Supporting Information's for

Formation of Self-assembled Ag Nanoparticles on DNA chains with Enhanced Catalytic Activity

Subrata Kundu*

Electrochemical Materials Science (ECMS) Division, CSIR-Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi-630006, Tamil Nadu, India.

* To whom correspondence should be addressed, *E-mail: skundu@cecri.res.in; subrata_kundu2004@yahoo.co.in*, Fax: +91 4565-241487; Tel: +91 4565-241487.

Instruments.

The synthesized self-assembled Ag NPs in DNA were characterized with several spectroscopic tools as given below. The UV-visible (UV-Vis) absorption spectra were recorded in a Hitachi (model U-4100) UV-Vis-NIR spectrophotometer equipped with a 1 cm quartz cuvette holder for liquid samples. The high resolution transmission electron microscopy (HR-TEM) analysis was done with a Tecnai model TEM instrument (Tecnai^{TM} G2 F20, FEI) with an accelerating voltage of 200 KV. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was recorded with a separate EDS detector incorporated with the same TEM instrument. A thin film of the DNA-Ag NPs chains was made in a glass substrate and the fabricated thin films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier Transform Infrared Spectroscopy (FT-IR) analyses. The XRD analysis was done with a scanning rate of 0.020 s^{-1} in the 2θ range 20-80° using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu Kα radiation (λ) 0.154178 nm). The XPS analysis was carried out using an ESCA model VG 3000 system X-ray photoelectron spectrometer with monochromatic Mg Kα line (1253.6 eV) radiation. The instrument integrates a magnetic immersion lens and charge neutralization system with a spherical mirror analyzer, which provides real time chemical state and elemental imaging using a full range of pass energies. The emitted photoelectrons were detected by the analyzer at a passing energy of 20 eV with energy resolution of 0.1 eV. The incident X-ray beam was normal to the sample surface, and the detector was 45° away from the incident direction. The analysis spot on the sample was 0.4 mm × 0.7 mm. The overall energy resolution was about 0.8 eV. Samples for the survey spectrum was recorded in the 0 – 700 eV kinetic energy by 1 eV steps where as high resolution scans with 0.1 eV steps were conducted over the following regions of interest: Ag 3d, O 1s and C 1s. The FT-IR analysis was done with the model Nexus 670 (FTIR), Centaurms 10X (Microscope) having spectral Range 4,000 to 300 cm^{-1} with a MCT-B detector. The UV-photoirradiation was done with 260 nm UV-lamp (UVP-Black Ray, B-100, AP High Intensity UV lamp) having lamp power was 100 watt cm^{-2} and working in 230 V-50HZ. The average illumination intensity of the UV light was ~ 13 mW/cm^2. The distance of the sample stage from the light source was approximately 19 cm. The sample solution was kept over a plastic box such that the UV light falls directly onto the sample solution. The spin coating was done with a spin coater purchased from Spektron instruments Inc, Chennai having highest rotating speed up to 8000/min. The pH value of different solutions was measured by a pH meter purchased from Eutech instruments (cyber scan, pH tutor) from Chennai, Tamilnadu.

Study with other reaction parameters.

In our present experiment, we varied the concentration of Ag(I) ions, concentration of DNA solutions, UV exposure time, and conducted experiment with free DNA bases. We observed that the formation of self-assembled Ag NPs on DNA take place at a particular concentration those are given in Table 1 in the main text. When we increase the concentration of Ag(I) ions ~ 0.5 (M), the Ag NPs formed aggregated nanostructure in DNA as shown in supporting Figure S-3A. We also studied our reaction with free DNA bases instead of polymeric DNA and observed the formation of spherical Ag NPs those are shown in supporting Figure S-3B. When we increase the DNA concentration very high, the Ag NPs are formed but agglomerated or precipitated within few minutes after the synthesis as shown in supporting Figure S-3C. We observed that the formation of DNA-Ag$^+$ complex is instantaneous and 3 hour UV exposure time is sufficient for the complete formation of the Ag NPs. Longer exposure time (8-10 hours) agglomerated the Ag NPs in DNA and gets precipitated in the solution (supporting Figure S-3D). Similarly, when we exposed UV light for a short period (~ 30 min to 1 hour), Ag particles are formed undefined shapes which indicates that their growth is not complete (not shown here). So all the above control experiment gives an in- depth idea about the reaction parameters but for definitive understanding further control experiments is warranted.

Supporting Figure S-1. The EDS spectrum of Ag NPs on DNA chains. The spectrum consists of different peaks for Cu, C, Ag, and P.

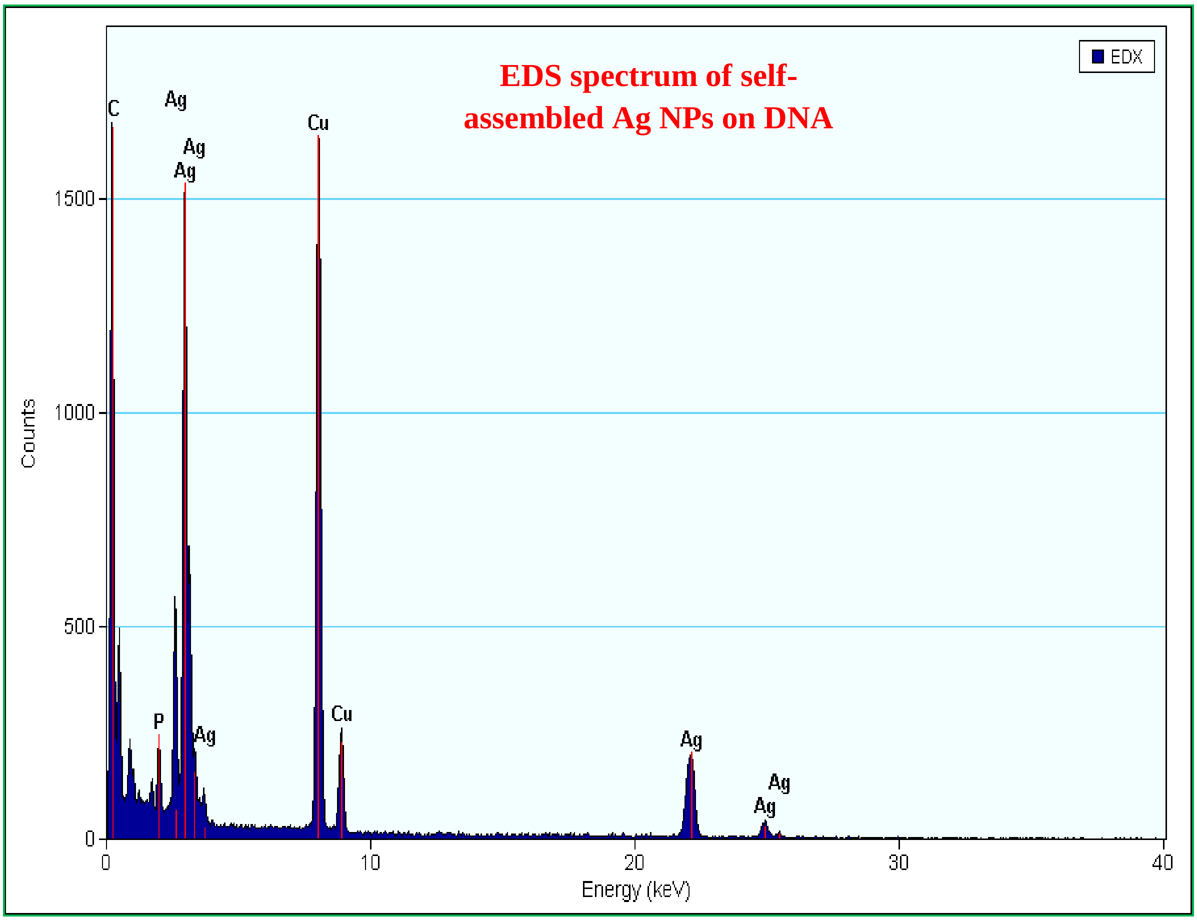


Figure S-1

Supporting Figure S-2. The XPS spectrum self-assembled Ag NPs on DNA chains. (A) shows the overall spectrum and (B) shows the spectrum of Ag (3d) region.

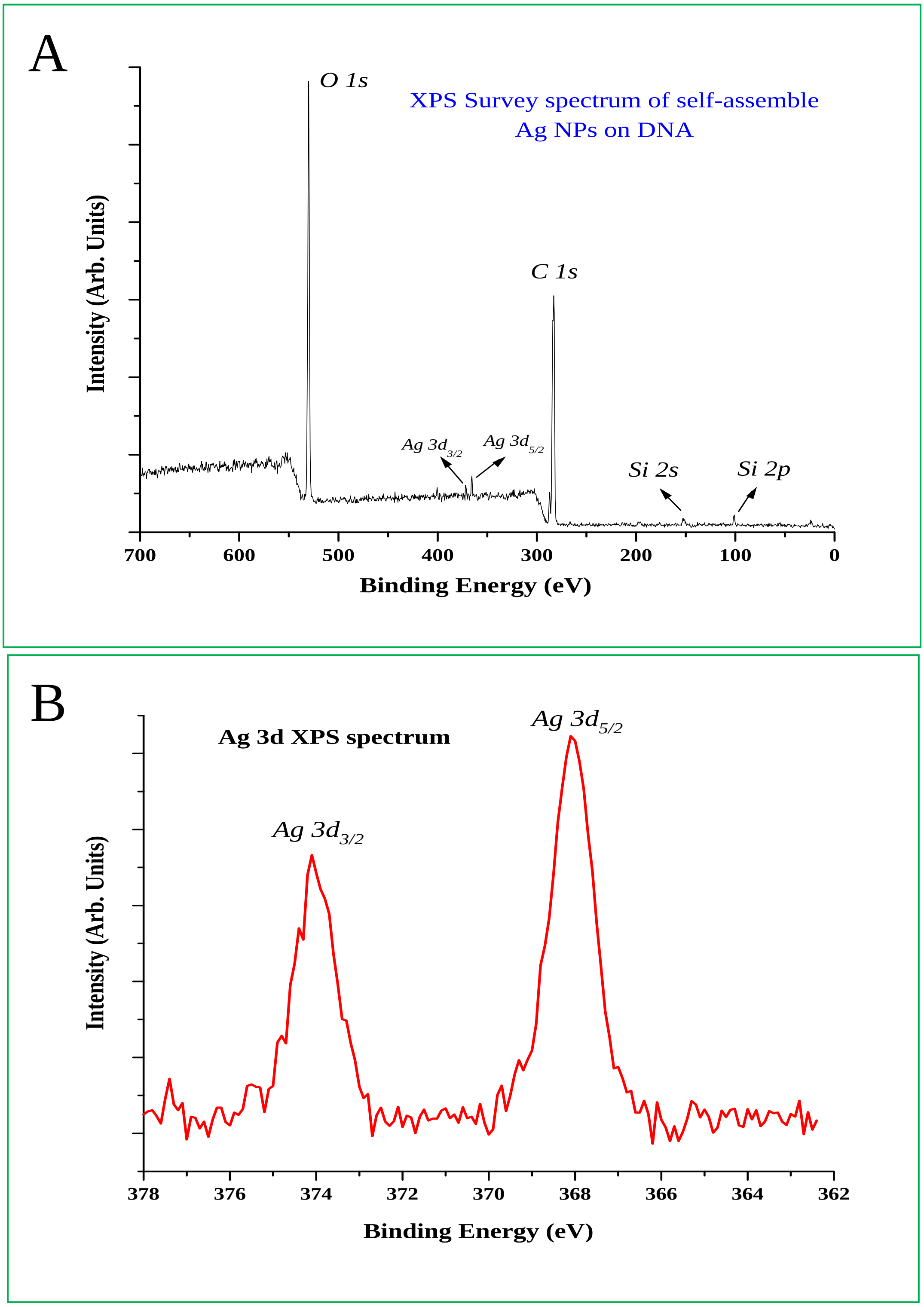


Figure S-2

Supporting Figure S-3. TEM images at various reaction conditions. (A) shows the image at high conc. of Ag(I) ions ~ 0.5 (M); (B) spherical Ag NPs when we used free DNA bases instead of polymeric DNA; (C) agglomerated Ag NPs on DNA at much higher DNA conc.; (D) image when we expose UV light for 8-10 hours.

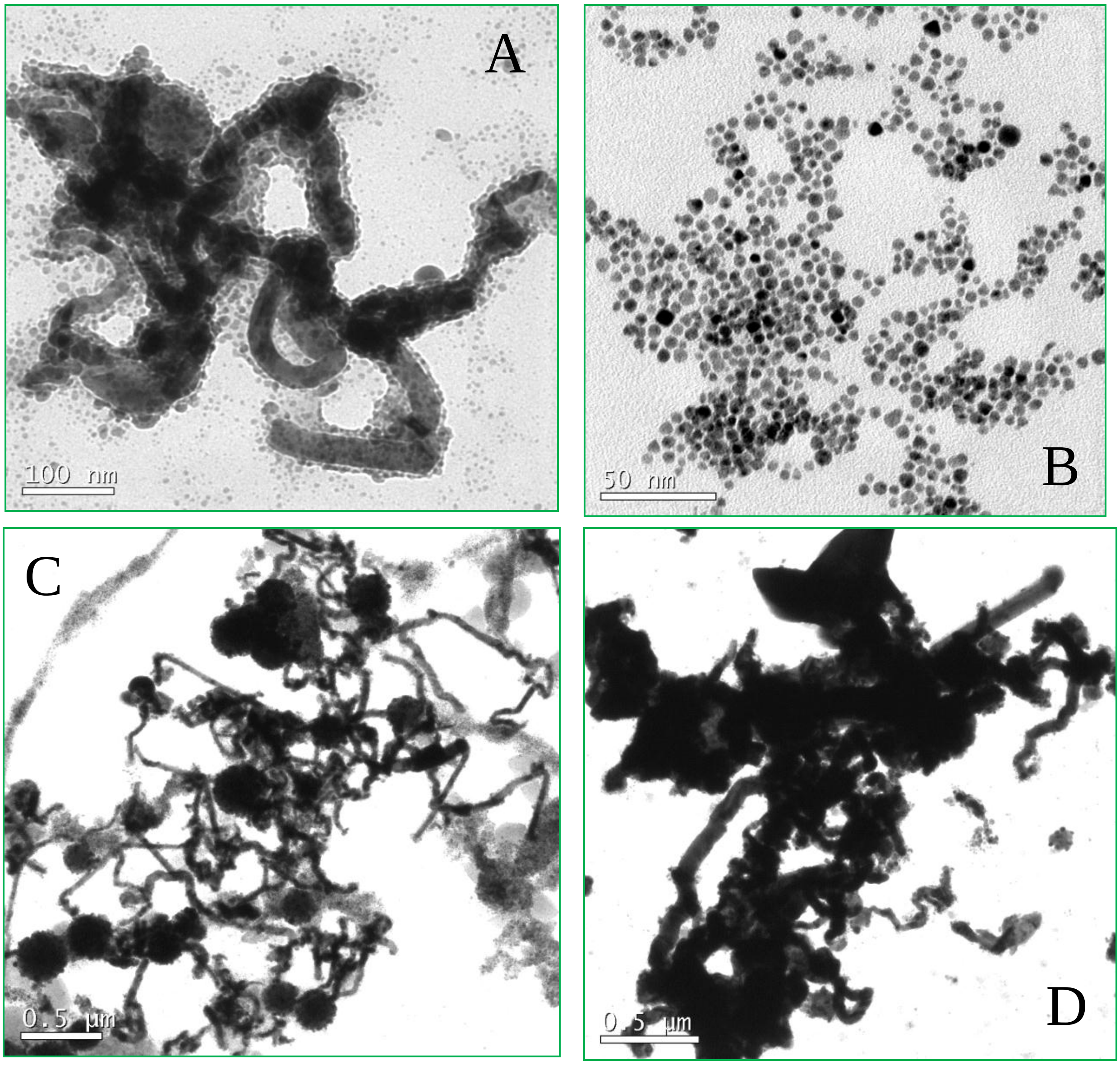


Figure S-3

Supporting Figure S-4. The ^{1}H NMR spectra of the final reduced product p-PDA.

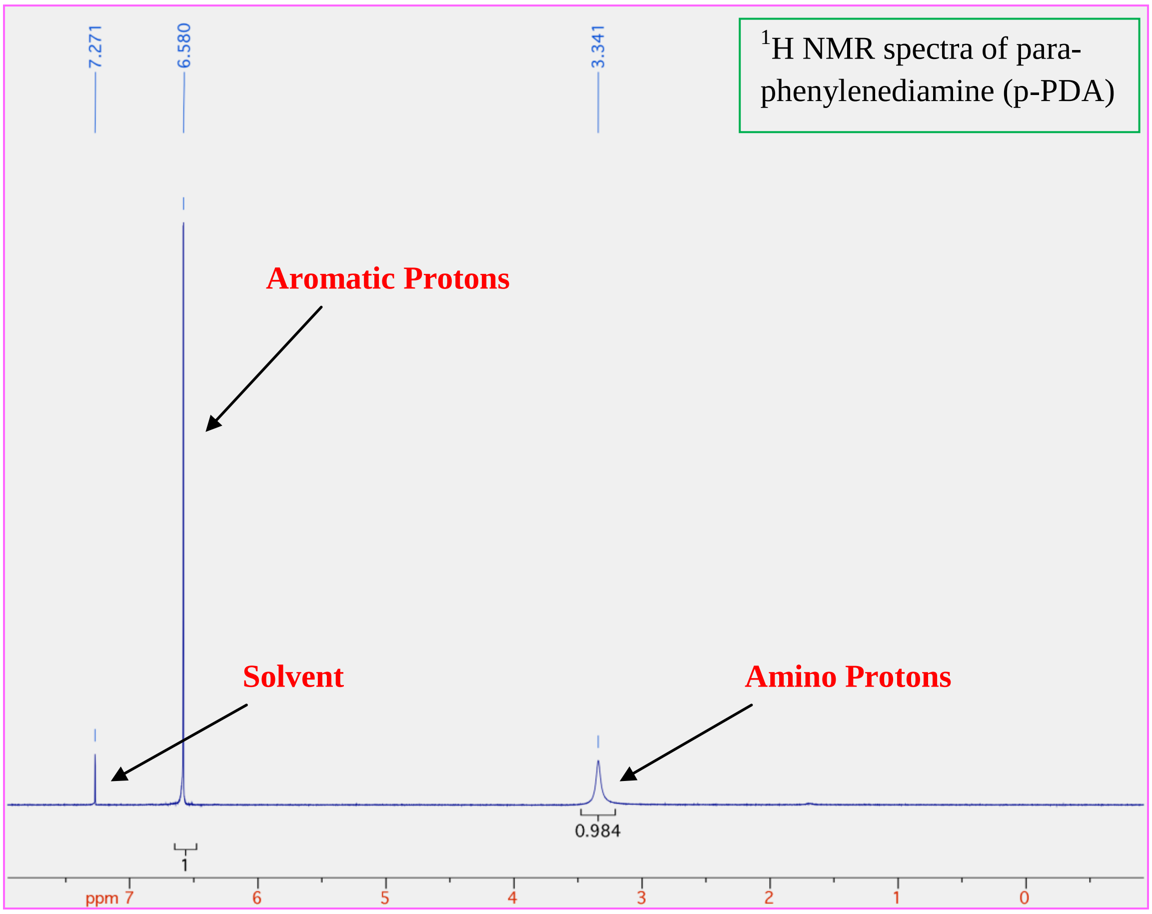


Figure S-4

Supporting Figure S-5. TEM image of the DNA-Ag NPs after used as catalyst for set 2.

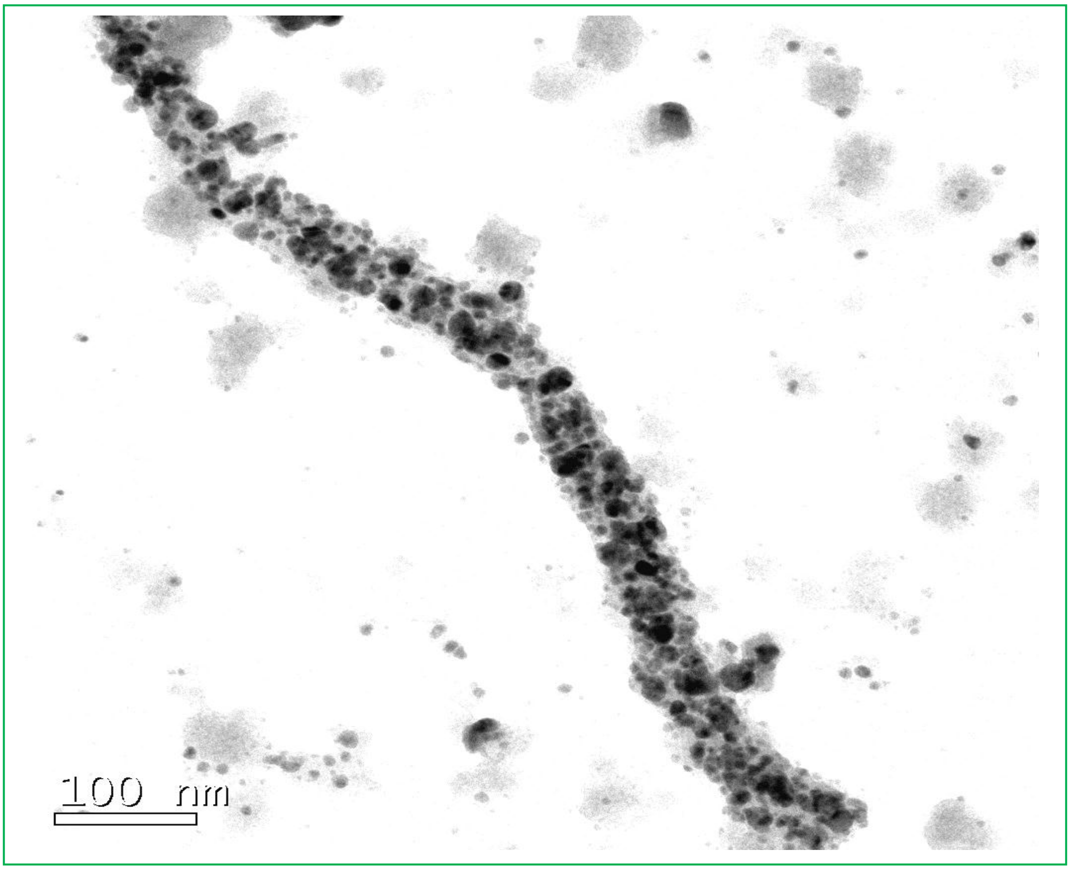
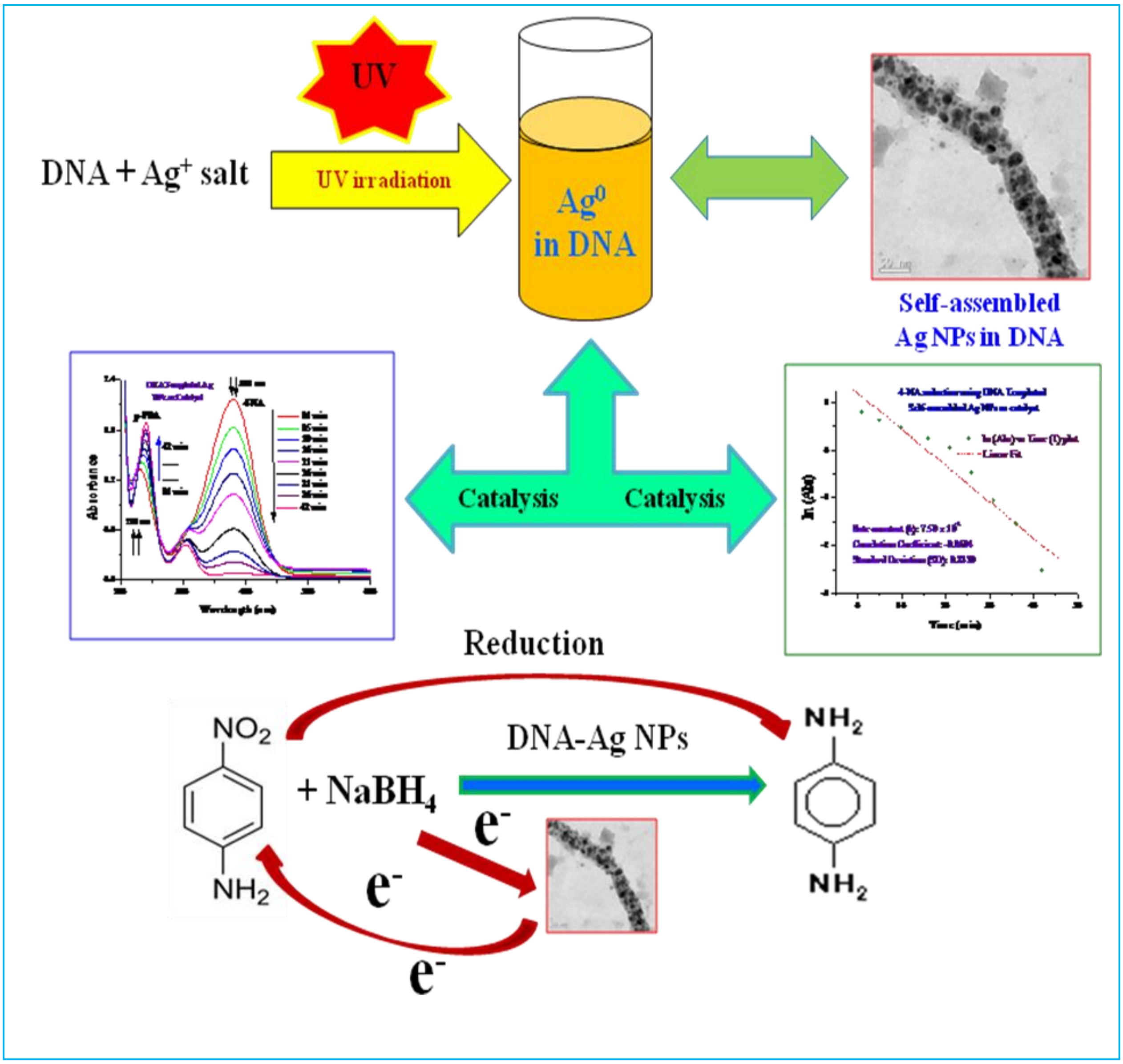


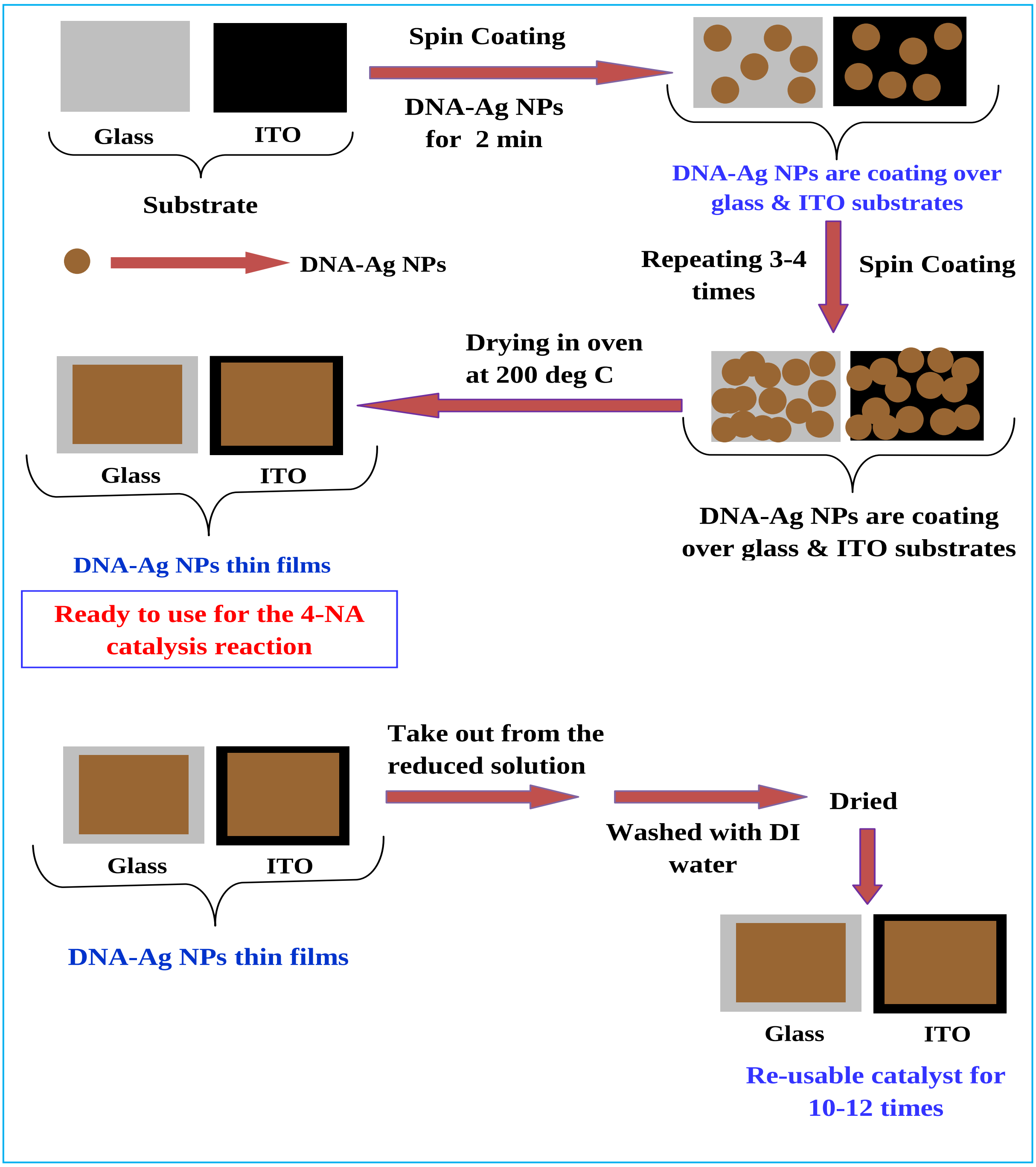
Figure S-5

Supporting Scheme S-1. The formation of self-assembled Ag NPs on DNA chains, their catalytic activity are shown schematically in scheme S-1.



Scheme S-1

Supporting Scheme S-2. The schematic presentation for the preparation of DNA-Ag NPs thin films over glass & ITO substrate for re-usability of the catalyst.



Scheme S-2