**Methodology**

**preparation of ZnO nanoparticles :**

Zinc acetate- 2-hydrate (ZAD) Zn(CH3COO)2.2H2O and Diethanolamine (DEA) NH(CH2CH2OH)2 -as stabilizer – were chosen as starting materials and ethanolic solution was used as a solvent. The concentration of ZAD and DEA were chosen to be 0.1 M and the precursor solution has been mixed thoroughly using magnetic stirrer at 60 ˚C for 30 min. the resultant solution was left for aging for 24 hours to obtain a collided, homogeneous solution. The homogenous solution was coating on the substrate consisting of glass plate with conductive thin film of indium-doped tin oxide (SnO2: In ITO, sheet resistance about 20 Ω cm-2) on one side using the dimensions of 1.0 × 1.5 cm2 which cleaned using the following solution respectively acetone[C3H6O],2-propanol and for 15 min for each solution separately in sonication bath (Ultrasonic LC 30H ELMA).Throughout the sonication treatment, DI-water(18.2 MΩ) was used to rinse the substrate after each solution. Then the ITO substrates were left in air for drying. The pre-cleaning of substrate is considered one of the most important keys of preparing ZnO nanoparticles seed layers with high quality since this procedure helps to get rid the residual organic solvent and undesired oxide layers that can cause random growth of seed layers.

The spin coating was conducted by using approximately 100 µL of the obtained colloid solution by using the spin coater (Midas System, SPIN-1200D) at 3000 rpm for 40 second to get one thin seed layer of ZnO nanoparticles which was exposed to the heat treatment using (Hot Plate Stirrer Digital Advanced, STERIPLAN, DURAN) for 15 min. between each successive spin coating steps for solvent evaporation and organic compounds removal. This procedure was repeated three recycles to provide three uniform dispersion layers of ZnO nanoparticles seed layers on ITO substrate. Afterward, the samples were annealed at 350 ◦C in order to obtain a well-crystallized film and the final decomposition of organic by- products varying for one hour with heating rate of 2˚C per min.



Figure 1 : schematic diagram of preparation of ZnO NPs/ZnO NRs/ITO

**Preparation of ZnO nanorods via hydrothermal method**

The hydrothermal growth solution (nutrient solution) composed of equimolar of zinc nitrate Zn(NO3)2.6H2O and hexamethylenetetramine (HMTA, C6H12N4) at the concentration 0.04 M and the pH value 6.5. The coated ZnO seed layers on ITO substrates were wet upside down facing the wall of sealable glass vials containing approximately 20 ml of the prepared growth aqueous solution. It was loaded into pre-heated silicon oil bath at110ºCfor four hours. It should be mentioned that the growth solution during the hydrothermal process was not refreshed. The obtained ZnO NRs were rinsed continuously after completing the hydrothermal process using (DI H2O) to remove the residual precursor, amino complexes, and avoid the accumulation of ZnO NRs caused by the water surface tension.

**Preparation of Bi2S3/ZnO NRAs nanocomposites via successive ionic layer and adsorption (SILAR ) method**

The preparation of Bi2S3/ZnO NRAs photoanode was done via successive ionic layer adsorption and reaction (SILAR). In this method, the pre-coated hydrothermally grown ZnO NRAs on ITO glass substrate is subjected to SlLAR adsorption steps. In the first step, the coated ZnO thin film was immersed in the cationic solution, which contains 3mM of bismuth nitrate Bi(NO3)3. 5H2O (sigma Aldrich,99%) for 60 sec. In the second step, coated ZnO NRs from the first step was dipped in deionized water (DIW) for 60 sec. to remove un-adsorbed (loosely bond). In the third step the resultant was dipped in the anionic solution consists of 30 mM of Na2S (FLAKE) for 60 sec followed by DIW rinsing for 60 sec. These four steps were considered as one cycle. The photoanodes were kept at ambient conditions to be used in PEC application. The coating process by SILAR method is shown schematically in Figure 2 .Meanwhile Equation illustrates the formation of Bi2S3 from SILAR method.



Figure 2 : Diagram of preparation Bi2S3/ZnO NRAs nanoparticles via SILAR method of cationic and ionic precursor ( =Bi3+ and = S2-)

$Bi^{3+}+S^{2-}→ Bi\_{2}S\_{3}$ ( 1 )