Supporting Information

Monitoring Hydrogen Evolution Reaction Catalyzed by MoS_2 Quantum Dots on a Single Nanoparticle Electrode

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Materials and methods

Reagents and Materials. Sulfuric acid (H_2SO_4) and Potassium Chloride (KCl) were obtained from Sigma-Aldrich Industrial Corporation. Silver nanoparticles (Ag NPs, capped with sodium citrate, 6.00 nM) with different sizes were purchased from nanoComposix company. All of the reagents were analytical grade and used without any purification. Ultra-pure water obtained from Milli-Q synthesis system was used to prepare stocking solution. 2H-phase MoS_2 QDs (10 nm) with negative charges were prepared according to the previous published paper.[1]

Fabrication and Characterization of Glass Nanopore. In short, glass capillary underwent ultrasound treatment in acetone and ultra-pure water solution separately for 30 min, and then dried under N_2 flow. The P-2000 laser puller (Sutter Instrument Co., Novato, CA) was employed to fabricate nanopore with ~80 nm diameter. The pulling program was set as follows: heat=650, filament=3, velocity=45, delay=170, pull=205. Zeiss Ultra plus scanning electron microscopy (SEM) was employed to characterize home- made nanopore, and the TEM (Transmission Electron Microscope) images and Energy Dispersive Spectroscopy (EDS) characterization were performed on JEM-2100f (JEOL Ltd.)

Electrochemical Experiments and Data Analysis. The mixture of MoS_2 QDs and 1.0 M H_2SO_4 solution was added to prepared nanopore using the micro-loader. The air at the tip of nanopore was removed by centrifuged at 5500 rpm/min for 6 min. 6 nM Ag NPs was diluted to 1.5 nM by 10.0 mM KCl solution and was added to the 2 mL centrifuged tube. The Ag/AgCl electrode embedded in the nanopore served as counter electrode and Ag/AgCl electrode embedded in the Ag NPs solution acted as working electrode. Axon 200B was employed to filter Data at 5 kHz. Sampling rate was controlled by DigiData 1440A converter and a PC running PClamp 10.4 (Axon Instrument, Forest City, CA) is 100 kHz. The raw data was analyzed by using our self-developed software.

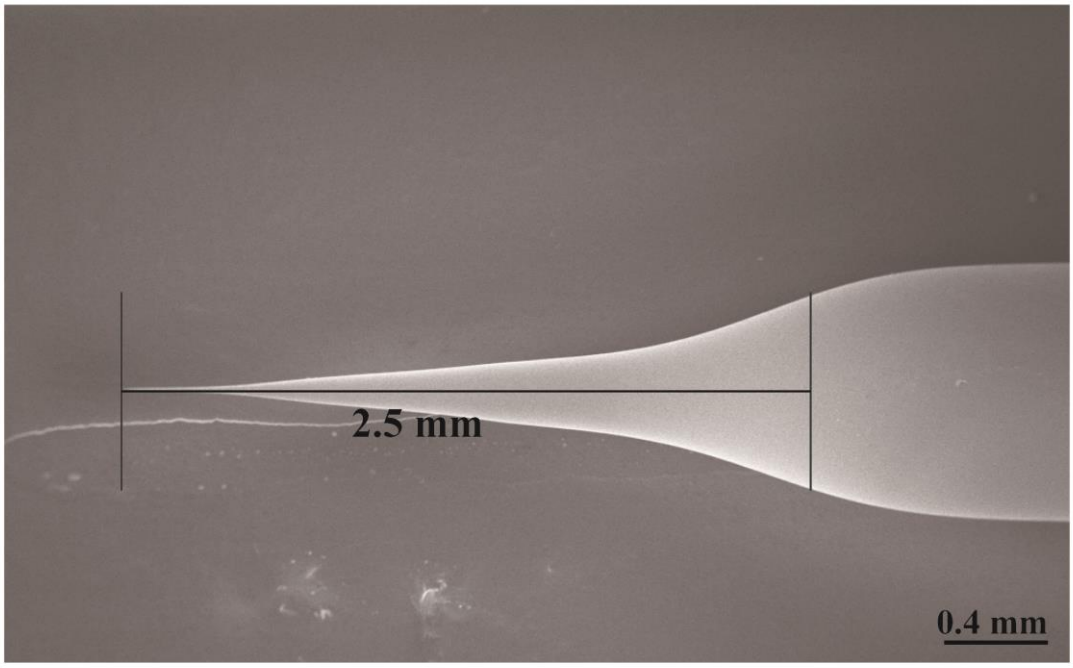

Figure S1. The side view of SEM characterization of prepared galss nanopore.

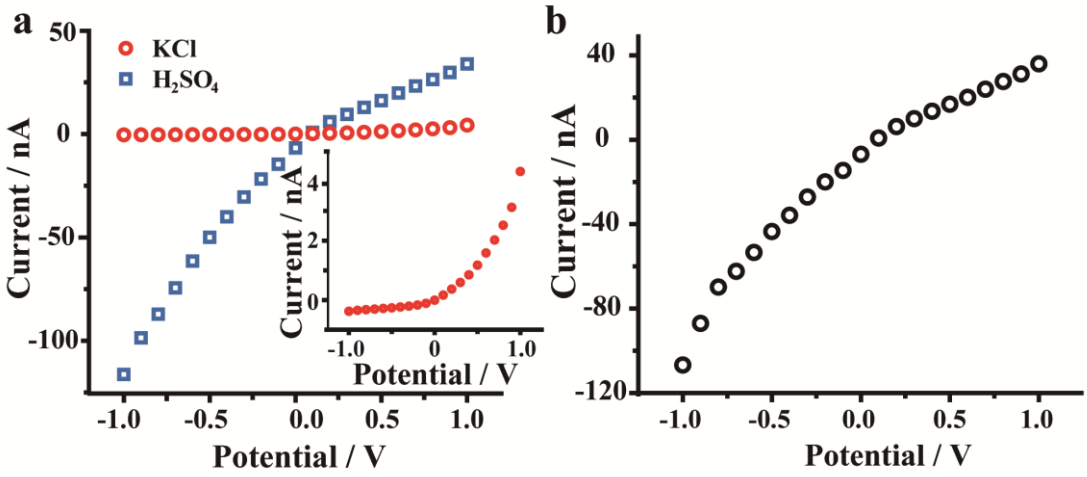

Figure S2. I-V response of bare nanopore with different solution inside the channel (red represents 10 mM KCl, blue represents 1.0 M H_2SO_4) the glass nanopore filled with KCl exhibits nonlinear I-V characteristic that is so-called current rectification (a), and I-V response of the glass nanopore after the experiment (b). (The Ag/AgCl electrode embedded in the nanopore served as counter electrode and Ag/AgCl electrode embedded in the Ag NPs solution acted as working electrode.)

In addition to the asymmetrical geometry of tip, the negative charges within the inner wall makes the nanopore present current rectification phenomenon when negative potential is applied inside the nanopore.[3] In the case of H_2SO_4, inner wall of glass nanopore turns to be positively charged, which contributes to an obviously reverse current rectification. It is worth noting that the rectification phenomenon still exists in the glass nanopore after the experiment, but the tendency of rectification phenomenon was weakened. We infer that the H_2SO_4 with high concentration flow out of the inner channel owing to the concentration gradience of electrolyte as the experiment progresses, and the concentration of H^+ decrease. Thus, besides electrical force and electroosmotic flow, concentration gradient of electrolyte probably is a factor driving MoS_2 QDs out of the inner channel.

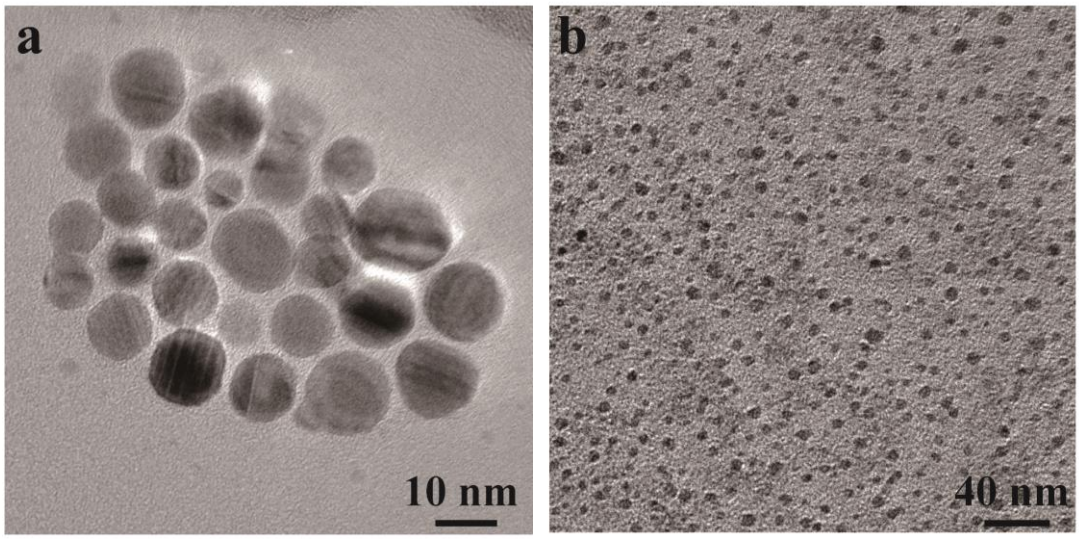

Figure S3. TEM images of Ag NPs (a) and MoS_2 QDs (b). According to the published paper, the prepared MoS_2 QDs are negatively charged.[1]

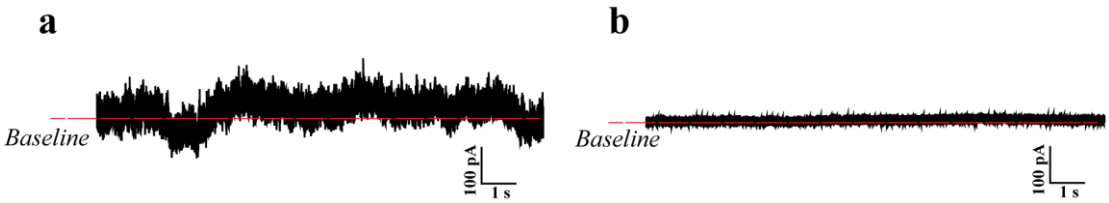

Figure S4. Ionic current traces in the absence of Ag NPs (a) and MoS_2 QDs (b). (Ag/AgCl electrode embedded in the nanopore served as counter electrode and Ag/AgCl electrode embedded in the Ag NPs solution acted as working electrode, a +950 mV biased potential was applied.)

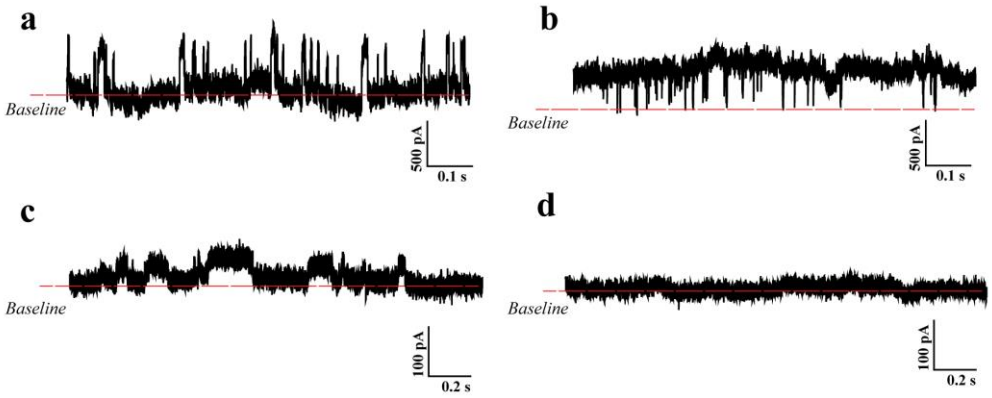

Figure S5. Ionic current traces of nanopore (the mixture of 1 M H_2SO_4, MoS_2 QDs, and 1.5 nM Ag NPs was added in the inner channel, 10 mM KCl was placed outside the nanopore) under +950 biased potential (a and b), +900 biased potential (c), and +800 biased potential (d).

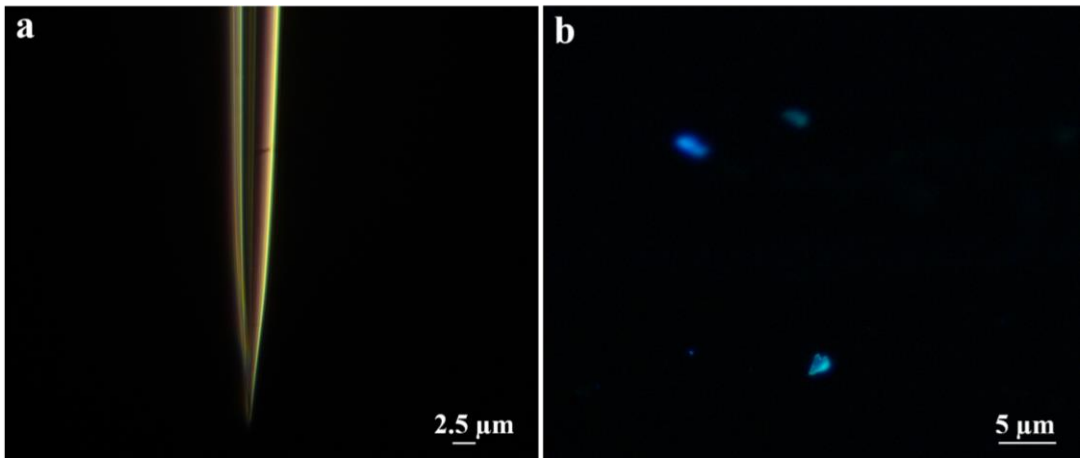

Figure S6. Dark-field image (a) and fluorescence image (b) of glass nanopore filled with MoS_2 QDs in 1.0 M H_2SO_4.

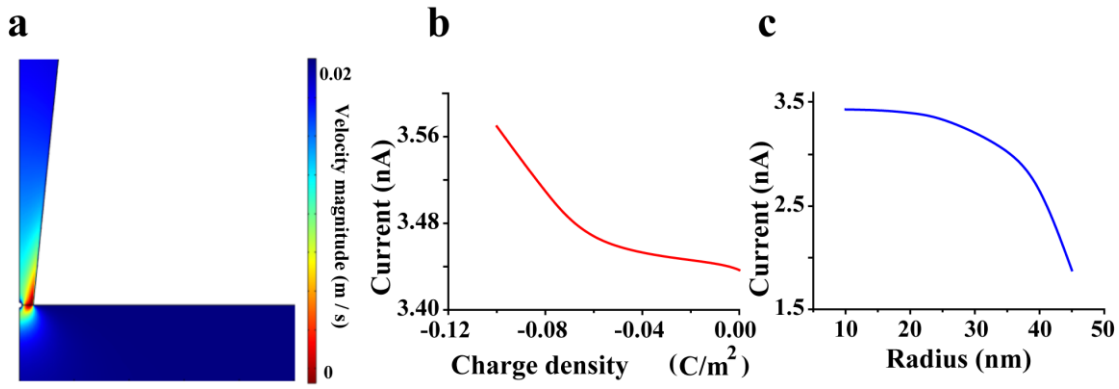

Figure S7. The FEM simulation of velocity distribution (the velocity increases near the tip and the direction of electroosmotic flow is from inside to outside of the nanopore) (a), the relationship between the charge density and ionic current (b) (We assume the diameter of nanocomposite is 20 nm and change the surface charge from -0.1 to 0.0 C/m^2.), the relationship between the radius of the nanocomposite and ionic current (In the simulation, the surface charge is set as -0.01 C/m^2 and the volume of nanocomposite increases from 20 nm to 80 nm owing to the generation of H_2 bubbles.) (c) along the position of the nanopore.

At beginning, a large number of the first type of signals exist. We infer that concentration difference of electrolyte between inside and outside the nanopore also is a force to drive the nanocomposites out of the orifice. It is impossible for nanocomposite to perform HER in a short residence time. As experiment processes, the concentration difference of electrolyte is weaken, which enable nanocomposite to attach on the orifice for a relatively long time, and HER catalyzed by MoS_2 QDs will happened on the single nanoparticle electrode. Consequently, plenty of the second type of signals pour out.

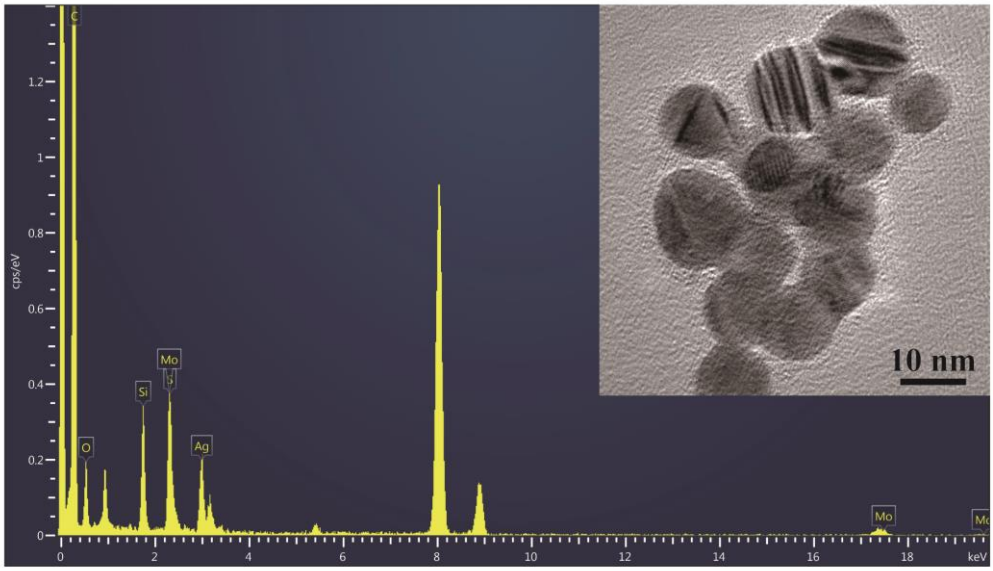

Figure S8. EDS characterization of composite of Ag NPs and MoS_2 QDs and the insert is the TEM characterization of the same composite.

We mixed Ag NPs and MoS_2 QDs in advance. The EDS result indicates the existence of Ag NPs and MoS_2 QDs in the composite, which also proves the bonding effect.

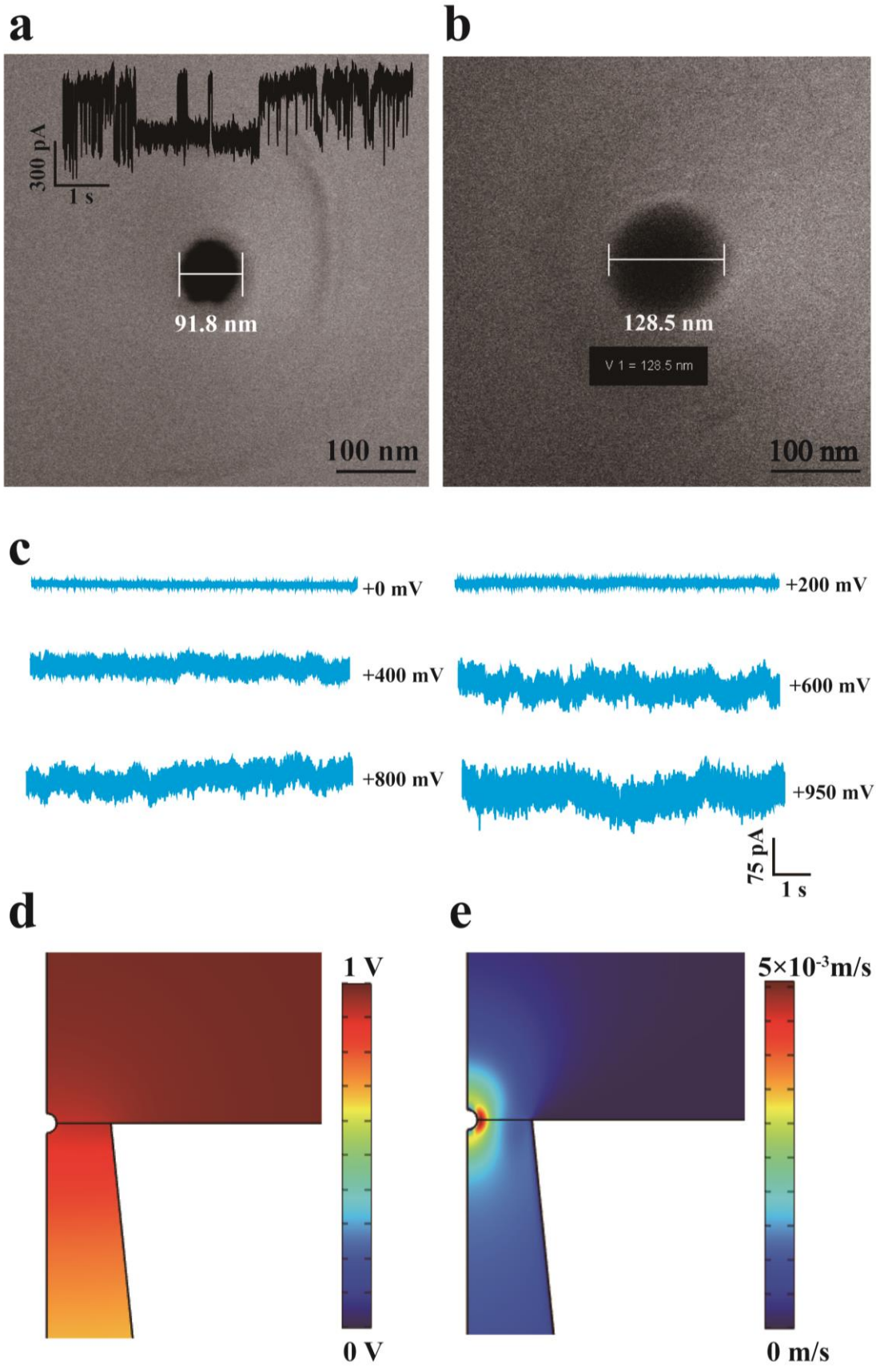

Figure S9. The vertical view of SEM characterization of prepared nanopore (a, b), the raw ionic current traces for glass nanopore shown in figure S 9b under a biased potential ranging from 0 mV to +950 mV,

the glass nanopore is filled with 1.0 M H_2SO_4 and MoS_2 QDs, then, the glass nanopore was inserted into the 6 nM Ag NPs diluted by 10 mM KCl solution (c), FEM simulation for biased potential drop long the position (d), and velocity distribution (e) of the glass nanopore with 128.5 nm pore size.

The glass nanopore near 90.0 nm is a candidate to conduct our experiment. For glass nanopore with large pore size, any signals were not monitored under a biased potential ranging from 0 mV to +950 mV, it is always believed that analytical method based on the nanopore lacks sufficient sensitivity when the volumes of analytes are much smaller than the diameter of the nanopore. [2] In addition, electrostatic interaction between surface charge of glass nanopore and ionic species will have effect on the ion transport process when the size of orifice is comparable to the diffuse double-layer (DDL). If the size of nanopore is large, electrostatic interaction would not affect the ion transport process.[3] Last but not the least, we can see from the Figure S9d and Figure S9e, the electric force and electroosmotic flow confined near the orifice are too weak to drive the the MoS_2 QDs out of the glass nanopore. Therefore, no signals appear when glass nanopore with larger orifice is employed.

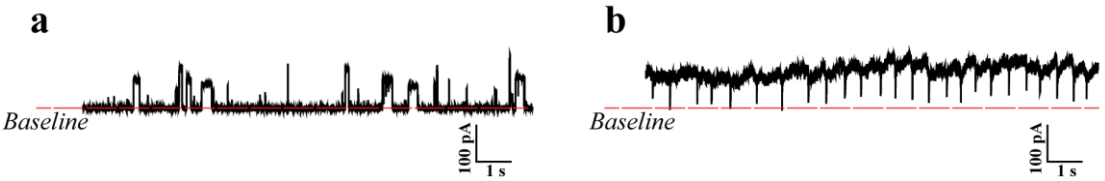

Figure S10. Increase in (a) and decrease on (b) the ionic current traces in the absence of H_2SO_4 (Iinner channel is filled with MoS_2 QDs in 10 mM KCl, 6 nM Ag NPs diluted by 10 mM KCl were placed outside the nanopore, the Ag/AgCl electrode embedded in the nanopore served as counter electrode and Ag/AgCl electrode embedded in the Ag NPs solution acted as working electrode, a +950 mV biased potential was applied.)

FEM simulation process for glass nanopore

The COMSOL Multiphysics software (COMSOL Inc., Burlington, MA, USA) is employed for the FEM simulation. The geometry of the model glass nanopore is set according to SEM images shown in Figure 1b and S1, which are r = 45 nm, $l_{nanopore}$= 25 μm, Θ = 6°. The surface charge on the glass nanopore and nanosphere are 0.01 C/m^2 and -0.01 C/m^2, respectively.[4,5] The diameter of nanocomposite of MoS_2 and Ag NPs is 20 nm, the reason of which is the sizes of MoS_2 and Ag NPs both are 10 nm. To simplify the simulation process, the system is regarded to be steady-state and all of processes happen in a 2D non-axisymmetric geometry. In addition, the nanocomposite locates at the tip of glass nanopore. Although the difference of electrolyte between *trans* and *cis* exists in our system owing to the presence of 1M H_2SO_4, we regard the inner wall of glass nanopore is positive charged wall, and, thus, the electrolytes inside and outside the nanopore could be set as 10 mM KCl.

The Nernst-Planck (NP) equation is used to compute the ionic flow, which includes the diffusion, migration, and convection terms.

$$\boldsymbol{J}_i = -D_i \nabla c_i - (z_i F/RT) D_i c_i \nabla \boldsymbol{\Phi} + c_i \boldsymbol{u} \qquad (1)$$

As mentioned in equation (1), $\boldsymbol{J}_i$ represents ion flow vector, F is Faraday's constant, T is the absolute temperature, $\boldsymbol{\Phi}$ is the potential, $\boldsymbol{u}$ is the position-dependent fluid. D_i, C_i, and Z_i represent the diffusion coefficient, the concentration, and the charge of species in the solution, respectively.

As for the relationship between the ion concentration and electric potential, Poisson equation is utilized to illustrate it.

$$\nabla^2 \boldsymbol{\Phi} = -F/\epsilon \sum_i z_i c_i \qquad (2)$$

Here, ϵ represents the dielectric constant of the medium.

In the stimulation, Navier-Sotkes equation is made use of to represent the flow distribution in the glass nanopore

$$\boldsymbol{u} \nabla \boldsymbol{u} = 1/\rho \, (-\nabla p + \eta \nabla^2 \boldsymbol{u} - F \, (\sum_i \sigma_i c_i) \nabla \boldsymbol{\Phi}) \qquad (3)$$

Therein, ρ and η are the density and viscosity of the fluid, respectively, and p is the pressure. p sets as 1×10^{-3} kg/m^3 and η sets as 1×10^{-3} Pa· s.

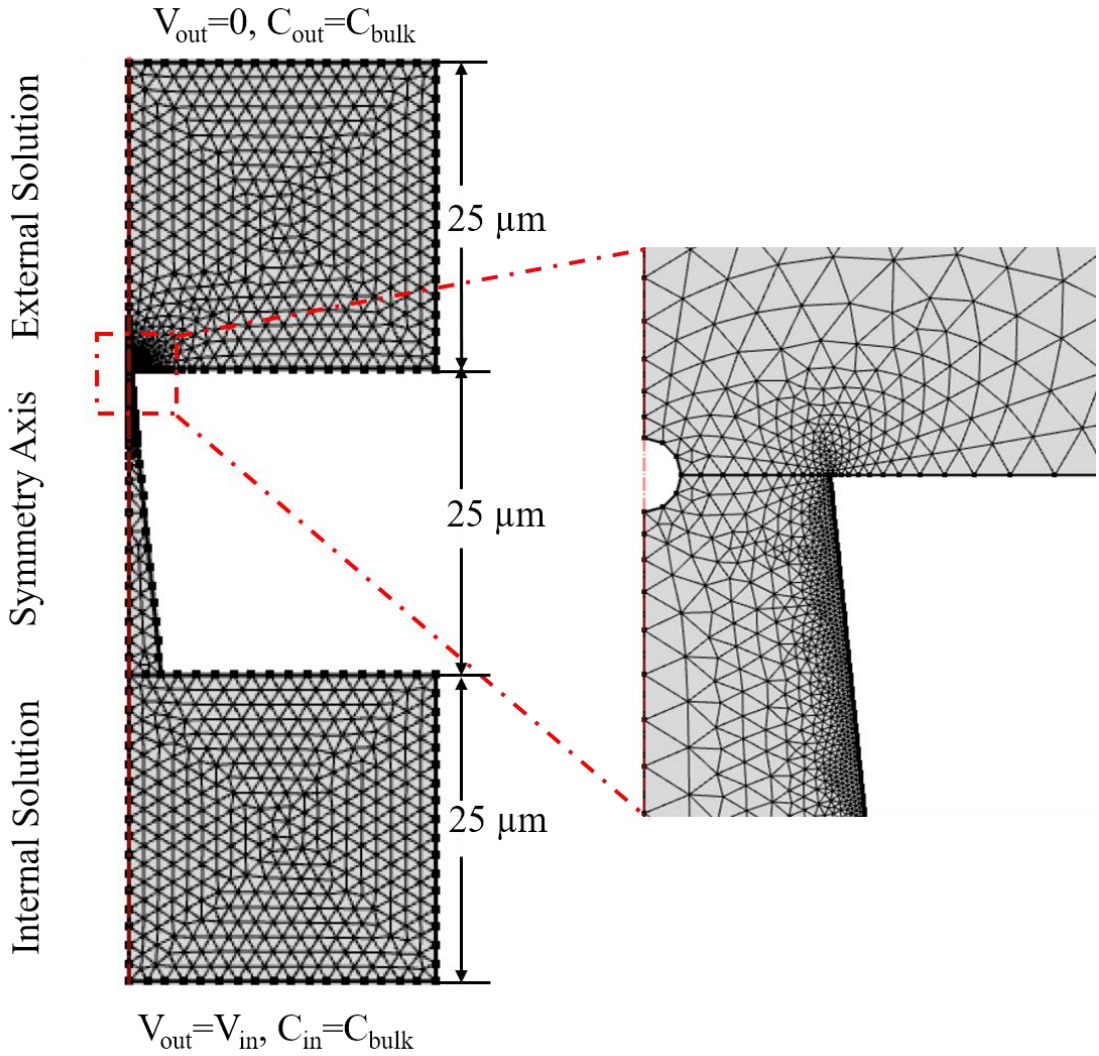

Figure S11. The geometry of nanopore, the boundary setting, and the mesh in the FEM simulation, the nanocomposite of MoS_2, Ag NPs, and H_2 nanobubble locates at the tip of nanopore, the electrolyte parameters for the ionic species were as (D_{k^+} = 1.957 × 10^{-9} m^2 /s, c_{K^+} = 10 mM, D_{Cl^-} = 2.032 × 10-9 m^2 /s, c_{Cl^-} = 10 mM at T = 298 K).

Reference

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