ELECTROCHEMICAL ELECTRODEPOSITION OF GALLIUM(III) AND INDIUM(III) IN AN IONIC LIQUID

Jie Zhang[1], Maozhong An[2], Wen Luo[1], Andreas Züttel[1]

[1]Laboratory of Materials for Renewable Energy (LMER), Institute of Chemical Sciences and Engineering (ISIC) Basic Science Faculty (SB), École polytechnique fédérale de Lausanne (EPFL) Valais/Wallis, Energypolis, Rue de l'Industrie 17, CP 440, CH-1951 Sion, Switzerland, email: jie.zhang@epfl.ch

[2]School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, China

Abstract

Electrodeposition is a simple, low cost, and easily industrialized method to prepare the gallium, indium, and their alloys, which show versatile applications in renewable energy related areas, for example CO_2 reduction [1-2] (Fig.1.). Gallium electrodeposition from aqueous solution is difficult to control because of the high overpotential and simultaneous hydrogen evolution reaction. The properties of large electrochemical window and almost non-volatility give ionic liquid great advantage for electrodepositing gallium-like metals. Therefore, We studied the electrodeposition behaviour of Ga(III) and In(III) ions in 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][TfO]) ionic liquid in order to lay the foundation for the preparation of gallium and indium related materials by electrodeposition.
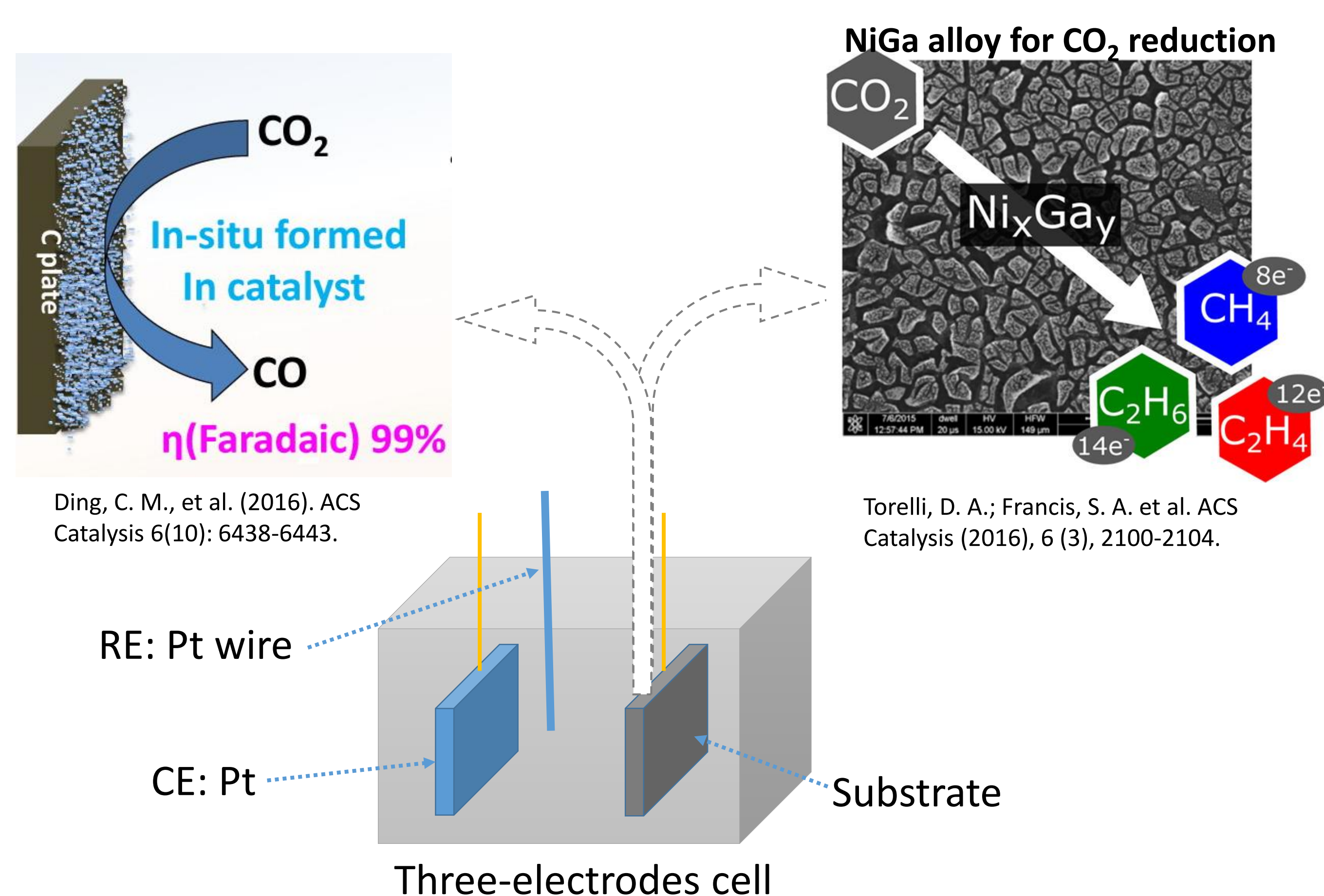
Fig. 1. Schematics of electrodeposition of gallium and indium related alloys for solar cell and CO_2 reduction applications

Electrochemical Behavior of Ga(III) Ions

Cyclic voltammetry study shows that both temperature and electrode material have a great impact on the electroreduction kinetics of Ga^{3+} ions in [BMIM][TfO] ionic liquid (Fig.2.). We obtained the diffusion coefficients (1.15×10^{-8} cm^2 s^{-1}) of Ga(III) ions and diffusion activation energy (47.11 KJ/mol) using three methods involving rotating disk electrode(RDE) (Fig.3.). The initial electrocrystallization of gallium on glassy carbon electrode (GCE) involves an instantaneous nucleation process, which is demonstrated by using non-linear fitting theoretical function to the current transients and SEM images of the initial deposition stage on GCE (Fig.4.). SEM images reveal that gallium deposits are composed of spherical particles. The effect of potential and temperature on the morphology of gallium deposits is demonstrated (Fig.5.). Similar methods are employed to investigate the electrodeposition process of indium in the same ionic liquid. There is an interesting result that we obtained octahedral indium particles by electrodeposition, which might be related to the interaction between [BMIM][TfO] and different oriented surfaces of indium (Fig.6.)
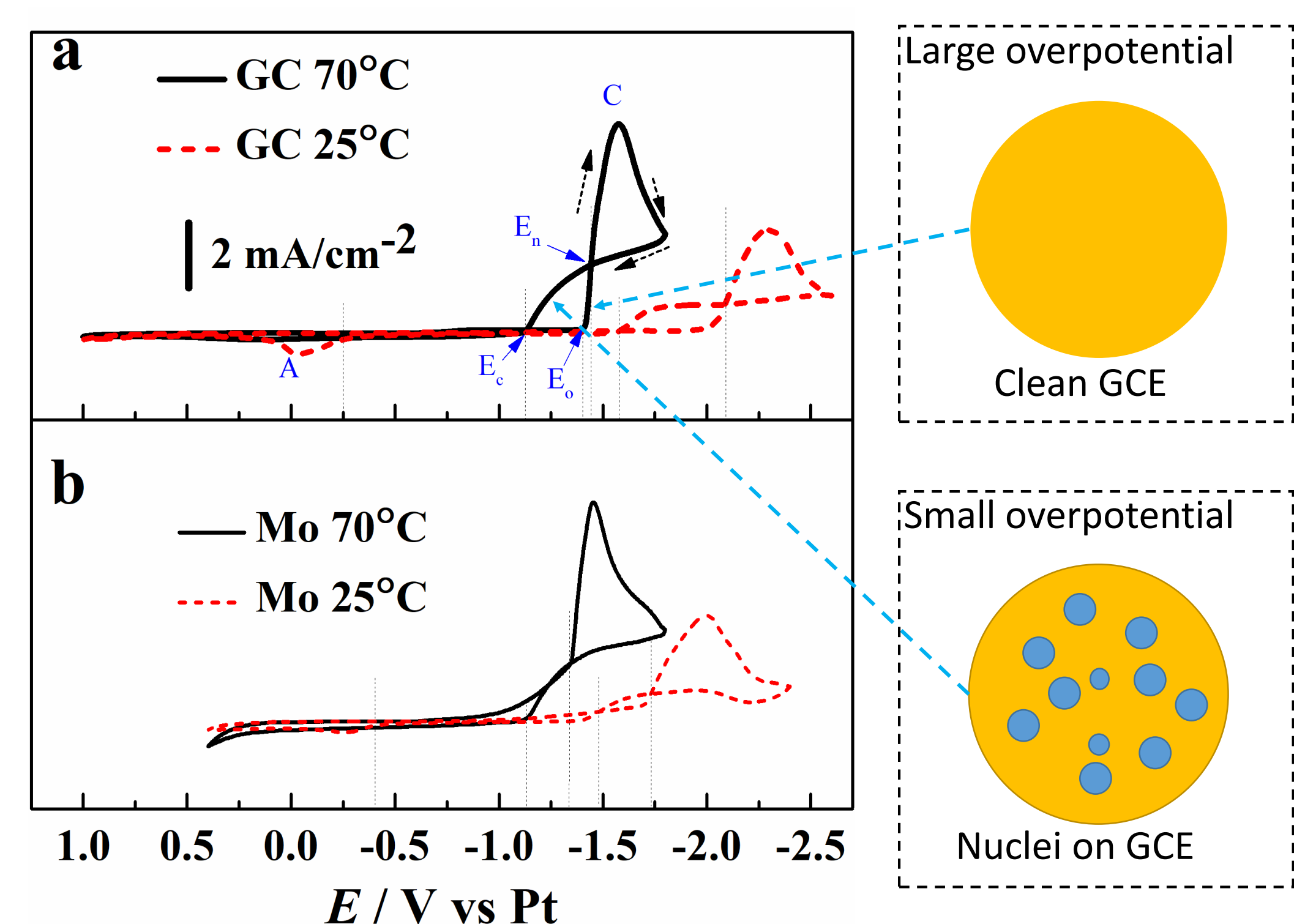

Fig. 2. Cyclic voltammograms of Ga(III) ions on glassy carbon and molybdenum electrodes in the ionic liquid at 25 ℃ and 70 ℃ with a scanning rate of 50 mV/s

Diffusion and Electrocrystallization of Gallium on Glassy Carbon Electrode
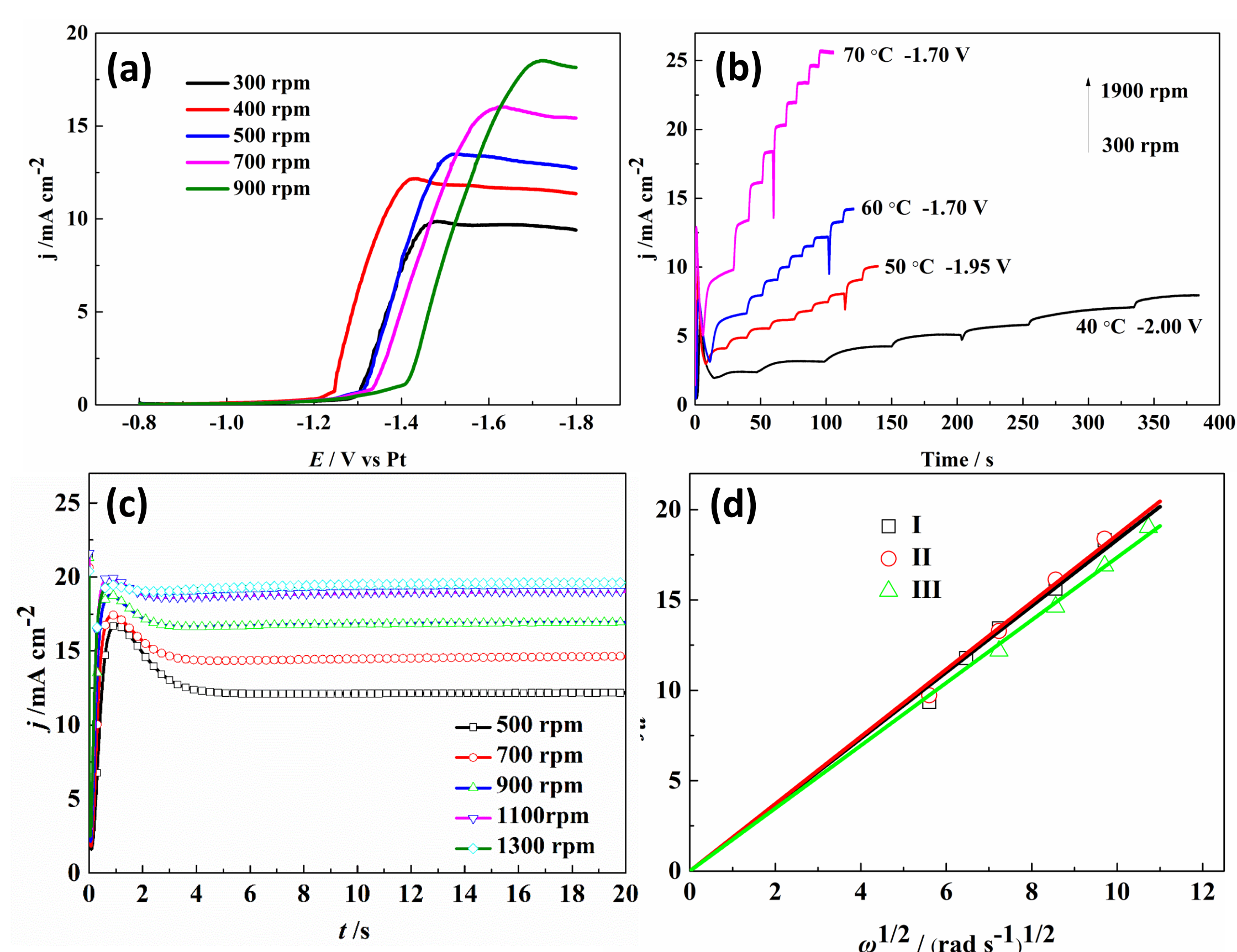

Fig. 3. (a) Voltammograms of the GC-RDE. (b) $j - t$ curves with staircase increasing rotating rate. (c) $j - t$ curves at various rotation rates. (d) Levich plots obtained from the three methods, in which (I) corresponds to (a), (II) to (b), and (III) to (c)
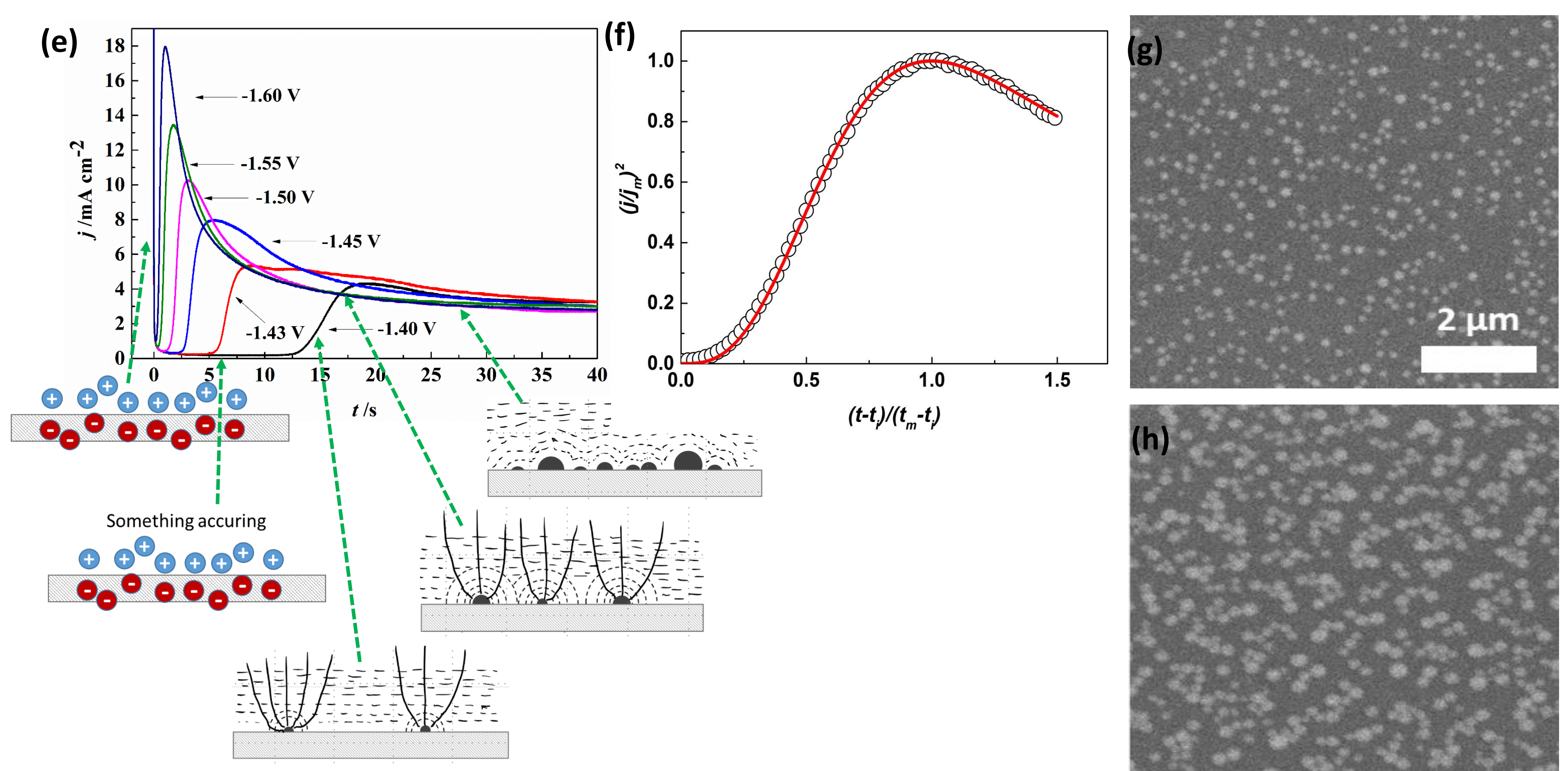

Fig. 4. (e) Current transients of GCE in the [BMIM][TfO] ionic liquid and schematics of the process corresponding to each stage. (f) Fitted current transients for nucleation kinetics parameters. SEM images of the initial stages of gallium electrodeposition with deposition time (g) 1s and (h) 2s(g)(h)
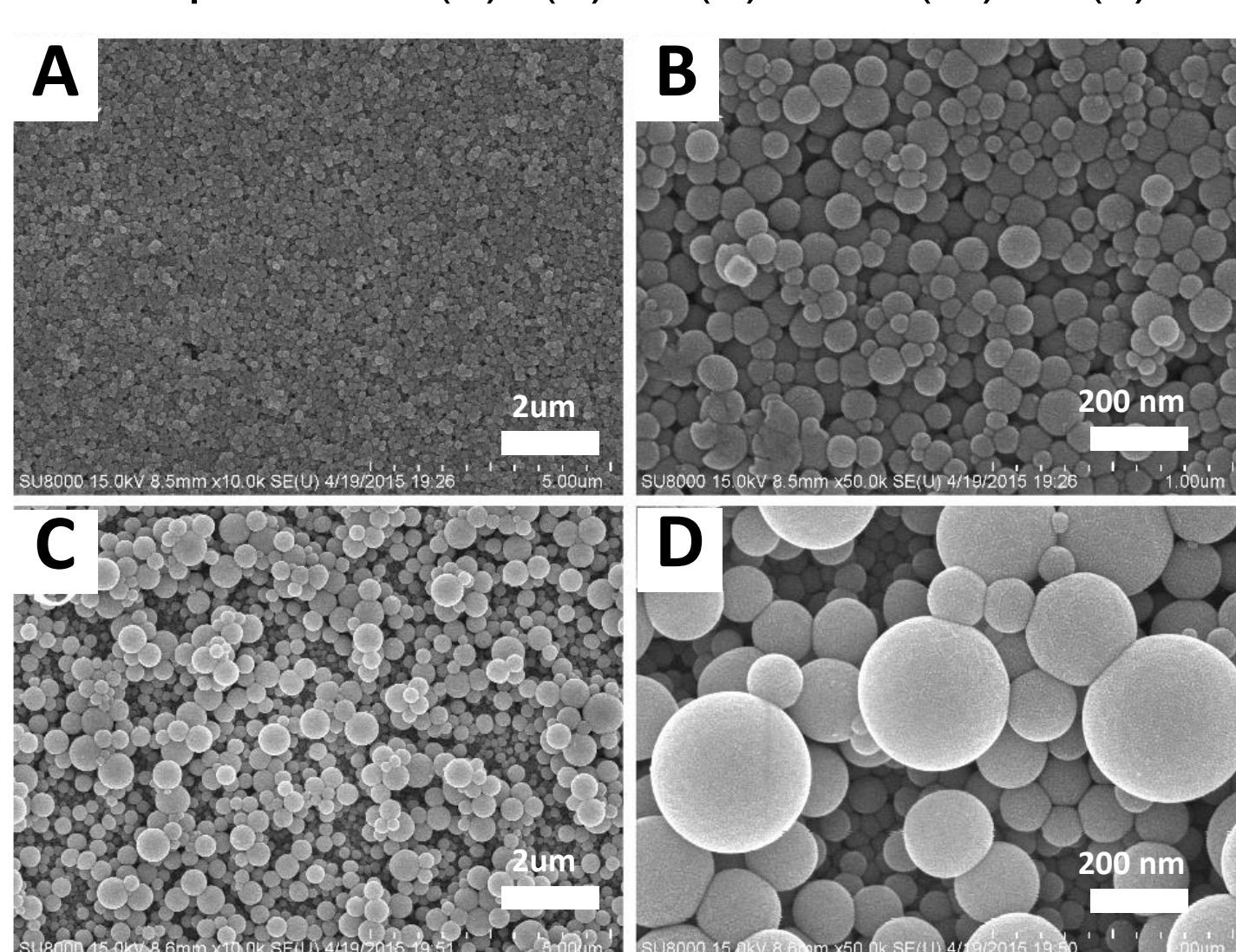

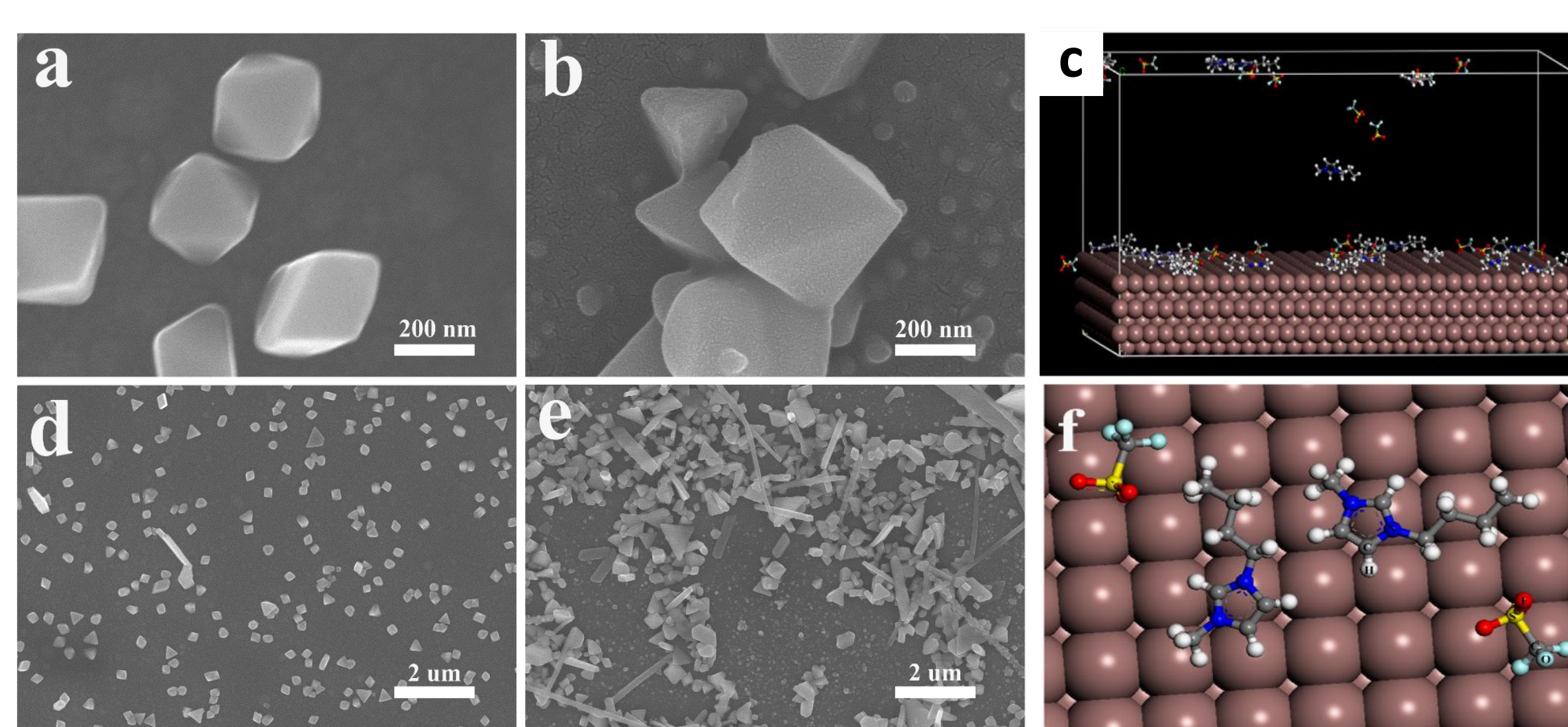Fig. 5. SEM images of the gallium films deposited at (A), (B) 25 ℃ and (C), (D) 40 ℃

Fig. 6. SEM images of indium particles deposited at (a), (d) -1.6 V vs Pt, (b), (e) -1.9 V vs Pt. (c) Results of molecular dynamic simulation of [BMIM][TfO] on In(002) surface. (f) Local top view of (c)

Conclusions

➢ Temperature extremely impacts the kinetics of the discharge of Ga(III) ions.
➢ Diffusion coefficient of Ga(III) ions in [BMIM][TfO] ionic liquid is very small (1.15×10^{-8} cm^2 s^{-1}).
➢ Nucleation of gallium on glassy carbon electrode is a instantaneous process.
➢ Above 30 ℃, temperature has almost no influence on the morphology of gallium deposits.
➢ Octahedral indium particles may resulted from the interaction between [BMIM][TfO] and different oriented surfaces.

References

[1] Ding, C. M., et al. ACS Catalysis **2016**, 6(10): 6438-6443.
[2] Torelli, D. A.; Francis, S. A. et al. *ACS Catalysis* **2016**, *6* (3), 2100-2104.
[3] Zhang, J.; An, M. et al. *Electrochim Acta* **2016**, *190*, 1066-1077.
[4] Zhang, J.; An, M.et al. *J Electrochem Soc* **2016**, *163* (13), D707-D709.