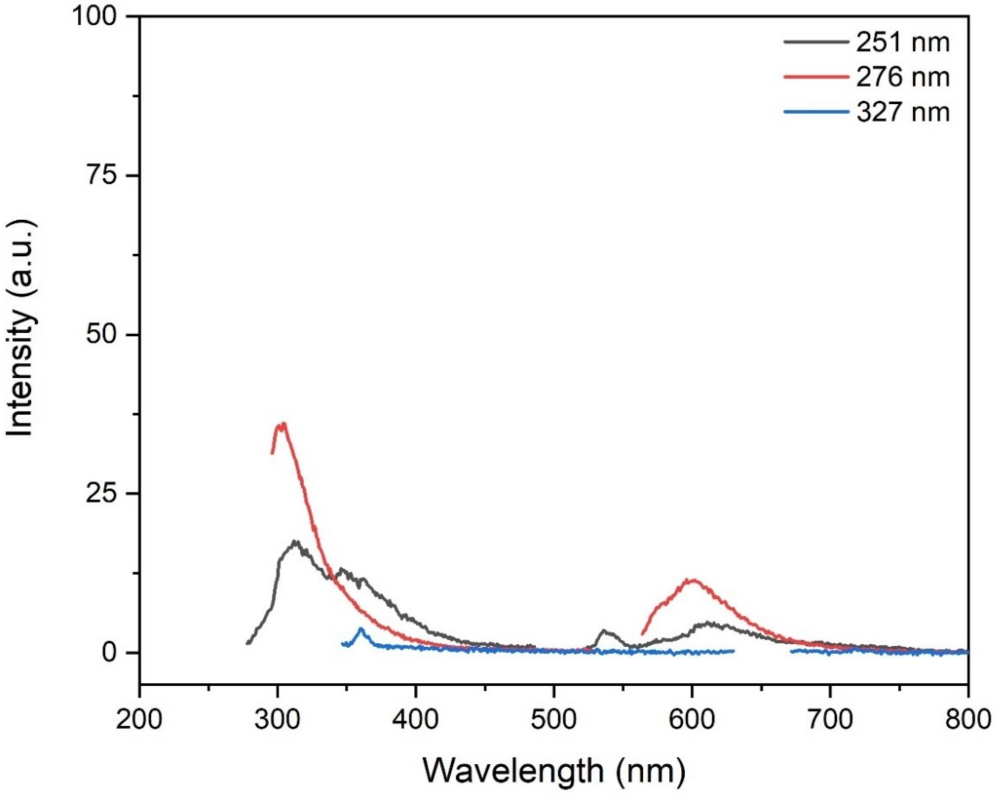


Figure S34: Photoluminescence spectra recorded at various excitation wavelengths (251nm, 276 nm, 327 nm) in methanol for CNPs synthesized at 25 °C for 4 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

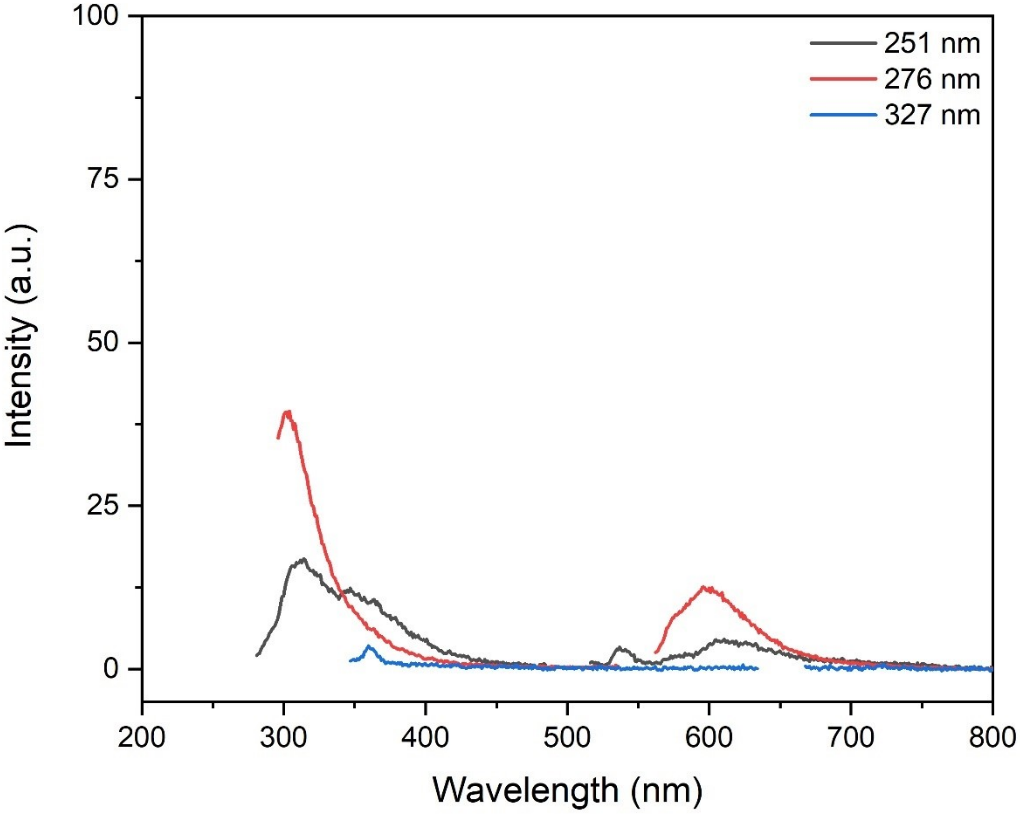


Figure S35: Photoluminescence spectra recorded at various excitation wavelengths (251nm, 276 nm, 327 nm) in methanol for CNPs synthesized at 50 °C for 4 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

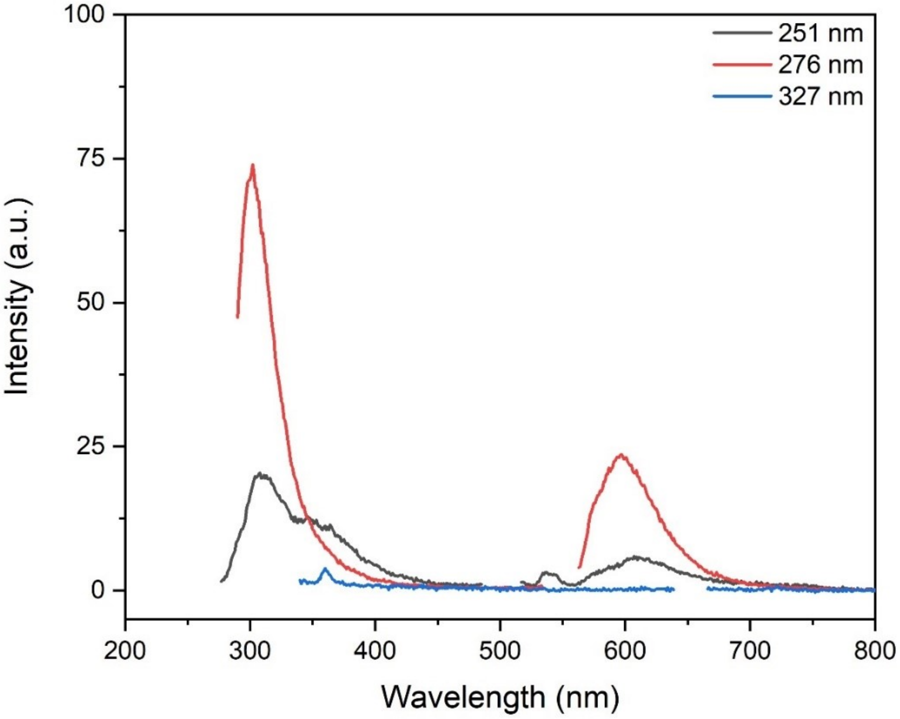


Figure S36: Photoluminescence spectra recorded at various excitation wavelengths (251nm, 276 nm, 327 nm) in methanol for CNPs synthesized at 70 °C for 4 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

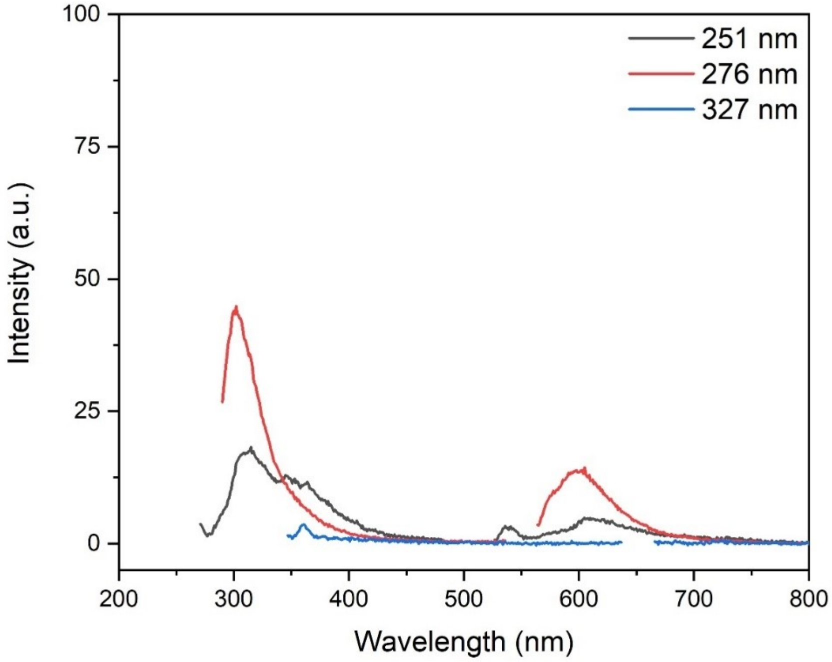


Figure S37: Photoluminescence spectra recorded at various excitation wavelengths (251nm, 276 nm, 327 nm) in methanol for CNPs synthesized at 25 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

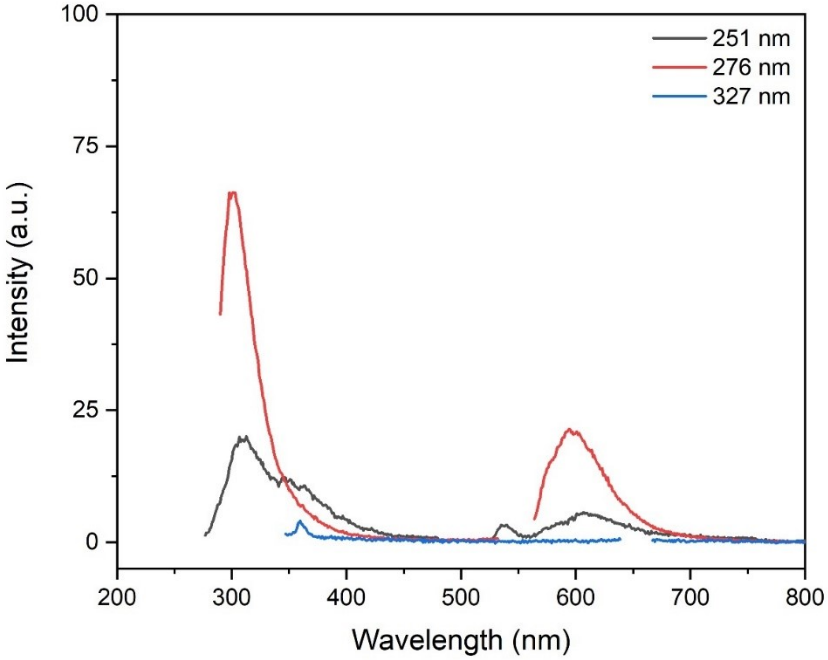


Figure S38: Photoluminescence spectra recorded at various excitation wavelengths (251nm, 276 nm, 327 nm) in methanol for CNPs synthesized at 50 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

UV-Visible Absorption Spectra of CNPs after UV irradiation

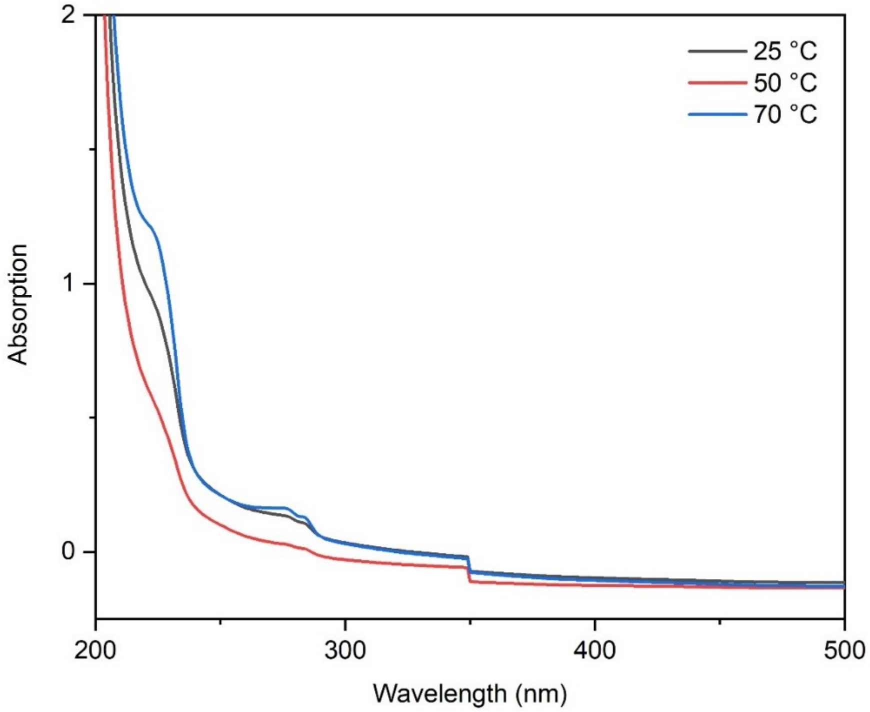


Figure S39: UV-vis absorption spectra of CNPs (reaction time= 4 h, various temperatures) recorded in methanol after 72 hours of UV-irradiation in acetonitrile.

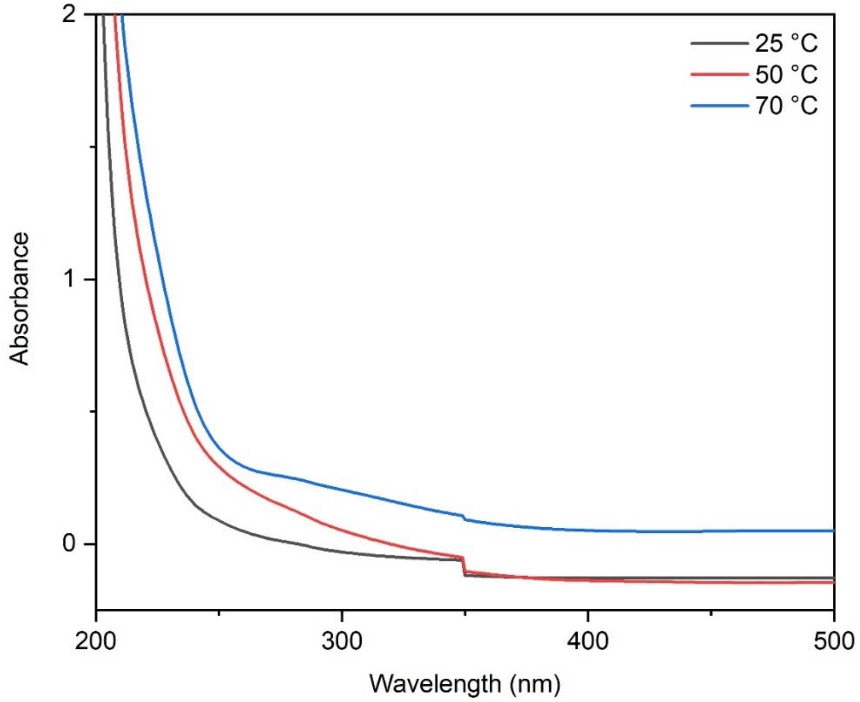


Figure S40: UV-vis absorption spectra of CNPs (reaction time= 16 h, various temperatures) recorded in methanol after 72 hours of UV-irradiation in acetonitrile.

Photoluminescence Spectra of CNPs after UV irradiation

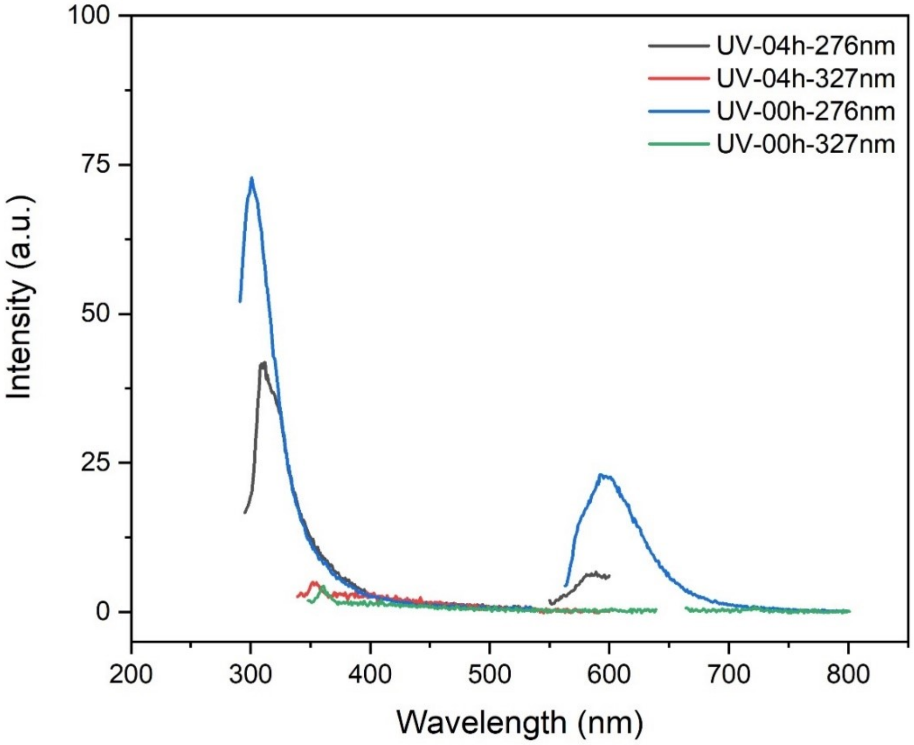


Figure S41: Photoluminescence spectra recorded in methanol before(00h) and after (04h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 70 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

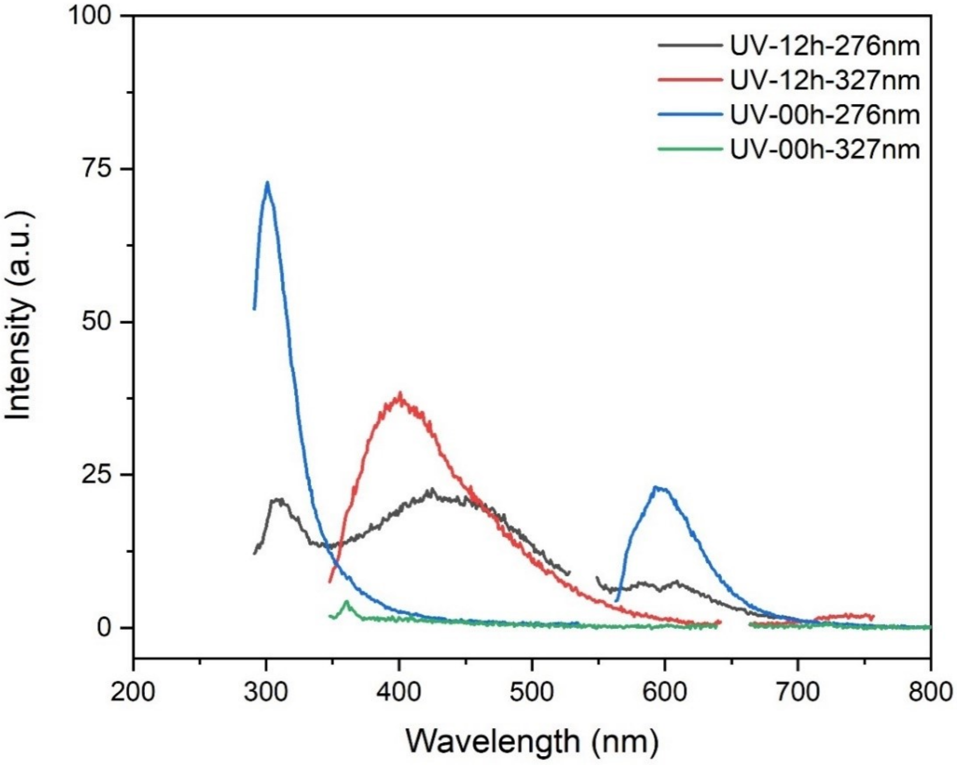


Figure S42: Photoluminescence spectra recorded in methanol before(00h) and after (12h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 70 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

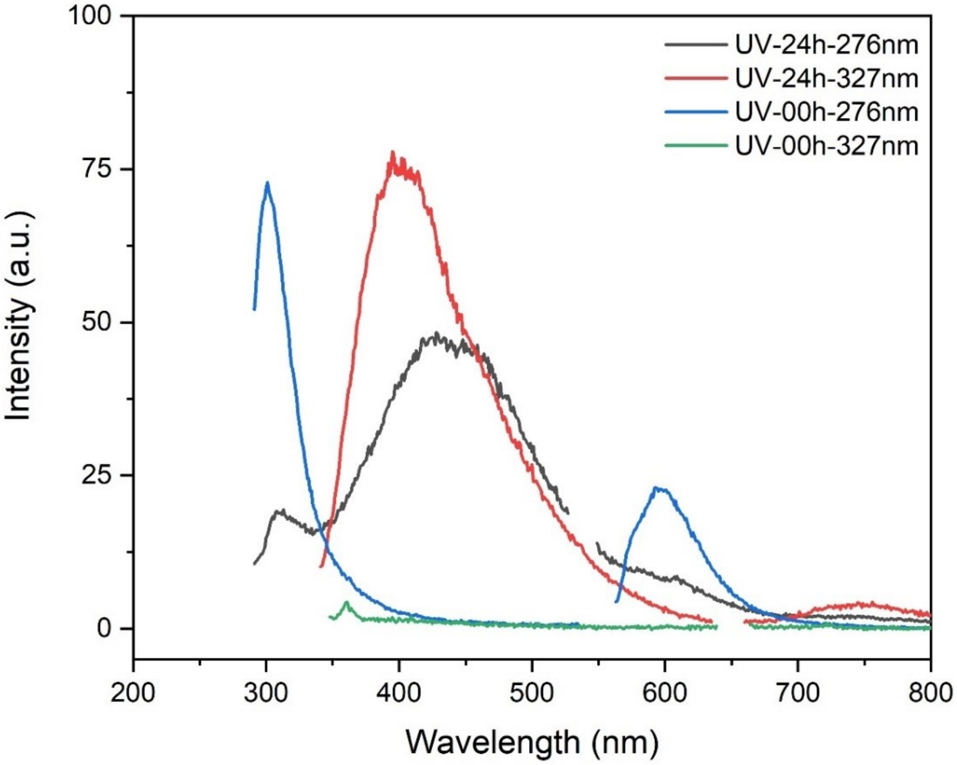


Figure S43: Photoluminescence spectra recorded in methanol before(00h) and after (24h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 70 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

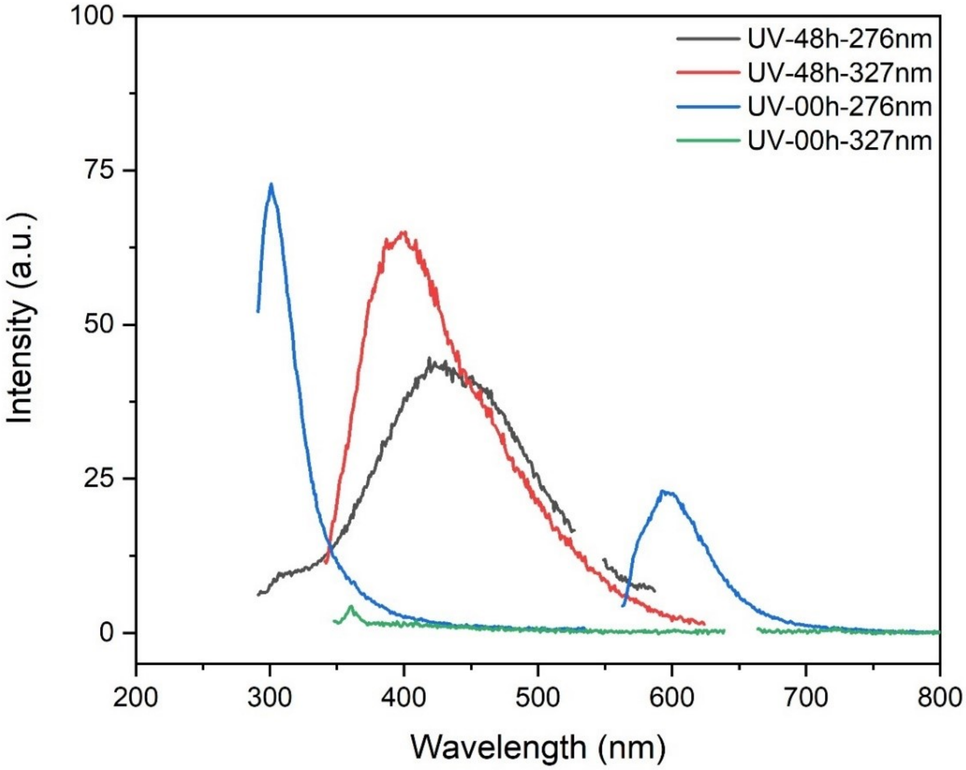


Figure S44: Photoluminescence spectra recorded in methanol before(00h) and after (48h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 70 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

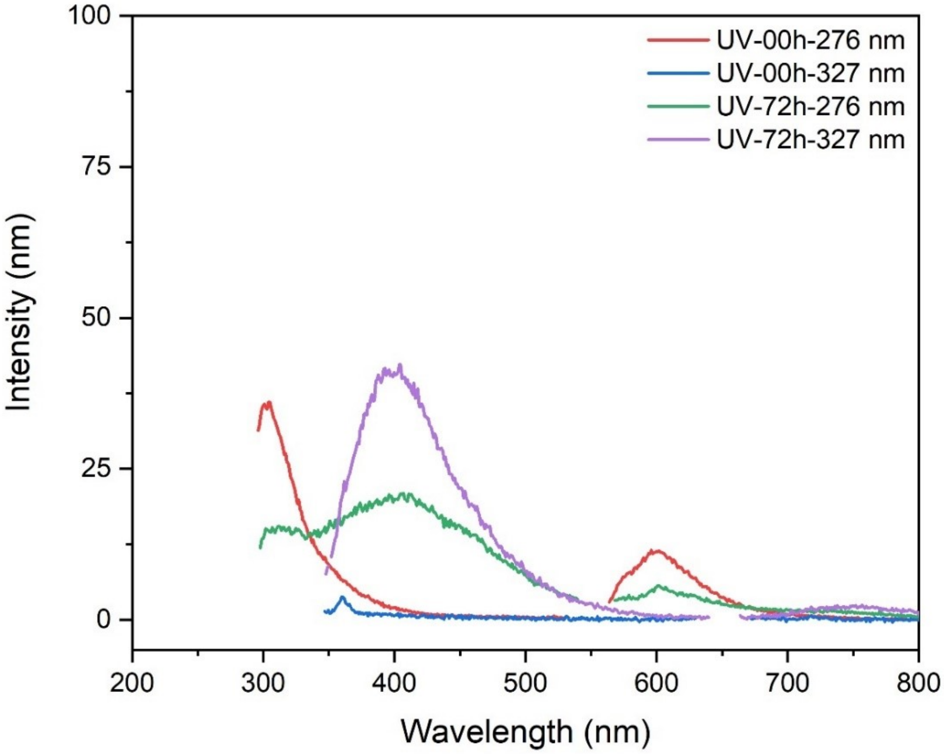


Figure S45: Photoluminescence spectra recorded in methanol before(00h) and after (72h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 25 °C for 4 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

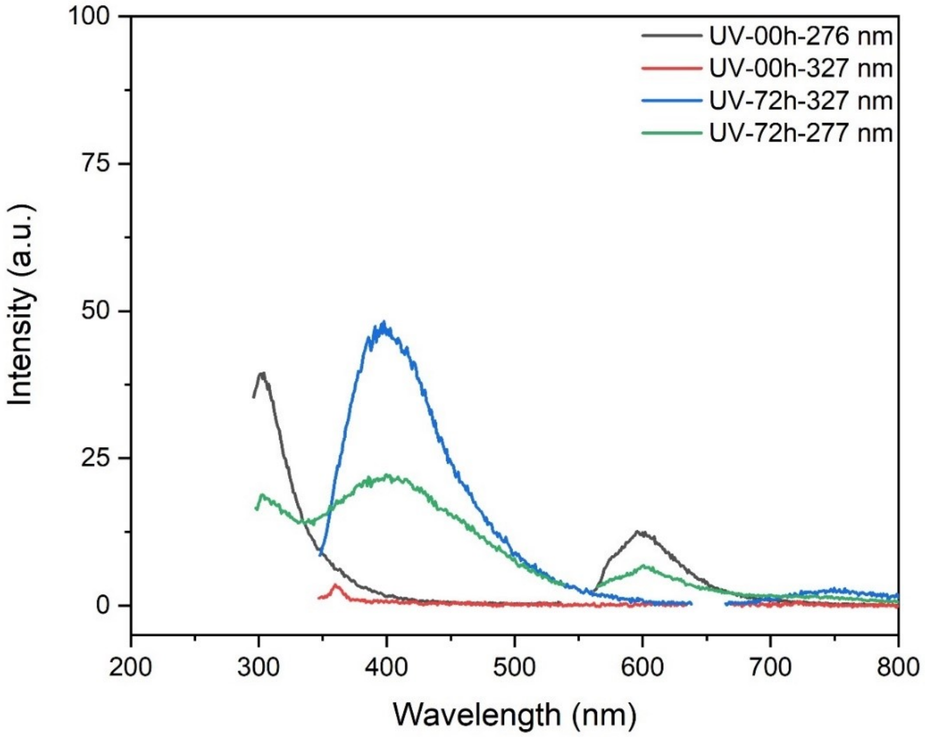


Figure S46: Photoluminescence spectra recorded in methanol before(00h) and after (72h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 70 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

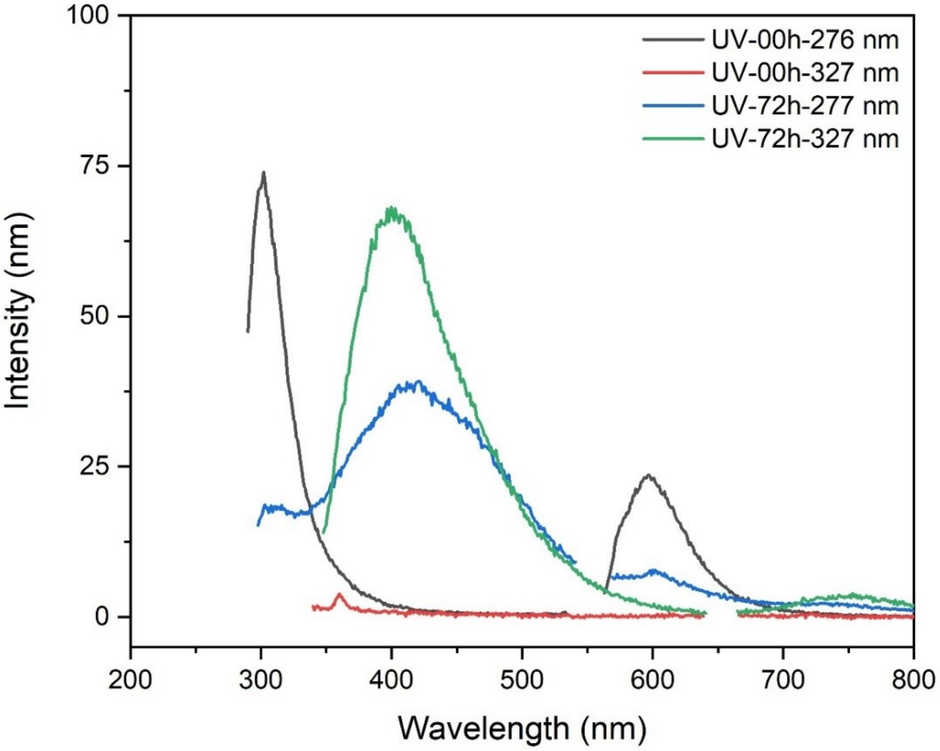


Figure S47: Photoluminescence spectra recorded in methanol before(00h) and after (04h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 70 °C for 4 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

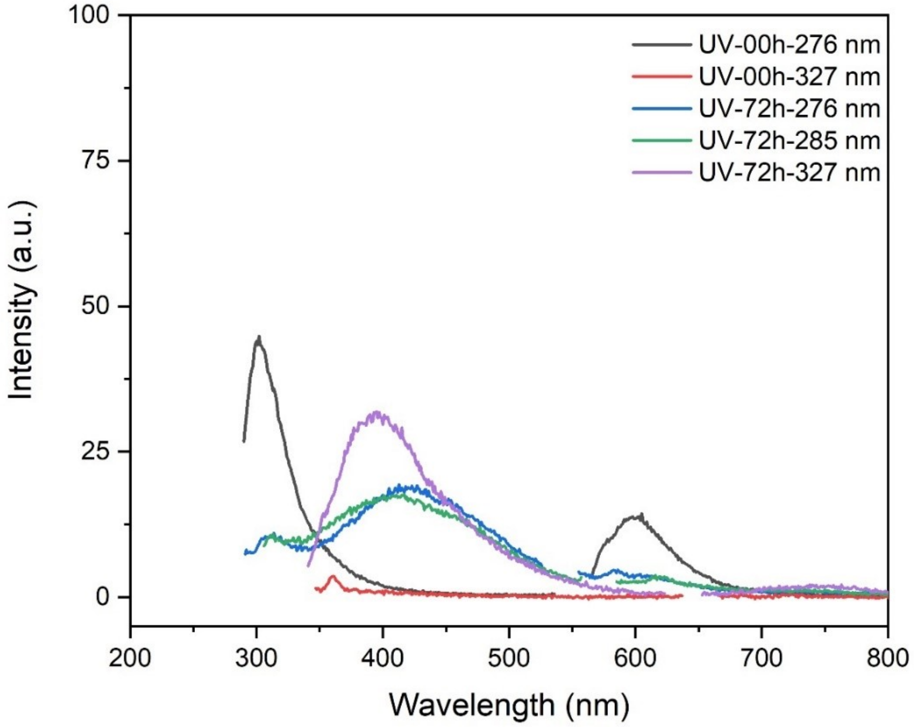


Figure S48: Photoluminescence spectra recorded in methanol before(00h) and after (72h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 25 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

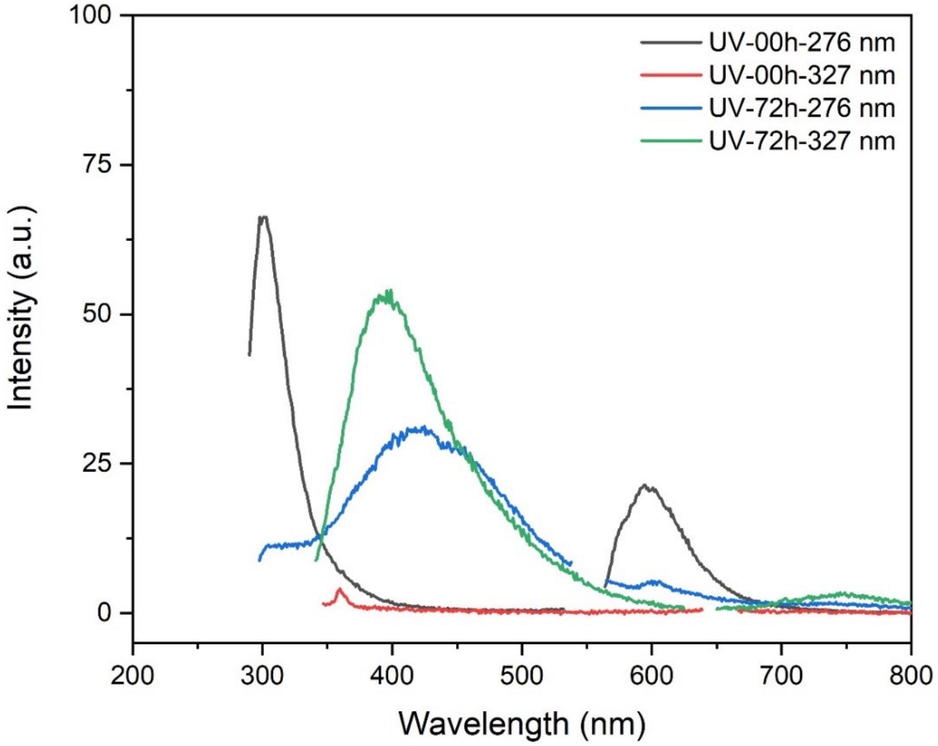


Figure S49: Photoluminescence spectra recorded in methanol before(00h) and after (72h) of UV (254nm) irradiation at various excitation wavelengths (276 nm, 327 nm) for CNPs dispersed in acetonitrile synthesized at 50 °C for 16 hours. The discontinuity of spectra is due to the removal of second harmonics peaks.

TEM images of CNPs after UV irradiation

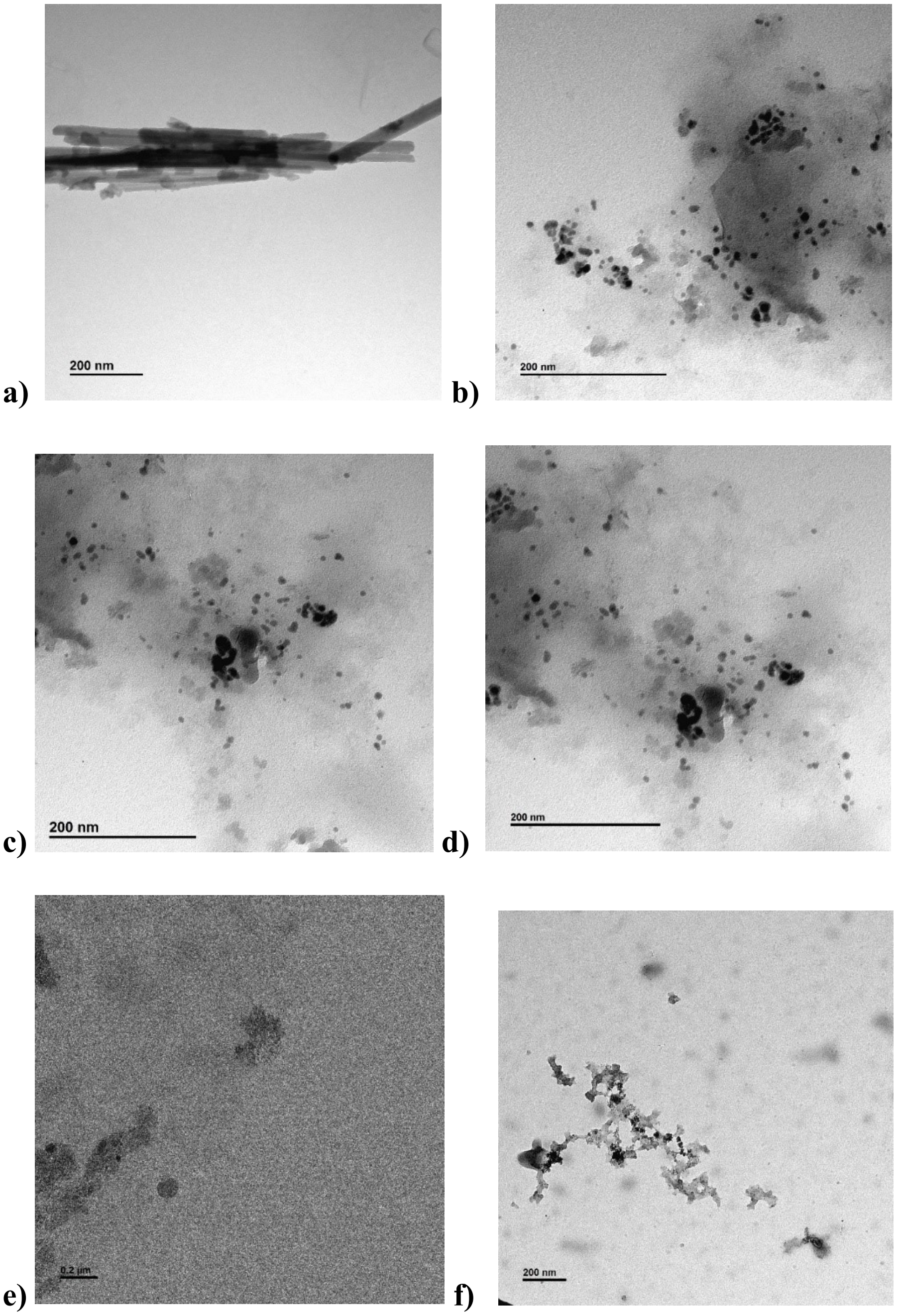


Figure S50: Representative TEM images of CNPs after 72 hours of UV-irradiation for CNPs synthesized for 4 hours at temperatures of 25 °C: a); 50 °C: b), c), d); 70 °C: e), f).

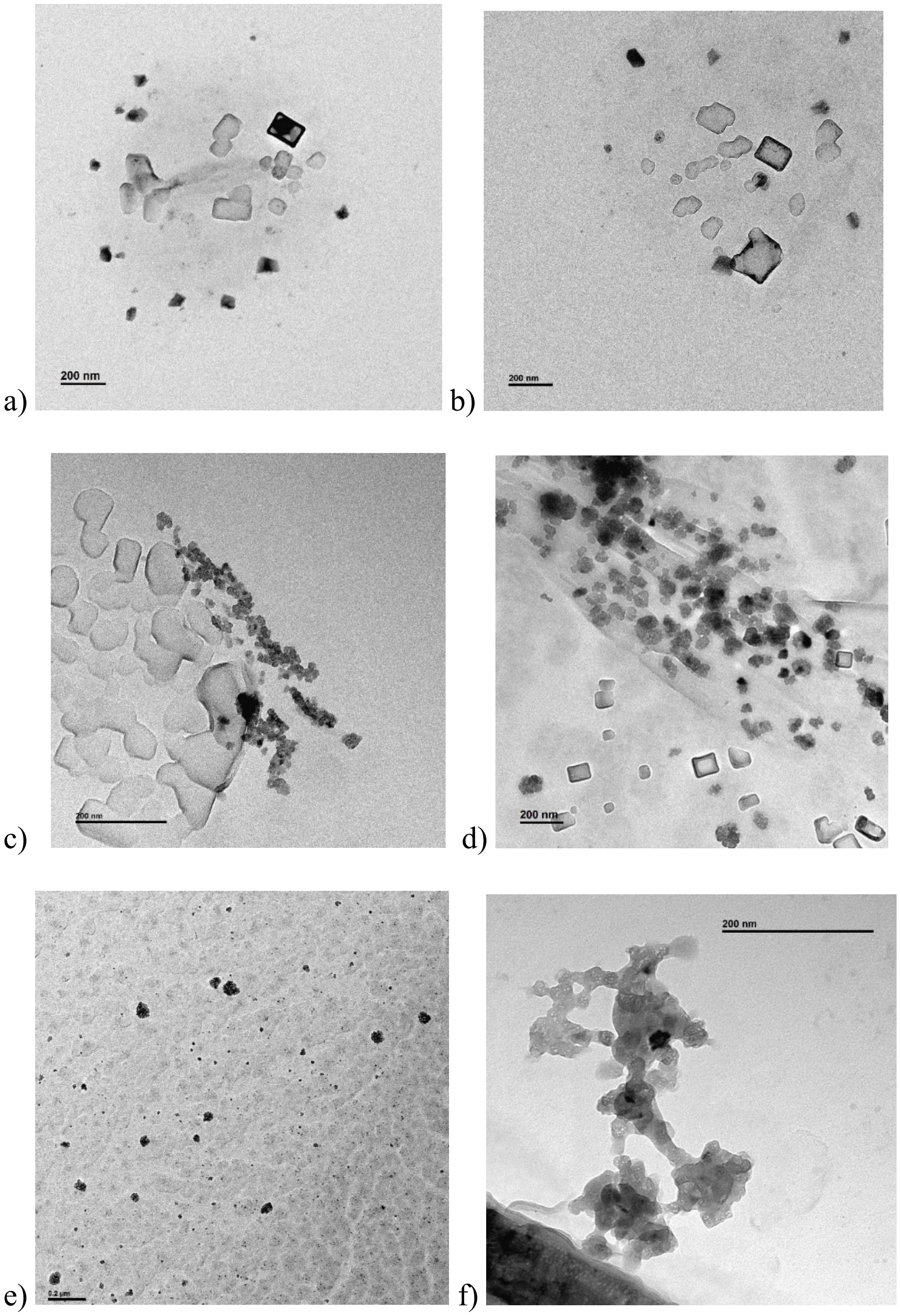


Figure S51: Representative TEM images of CNPs after 72 hours of UV-irradiation for CNPs synthesized for 16 hours at temperatures of 25 °C: a), b); 50 °C: c), d); 70 °C: e), f).

XPS Spectra of CNPs after UV irradiation

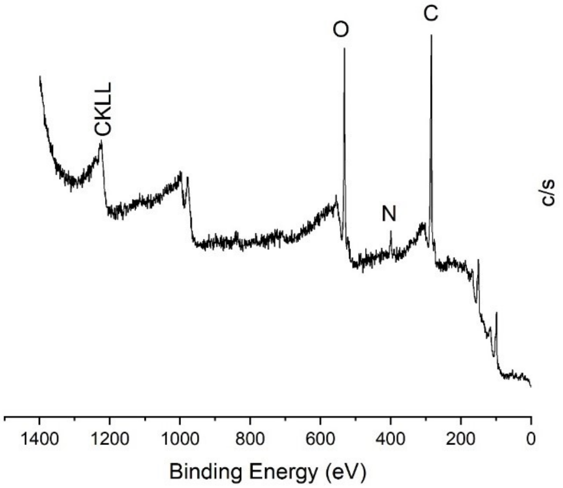


Figure S52: XPS survey spectrum for CNPs after 72 hours of UV irradiation for CNPs synthesized at 25 °C for 4 hours.

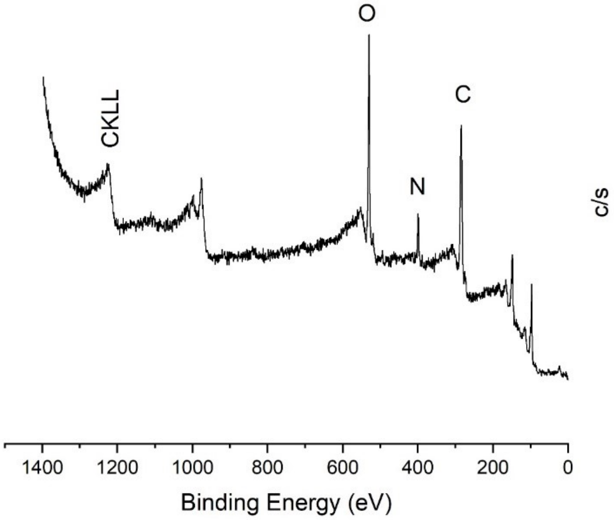


Figure S53: XPS survey spectrum for CNPs after 72 hours of UV irradiation for CNPs synthesized at 50 °C for 4 hours.

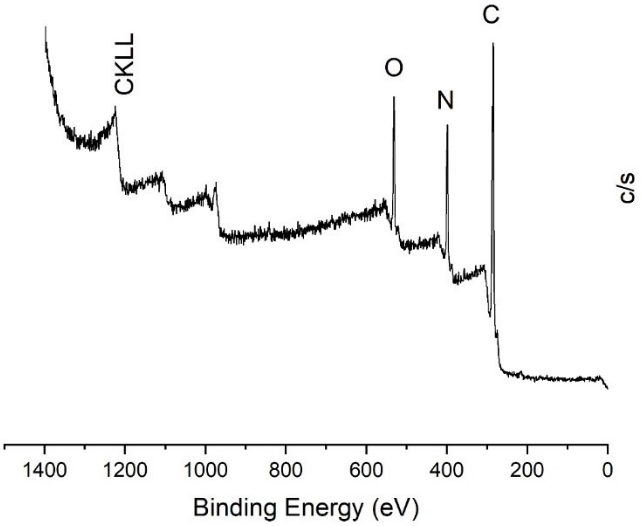


Figure S54: XPS survey spectrum for CNPs after 72 hours of UV irradiation for CNPs synthesized at 70 °C for 4 hours.

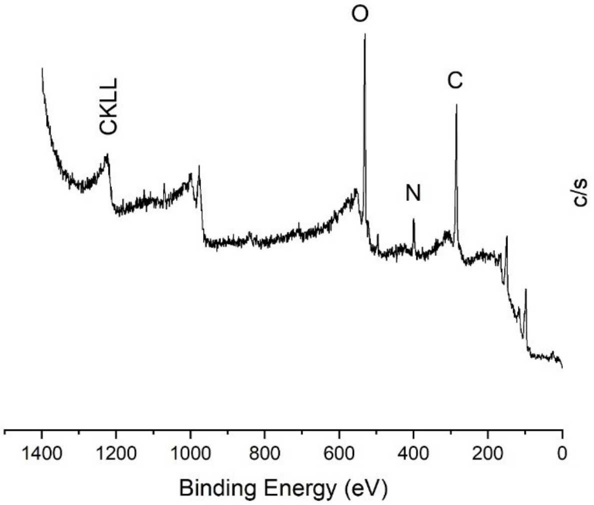


Figure S55: XPS survey spectrum for CNPs after 72 hours of UV irradiation for CNPs synthesized at 25 °C for 16 hours.

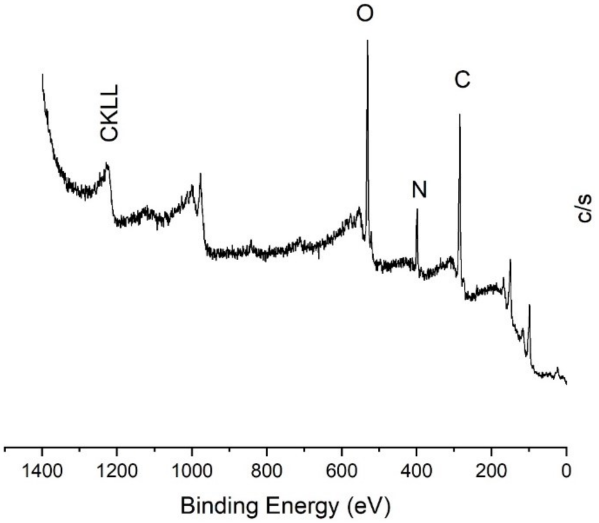


Figure S56: XPS survey spectrum for CNPs after 72 hours of UV irradiation for CNPs synthesized at 50 °C for 16 hours.

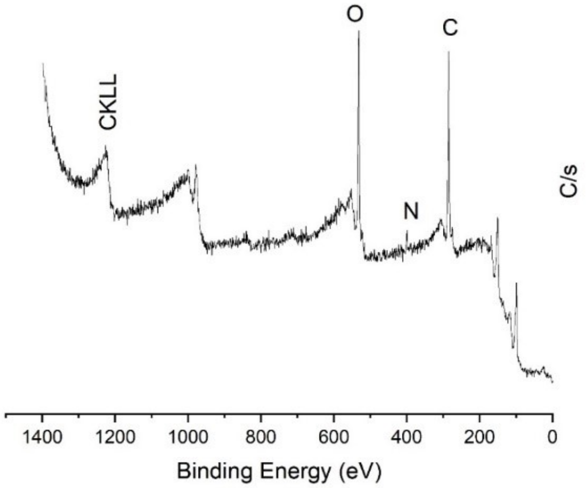


Figure S57: XPS survey spectrum for CNPs after 72 hours of UV irradiation for CNPs synthesized at 70 °C for 16 hours.

Table S11: Summary of atomic % values of elements (C, O, N) from XPS survey spectra in CNPs after 72 hours of UV irradiation

Reaction Temperature	Reaction Time	C	O	N	O/C
25 °C	4 h	69.1	26.3	4.2	0.38
50 °C	4 h	63.7	26.9	9.5	0.42
70 °C	4 h	69.1	19.2	11.6	0.28
25 °C	16 h	59.2	31.2	9.2	0.53
50 °C	16 h	58.3	29.2	12.5	0.50
70 °C	16 h	64.6	31.8	3.6	0.49

Table S12: Summary of the ratio of atomic % values of carbon and oxygen from XPS survey spectra in CNPs before UV-irradiation and after 72 hours of UV irradiation

		O/C	
Reaction Temperature	**Reaction Time**	**Before UV**	**After UV**
25 °C	4 h	0.25	0.38
50 °C	4 h	0.20	0.42
70 °C	4 h	0.23	0.28
25 °C	16 h	0.23	0.53
50 °C	16 h	0.26	0.50
70 °C	16 h	0.17	0.49

X-Ray Induced Auger Electron Spectroscopy (XAES)

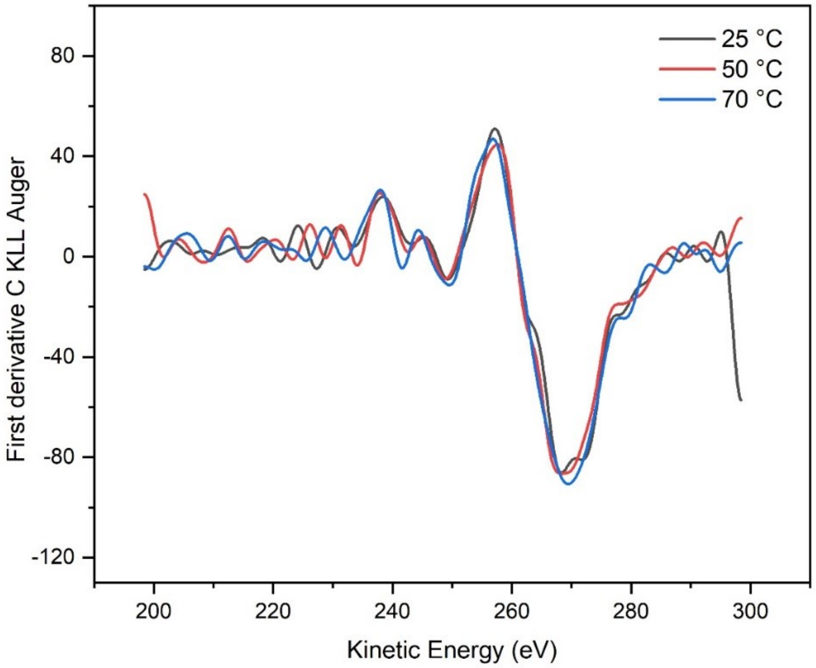


Figure S58: First derivative CKLL XAES spectra recorded after 72 hours of UV irradiation for CNPs synthesized at 4 hours with temperature variations.

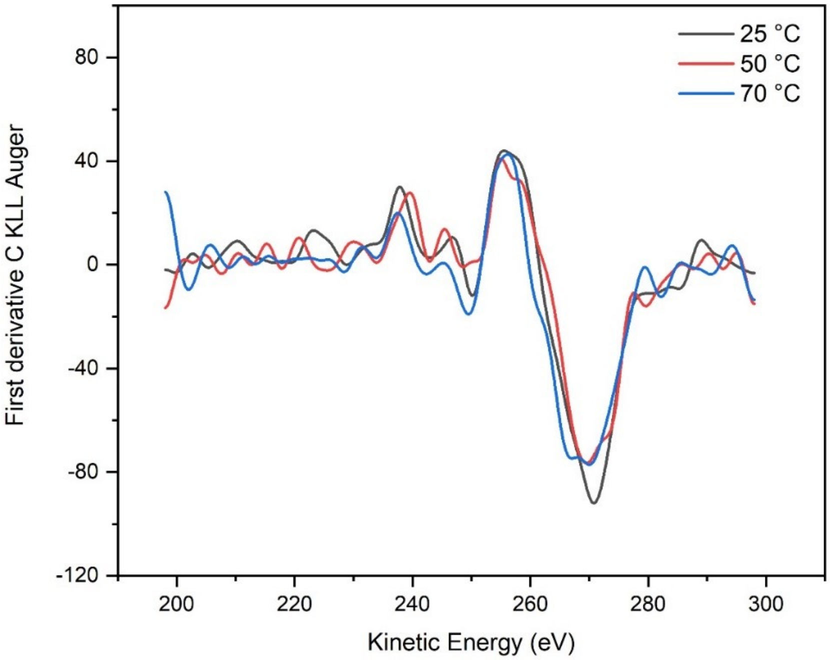


Figure S59: First derivative CKLL XAES spectra recorded after 72 hours of UV irradiation for CNPs synthesized at 16 hours with temperature variations.

Table S13: D-parameter values calculated from the first derivative CKLL XAES spectra for CNPs after UV irradiation

Reaction Temperature	*Reaction Time*	*D-Parameter*
25 °C	4 h	11.18
50 °C	4 h	12.56
70 °C	4 h	13.93
25 °C	16 h	15.27
50 °C	16 h	14.43
70 °C	16 h	13.83

Table S14: Comparison of D-parameter values for CNPs before UV-irradiation and after 72 hours of UV irradiation

Reaction Temperature	**Reaction Time**	**D-Parameter**	
		Before UV-irradiation	**After UV-irradiation**
25 °C	4 h	12.18	11.18
50 °C	4 h	12.74	12.56
70 °C	4 h	13.49	13.93
25 °C	16 h	12.88	15.27
50 °C	16 h	13.57	14.43
70 °C	16 h	11.48	13.83

FT-IR of CNPs after UV irradiation

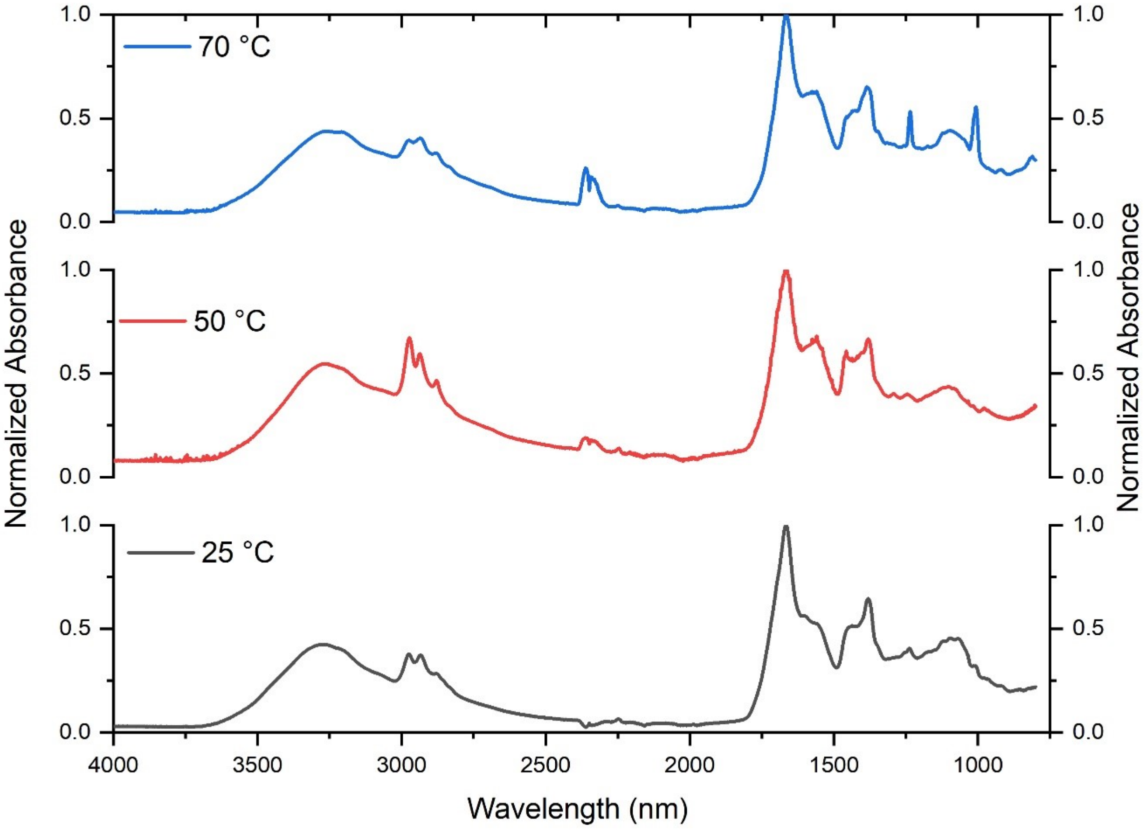


Figure S60: FT-IR spectra recorded in ATR mode for CNPs synthesized at 4 hours with variations in temperature after 72 hours of UV irradiation.

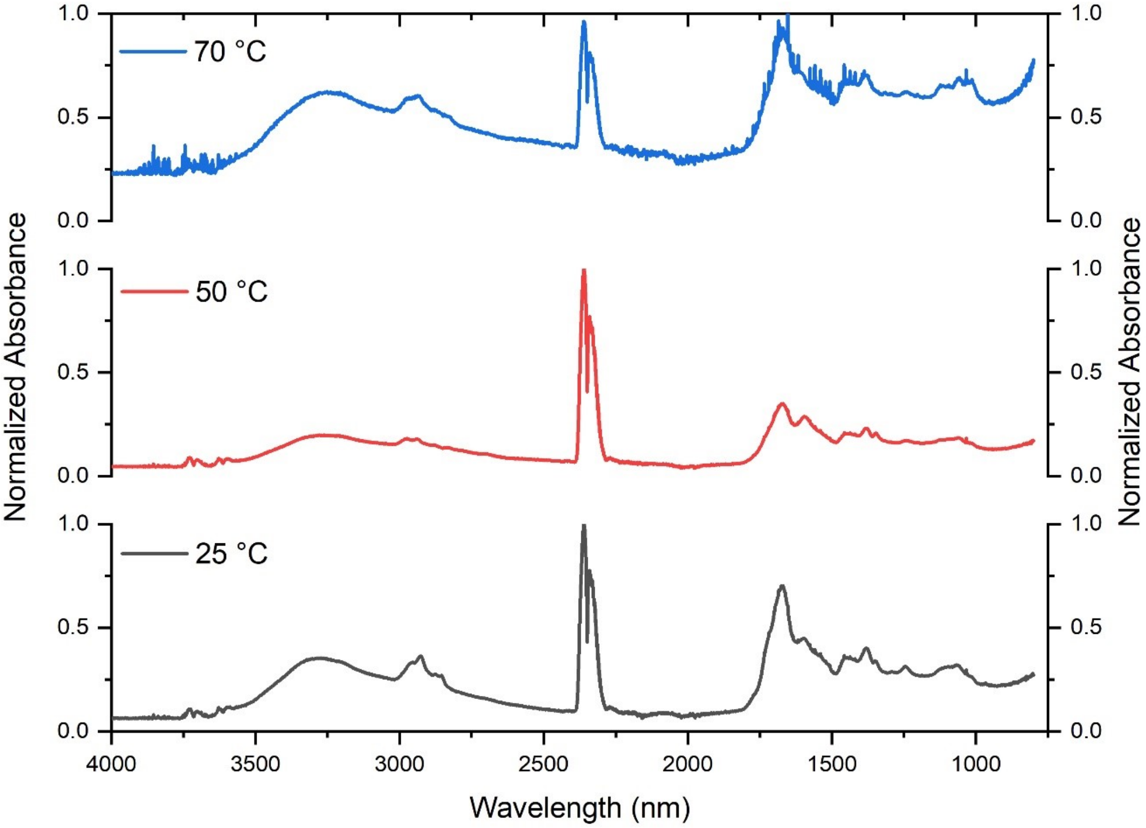


Figure S61: FT-IR spectra recorded in ATR mode for CNPs synthesized at 16 hours with variations in temperature after 72 hours of UV irradiation.

High-Resolution XPS C1s Spectra of CNPs after UV irradiation

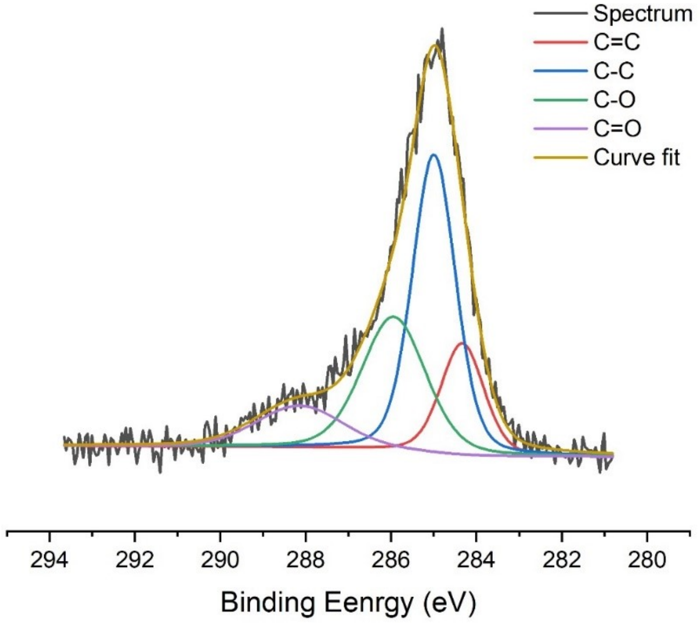


Figure S62: Curve fit spectra of high-resolution XPS C1s spectrum after 72 hours of UV irradiation for CNPs synthesized at 25 °C for 4 hours.

Table S15: Summary of the curve-fit data for Figure S62

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	283.65	0	91	1.31	75	141	11.87	1.2
C-C	284.77	1.12	269	1.82	75	583	49.08	
C-O	286.38	2.74	145	2.16	75	374	31.45	
C=O	288.08	4.43	41	1.93	85	41	7.61	

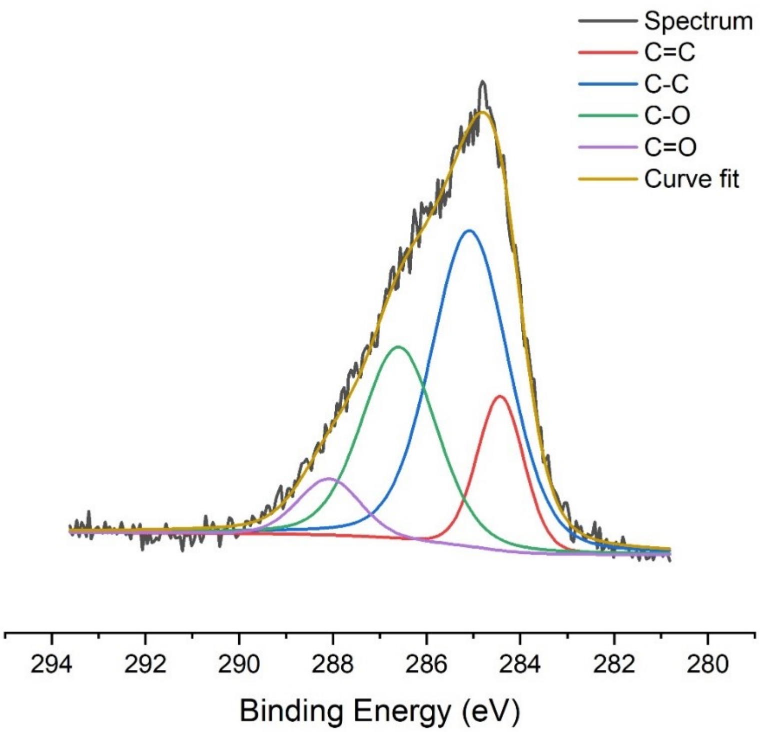


Figure S63: Curve fit spectra of high-resolution XPS C1s spectrum after 72 hours of UV irradiation for CNPs synthesized at 50 °C for 4 hours.

Table S16: Summary of the curve-fit data for Figure S63

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.43	0	141	1.18	85	189	14.03	1.22
C-C	285.08	0.65	288	1.96	75	671	49.79	
C-O	286.59	2.16	176	1.89	75	395	29.34	
C=O	288.08	3.65	52	1.56	85	92	6.85	

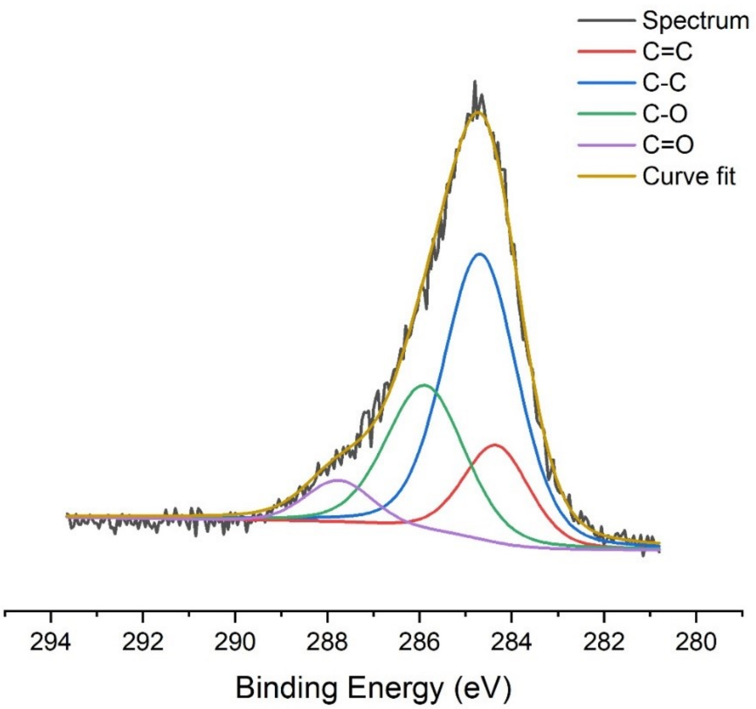


Figure S64: Curve fit spectra of high-resolution XPS C1s spectrum after 72 hours of UV irradiation for CNPs synthesized at 70 °C for 4 hours.

Table S17: Summary of the curve-fit data for Figure S64

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.33	0	115	1.69	75	232	15.54	1.63
C-C	284.68	0.35	336	1.89	75	757	50.75	
C-O	285.88	1.55	170	2	75	406	27.21	
C=O	287.75	3.42	50	1.69	85	97	6.5	

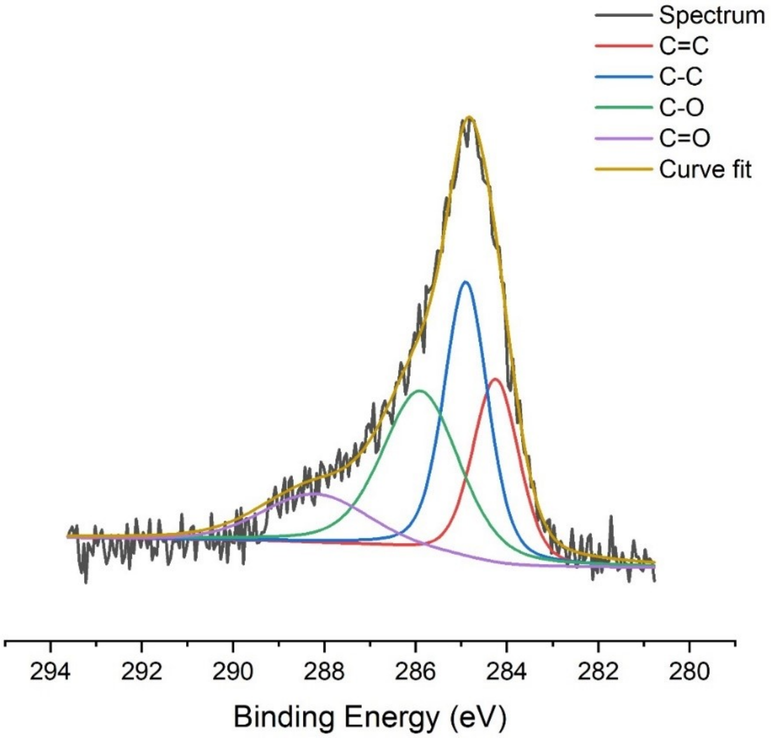


Figure S65: Curve fit spectra of high-resolution XPS C1s spectrum after 72 hours of UV irradiation for CNPs synthesized at 25 °C for 16 hours.

Table S18: Summary of the curve-fit data for Figure S65

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.24	0	140	1.19	75	200	21.83	1.17
C-C	284.9	0.65	211	1.14	65	297	32.51	
C-O	285.89	1.65	122	1.99	65	301	32.91	
C=O	288.2	3.95	37	2.73	85	117	12.75	

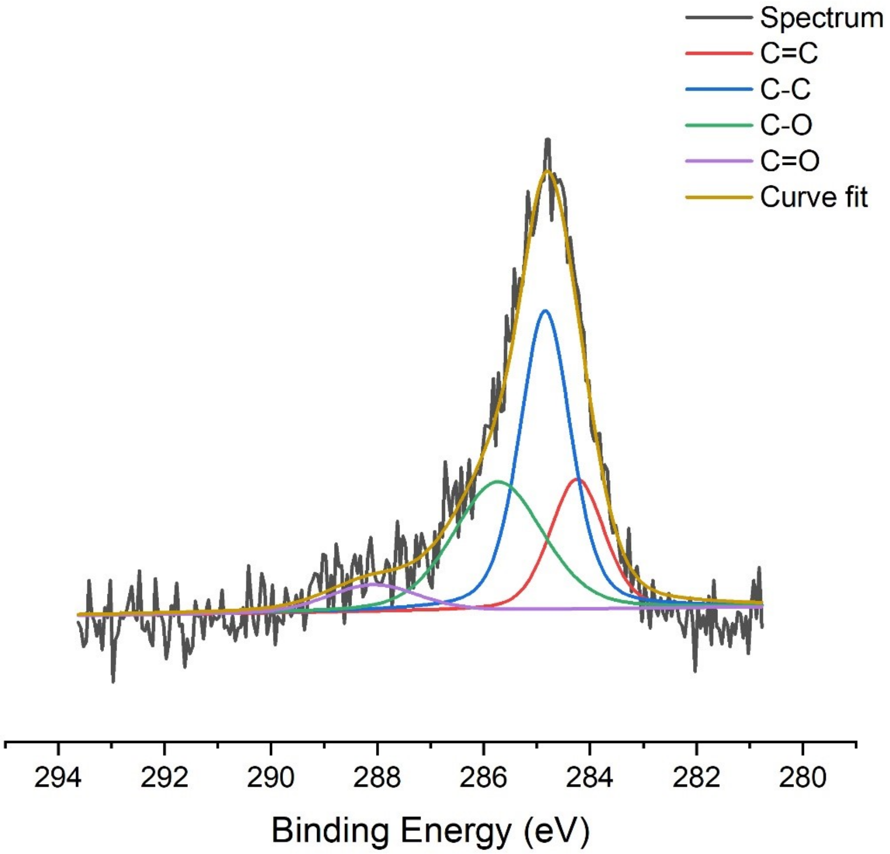


Figure S66: Curve fit spectra of high-resolution XPS C1s spectrum after 72 hours of UV irradiation for CNPs synthesized at 50 °C for 16 hours.

Table S19: Summary of the curve-fit data for Figure S66

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.24	0	66	1.19	75	94	19.01	1.11
C-C	284.24	0.6	153	1.14	65	215	43.29	
C-O	285.73	1.49	66	1.99	75	155	31.29	
C=O	288.08	3.84	14	1.99	85	31	6.3	

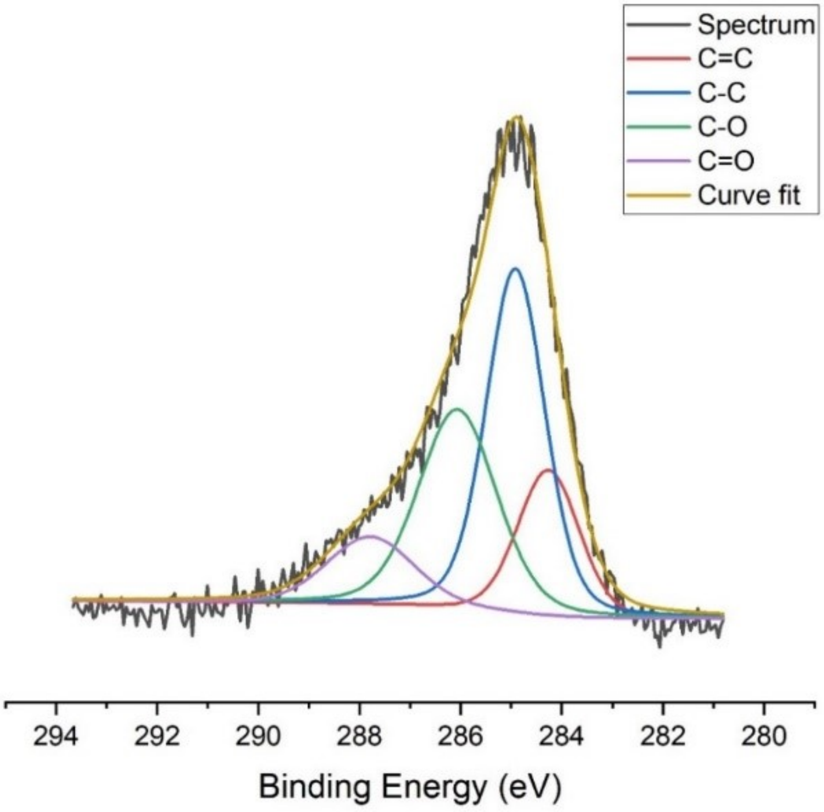


Figure S67: Curve fit spectra of high-resolution XPS C1s spectrum after 72 hours of UV irradiation for CNPs synthesized at 70 °C for 16 hours.

Table S20: Summary of the curve-fit data for Figure S67

	Peak (eV)	*Delta*	*Height*	*FWHM*	*% Gauss*	*Area*	*% of total area*	*Chi Square*
C=C	284.62	0	163	1.74	100	301	27.11	1.29
C-C	285.1	0.47	230	1.9	100	466	41.91	
C-O	286.22	1.6	75	2.45	95	201	18.08	
C=O	287.59	2.96	64	3.06	95	143	12.9	

Table S21: Summary of functional groups extracted from curve-fit data of XPS C1s spectra of CNPs 72 hours after UV irradiation

Reaction Temperature	*Reaction Time*	*C=C (%)*	*C-C (%)*	*C-O (%)*	*C=O (%)*	*CO : CC*
25 °C	4 h	11.87	49.08	31.45	7.61	**0.64**
50 °C	4 h	15.54	50.75	27.21	6.5	**0.51**
70 °C	4 h	14.03	49.79	29.34	6.85	**0.57**
25 °C	16 h	21.83	32.51	32.91	12.75	**0.84**
50 °C	16 h	19.01	43.41	31.29	6.3	**0.60**
70 °C	16 h	17.17	40.49	31.08	1.26	**0.56**

Table S22: Comparison of CO/CC ratio for CNPs before UV irradiation and after 72 hours of UV irradiation from XPS C1s spectra

Reaction Temperature	*Reaction Time*	*CO/CC*	
		Before UV	**After UV**
25 °C	4 h	0.30	0.64
50 °C	4 h	0.41	0.51
70 °C	4 h	0.39	0.57
25 °C	16 h	0.26	0.84
50 °C	16 h	0.40	0.60
70 °C	16 h	0.51	0.56

Picture of CNP samples

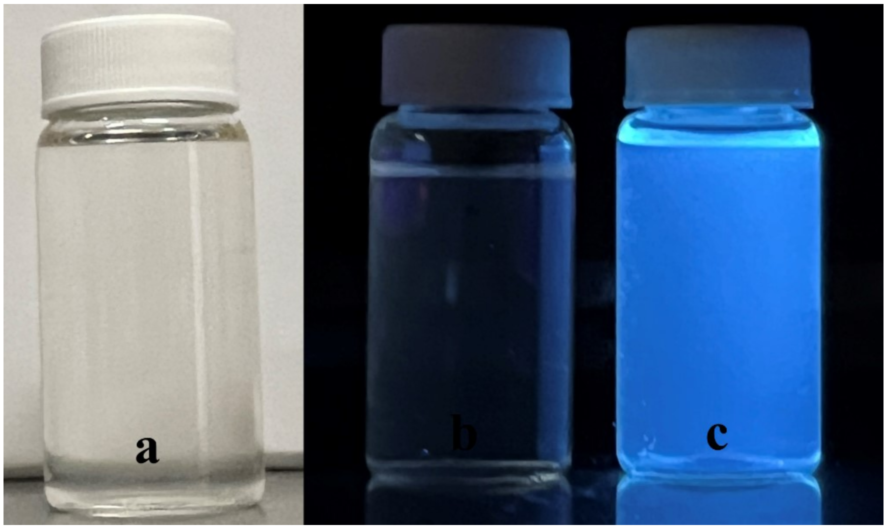


Figure S68: Emission of CNPs synthesized at 25 °C for 4 hours, observed a) in daylight, b) under UV lamp, c) CNPs after 72 hours of UV irradiation under UV lamp.

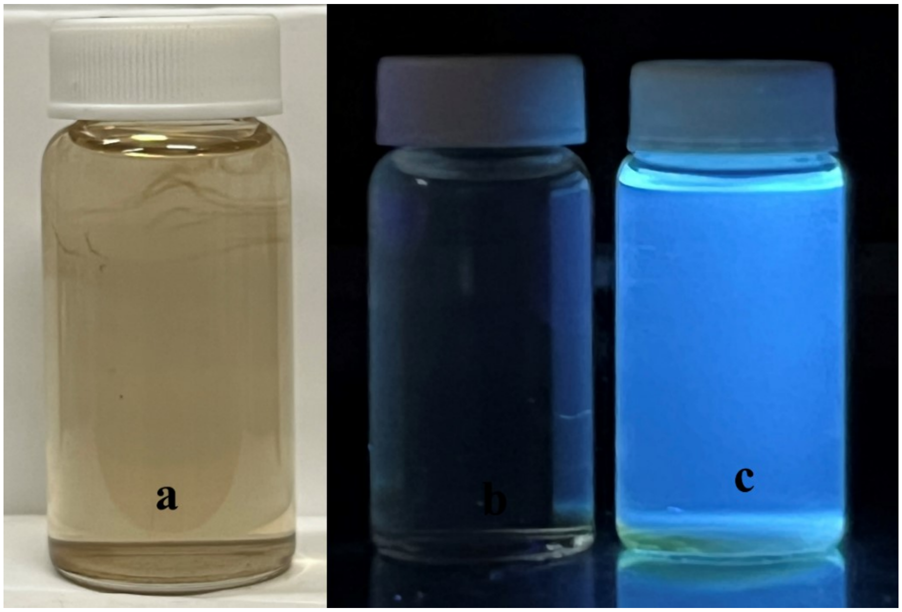


Figure S69: Emission of CNPs synthesized at 50 °C for 4 hours, observed a) in daylight, b) under UV lamp, c) CNPs after 72 hours of UV irradiation under UV lamp.

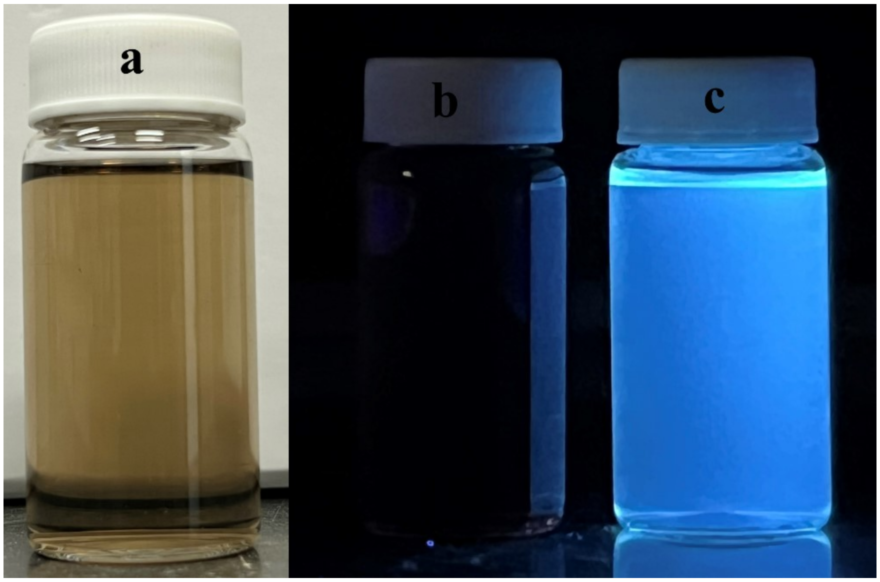


Figure S70: Emission of CNPs synthesized at 70 °C for 4 hours, observed a) in daylight, b) under UV lamp, c) CNPs after 72 hours of UV irradiation under UV lamp.

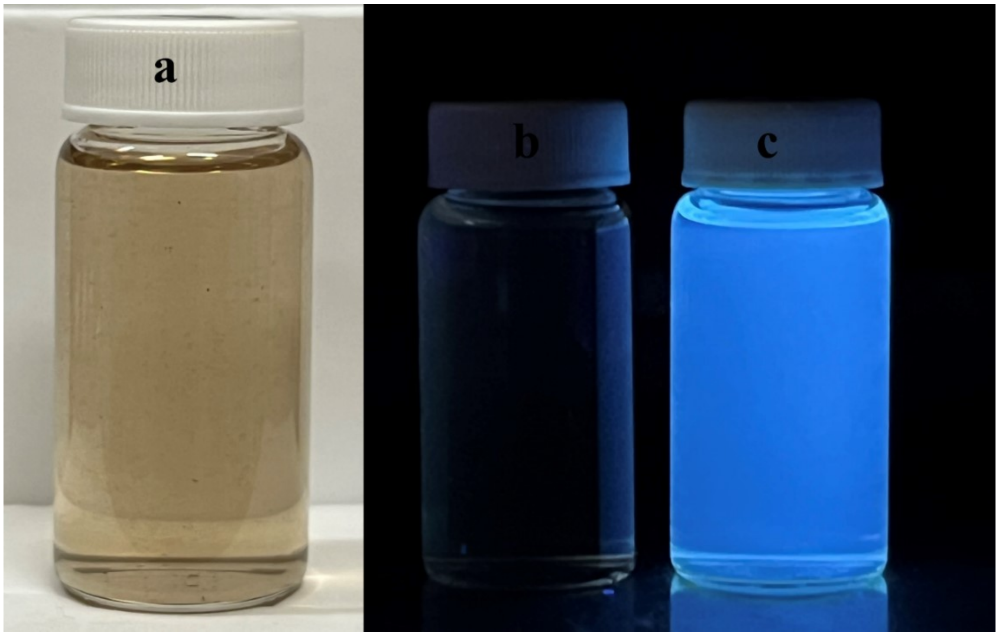


Figure S71: Emission of CNPs synthesized at 25 °C for 16 hours, observed a) in daylight, b) under UV lamp, c) CNPs after 72 hours of UV irradiation under UV lamp.

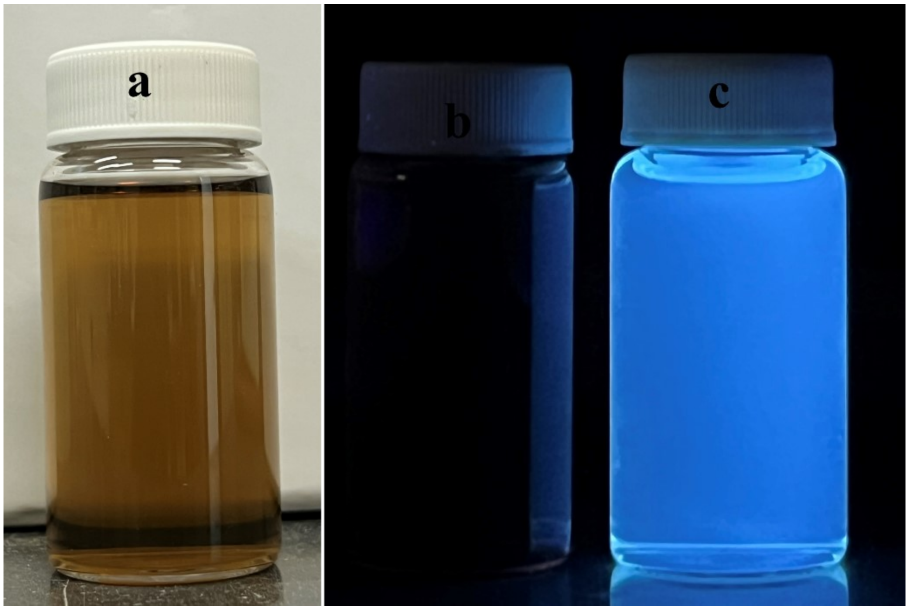


Figure S72: Emission of CNPs synthesized at 50 °C for 16 hours, observed a) in daylight, b) under UV lamp, c) CNPs after 72 hours of UV irradiation under UV lamp.