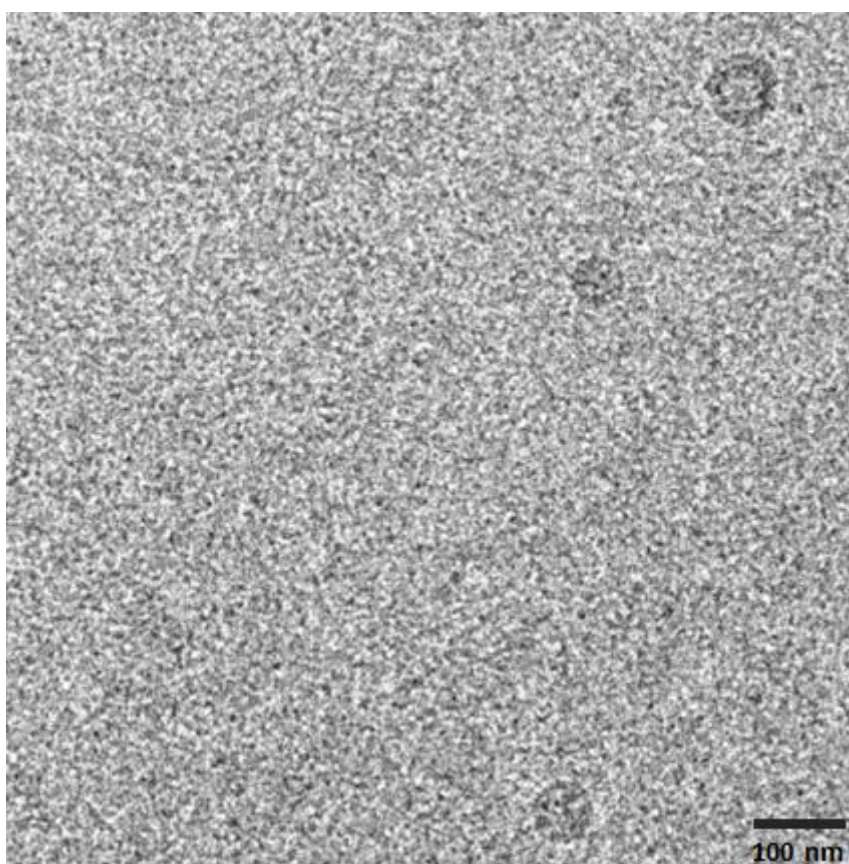


Electronic Supplementary Information (ESI)

For

**An amplification-free electrochemical detection of exosomal miRNA-21 in serum samples**

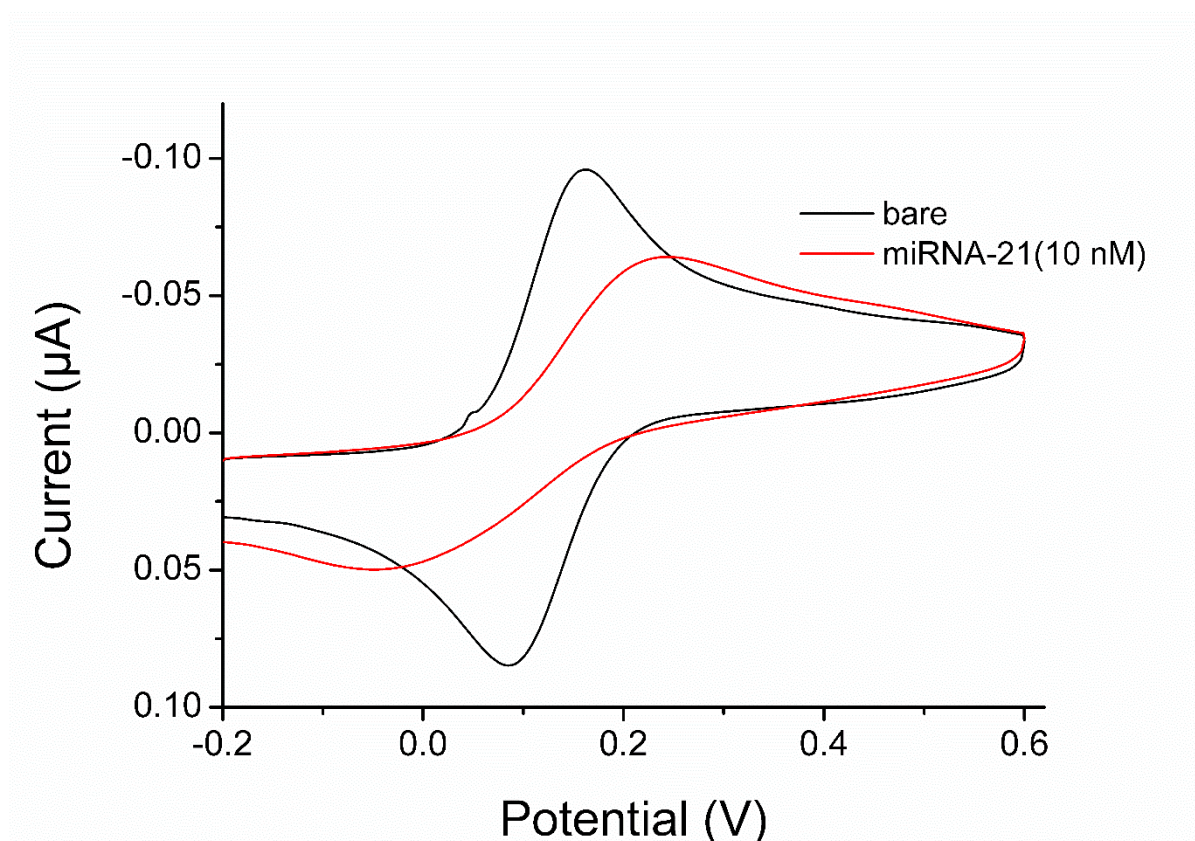
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**Fig. S1.** Cryo-TEM images of SW-48 cell derived exosomes confirming size and shape of vesicles.

## Characterization of miRNA-21 on gold surface by cyclic voltammetry (CV)

As our assay relies on the electron transfer reaction of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ , we characterized our sensor *via* performing cyclic voltammetry (CV) of unmodified (bare) and modified (subsequent absorption of target miRNA-21 on gold surface) SPE-Au. As can be seen below (Fig S2), a well-defined cathodic and anodic peaks for the  $[\text{Fe}(\text{CN})_6]^{3-}$  system were obtained at 95 mV and 185 mV (vs. Ag/AgCl) at bare SPE-Au, where upon adsorption of miRNA onto the electrode surface, current was reduced with less cathodic and anodic peak current and enhanced peak separation. These CV responses could be explained by the fact that due to the coulombic repulsion among the negatively charged  $[\text{Fe}(\text{CN})_6]^{3-}$  with negatively charged RNA strands,  $[\text{Fe}(\text{CN})_6]^{3-}$  molecules tend to repel out from the electrodes which hinders the electron transfer process, thereby reducing the current response and increasing the peak separation.



**Fig. S2.** Characterization of the gold screen printed electrodes Au-SPE (DRP-C250BT.) Cyclic voltammogram (CV) obtained at unmodified (bare) and target miRNA-21-modified electrode in 10 mM PBS containing 2.5 mM  $[\text{K}_3\text{Fe}(\text{CN})_6]$  and 2.5 mM  $[\text{K}_4\text{Fe}(\text{CN})_6]$ .