

## Supporting Information

### Size Dependent Quantized Double Layer Charging of Monolayer Protected Silver Nanoparticles

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## 1 Synthesis of MP-AgNPs:

Biphasic mixture of 25ml of 80 mM tetra butyl ammonium bromide in toluene and 10ml of 30 mM aqueous solution of AgNO<sub>3</sub> in a round bottom flask was stirred for ca. 20 min. Into this biphasic mixture, varying amounts of dodecane thiol (DDT) viz. 0.03, 0.05, 0.07, 0.1 and 0.12 ml were added for synthesis of MP-AgNPs *I, II, III, IV* and *V*, respectively. Immediately after DDT addition, 10ml of 0.4 M ice-cold NaBH<sub>4</sub> solution were added with continuous stirring. Color of the solution turned turbid to dark brown. Solution was allowed to stir for additional three hours and then organic layer separated. MP-AgNPs were extracted by adding 400ml of ethanol into 25ml of sol with constant stirring and kept in a deep freezer at 0 °C for 4 hours. Dark brown precipitate settled down at the bottom. The colorless supernatant was decanted and the precipitate redissolved in 25ml of toluene. The procedure was repeated thrice to remove excess of tetra butyl ammonium bromide. The extracted precipitate was then subjected to size selective separation.

## 2 Size Selective Separation:

Extracted precipitate was dissolved in 10ml of toluene and the dispersion centrifuged at 5000 rpm for 7 min to remove the agglomerated bigger particles. Ethanol was added drop wise to the supernatant till a separate layer was developed and kept without disturbance for one hour for complete separation of two layers. The upper layer was comparatively faint and slight amount of precipitate settled at bottom. Upper layer was slowly separated and discarded. Lower layer was separated and centrifuged at 5000 rpm for 5min. Same procedure was repeated. Final product was vacuum dried and used immediately for electrochemical study.

## Details of XRD Analysis:

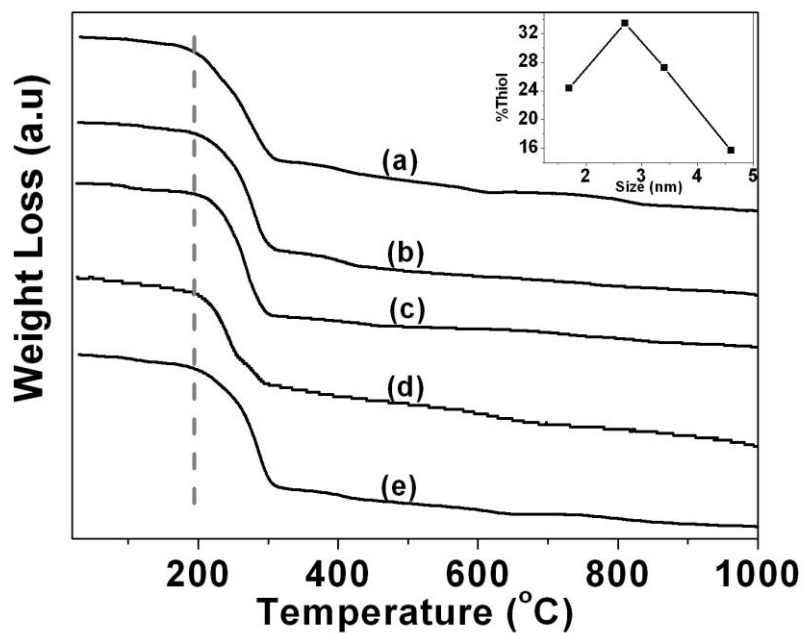
Table 1: Peak positions and phase analysis of XRD data. The JCPDS files 4-783, 19-1155, 22-472 and 40-909 have been used to fit the Ag, Ag<sub>2</sub>O, AgO and Ag<sub>2</sub>O<sub>3</sub> phases, respectively.

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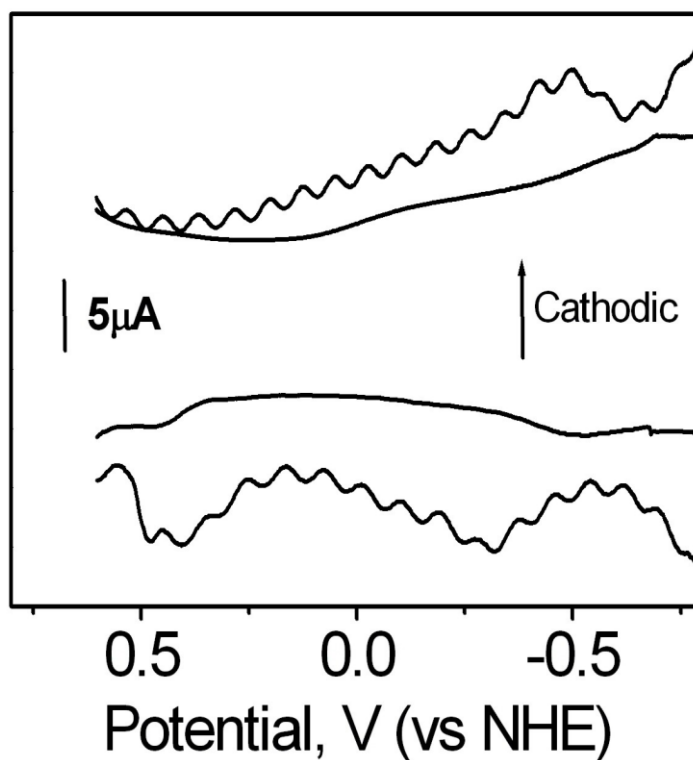
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No./ MP- AgNPs	I	II	III	IV	V
1		31.4 (AgO)			
2	32.4 (AgO)	32.4 (AgO)			
3	33.4 (AgO)				
4	34.4 (AgO)	34.4 (AgO)			
5	36.6 (Ag <sub>2</sub> O <sub>3</sub> )	36 (Ag <sub>2</sub> O <sub>3</sub> )			
6	38.2 (Ag)	38.2 (Ag)	38.2 (Ag)	38.2 (Ag)	38.2 (Ag)
7	38.8 (Ag <sub>2</sub> O)	38.8 (Ag <sub>2</sub> O)	38.8 (Ag <sub>2</sub> O)		
8	41.2 (Ag <sub>2</sub> O <sub>3</sub> )				
9	44.2 (Ag)	44.2 (Ag)	44.2 (Ag)	44.2 (Ag)	44.2 (Ag)
10	51.2 (Ag <sub>2</sub> O)	51.8 (Ag <sub>2</sub> O)			
11	56 (Ag <sub>2</sub> O)				
12	64.4 (Ag)	64.6 (Ag)	64.6 (Ag)	64.6 (Ag)	64.4 (Ag)
13	77.6 (Ag)	77.4 (Ag)	77.4 (Ag)	77.4 (Ag)	77.4 (Ag)

From XRD analysis, in addition to cubic phase of silver, AgO, Ag<sub>2</sub>O and Ag<sub>2</sub>O<sub>3</sub> phases of silver oxide were observed. However, from XPS analysis suggest AgO and Ag<sub>2</sub>O phase. An existence of Ag<sub>2</sub>O<sub>3</sub> phase of silver in XRD was attributed to the in situ transformation of silver due to the high energy source used in XRD than the XPS.



**Fig. S1:** Comparative TGA recorded in N<sub>2</sub> atmosphere for MP-AgNPs prepared at molar ratios of Ag<sup>+</sup>:DDT namely (a) 1:1.75, (b) 1:1.45, (c) 1:1, (d) 1:0.75 and (e) 1:0.44. These are labeled as **I**, **II**, **III**, **IV** and **V**, respectively. Inset shows variation in percent weight loss with size of MP-AgNPs.



**Fig. S2:** Comparison of differential pulse voltammograms for without (a) and with (b) MP-AgNPs. The multiple peaks with enhancement in current for (b) proves the electrochemical process is due to the MP-AgNPs.