

Supporting information

Electrochemical Detection of Azidothymidine on Modified Probes based on Chitosan Stabilised Silver Nanoparticles Hybrid Material

Preeti Tiwari, Ashish Kumar and Rajiv Prakash*

School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi-221005, India.

Tel.: +91 9935033011, Fax: +91 542-2368707

*Corresponding Author: rprakash.mst@iitbhu.ac.in

[A] Catalytic effect of Ch@Ag NPs/GCE:

The catalytic effect of Ch@Ag NPs/GCE is compared with commercial Ag electrode towards AZT reduction as shown in figure S1. In this experiment, change in reduction current (Δi) is calculated for two different concentrations of AZT by performing CV at fixed scan rate for both the electrodes. We observed $\Delta i=1.44 \mu\text{A}$ for commercial Ag and $\Delta i=2.24 \mu\text{A}$ for Ch@Ag NPs/GCE, indicating better catalytic effect of Ch@Ag NPs/GCE. This catalytic effect is due to coordination of AZT with modified electrode and large energetic surface of Ag NPs.

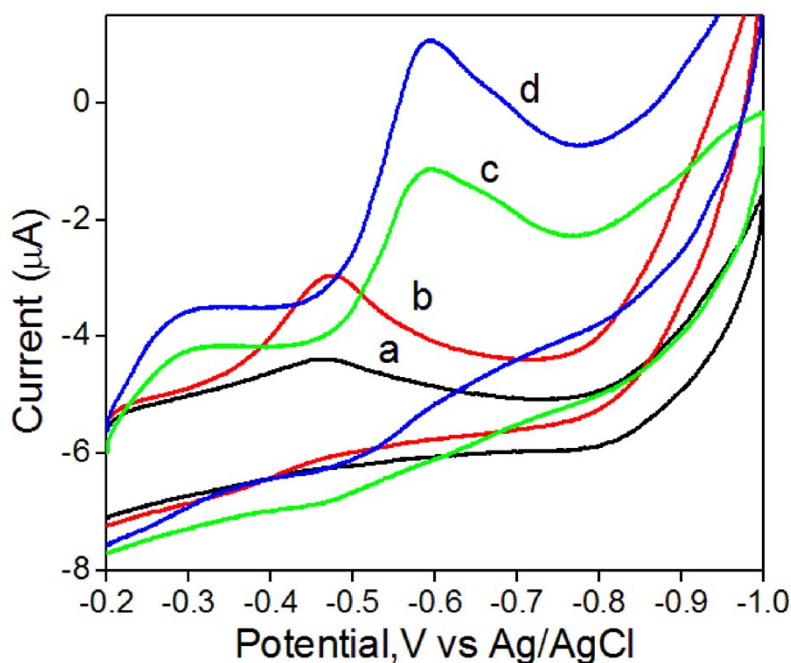


Figure S1: CV of 295 μM and 439 μM AZT over commercial Ag electrode (a & b) and Ch@Ag NPs/GCE (c & d) at scan rate 50 mV/s.

[B] Time dependent CV of AZT:

The reliability of as-modified Ch@Ag NPs/GCE electrode is checked with respect to time interval at scan rate of 50 mV/s as shown in figure S2. In this technique CV of fixed concentration of AZT reduction is performed at constant scan rate for several cycles (as shown in figure S2-a) and then again scanned after a time 10, 15, 20 minute (as shown in figure S2-b to figure S1-d). We observed that our modified electrode exhibits constant peak voltage and current initially for more than 10 cycles as shown by overlapped thick green colour curve. However, reduction current goes on decreasing gradually at constant reduction potential whenever scanning is again started after 10, 15 and 20 minutes. It means that the active sites of modified electrode are blocking/ poisoning by AZT.

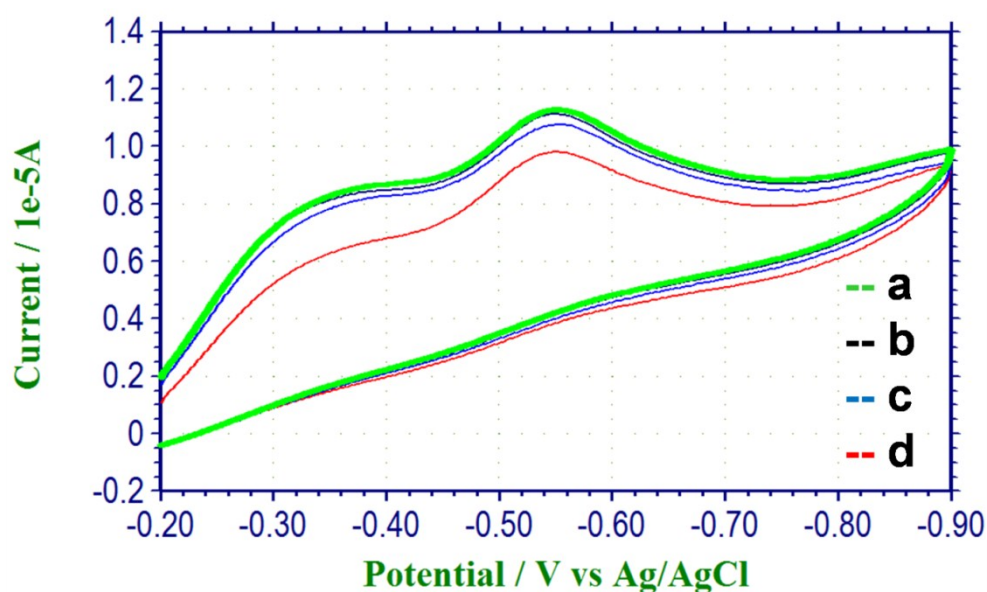


Figure S2: CV of 100 μ M AZT over Ch@Ag NPs/GCE at scan rate 50 mV/s.

[C] AZT detection using Ch@Ag NPs by DPV

Similar to CV results, we again observed successive increase in reduction peak current on serial addition of AZT in PBS (pH=7.6). But the stage of saturation of Ch@Ag NPs/GCE is observed herein after eleventh addition of AZT. This observation can be better visualized in corresponding calibration plot of DPV response as shown in figure S3-II.

The LOD of as-prepared Ch@Ag NPs/GCE is calculated by DPV as 1 μM and sensitivity 0.022 $\mu\text{A}/\mu\text{M}$ in PBS at S/N: 3.

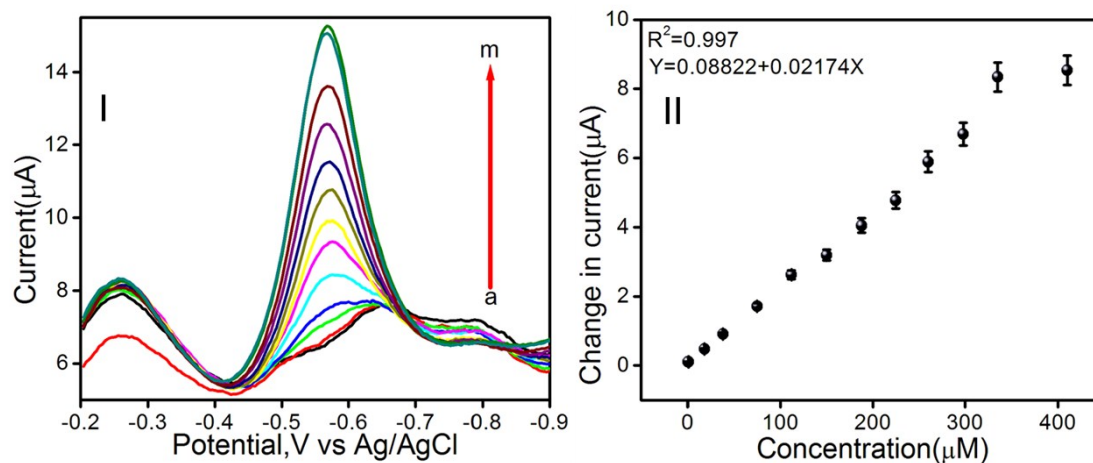


Figure S3: (I) DPV response of Ch@Ag NPs/GCE in PBS at pH=7.6 after serial addition of AZT from 1 μM to 410 μM concentration (a-m; a=blank current, b=1 μM , c=18 μM , d=38 μM , e=75 μM , f=112 μM , g=150 μM , h=188 μM , i=225 μM , j=260 μM , k=298 μM , l=335 μM , m=410 μM) and (II) corresponding calibration plot showing AZT concentration vs. change in reduction current with good correlation coefficient of 0.997.

[D] Mechanism of AZT electrocatalysis over Ch@Ag NPs: Role of Ag NPs

It is well known that nano particles have ability to agglomerate together due to its high surface energy. However stabilization of such particles using polymers is one of the choices with slight compensation in its surface energy recognised for its activity. In case of Ch@Ag NPs, the role of Ch is to stabilize Ag NPs and provides availability for the interaction with electron rich species like AZT. During AZT detection over Ch@Ag NPs/SPGE in presence of phosphate buffer (pH=7.6), it is expected that AZT adsorbs on Ag surface (as shown in figure S4) and azide group present in AZT exhibits electro-reduction to primary amine ($-\text{NH}_2$) on application of -0.60 V. After that this amino group undergoes protonation with available H^+ ions and leaving the surface of Ag NPs. Here this modification is showing large current and better detection limit in comparison to bare or without modified electrodes. This catalytic effect is explained based on coordination of AZT with modified electrode and large energetic surface of Ag NPs.

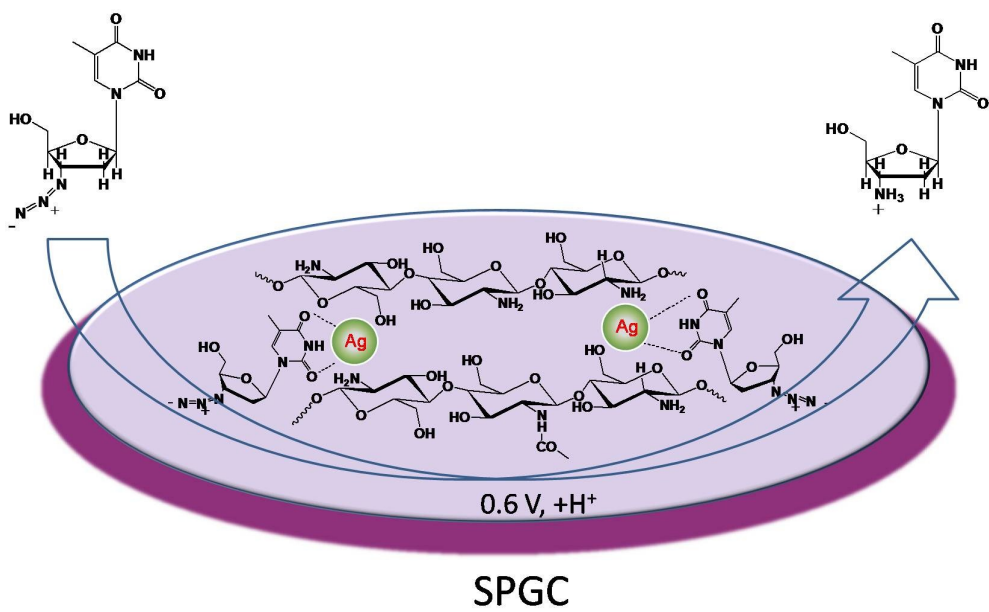


Figure S4: Proposed mechanism of AZT electro-catalysis over Ch@Ag NPs.