Electronic Supplementary Information

Morphologic dependence of silver electrodeposits by changing the ionic liquid solvent and the deposition parameters: Experimental and modelling approaches

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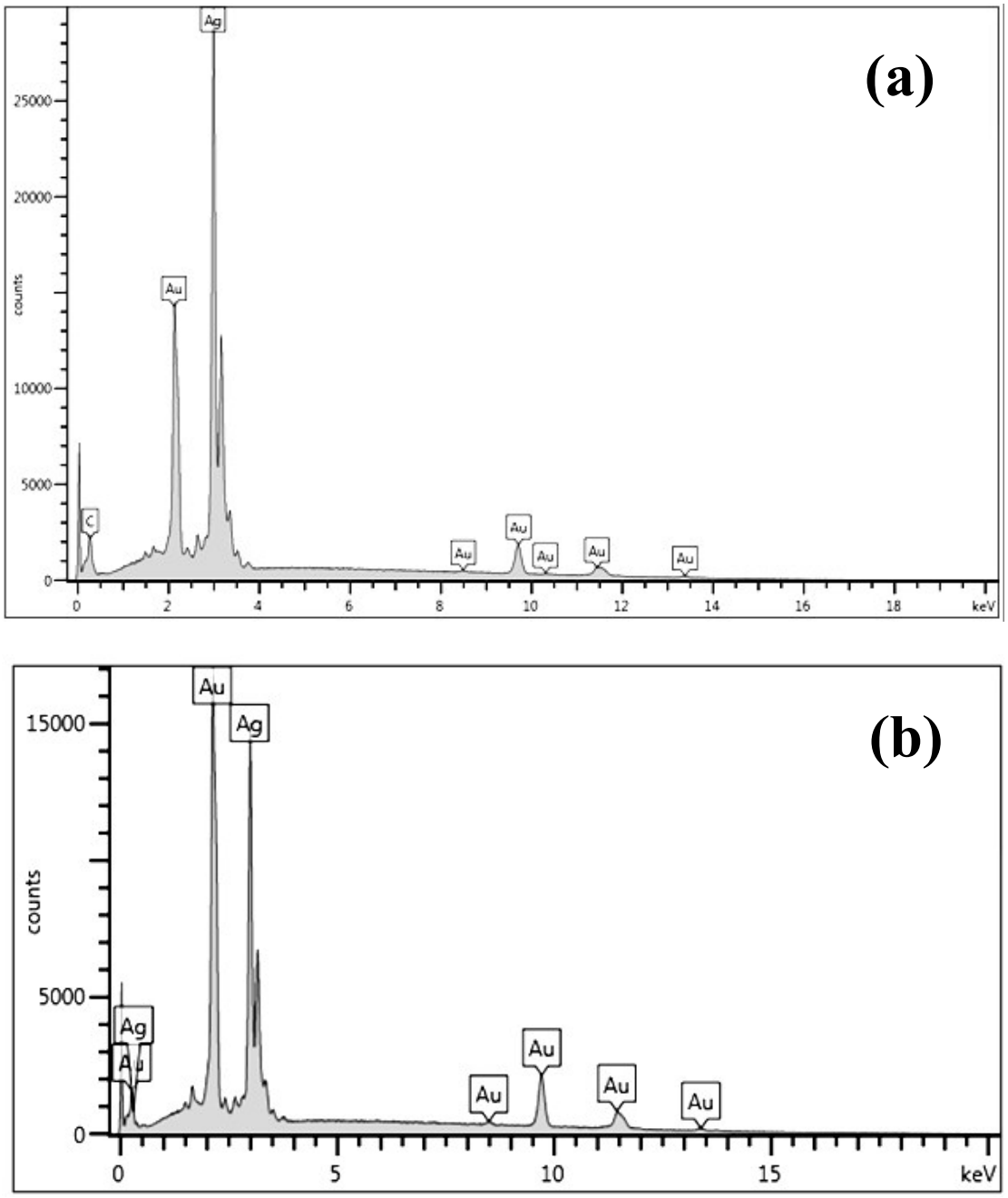

Fig. S1: EDS spectrum of Ag coatings obtained by galvanostatic deposition (30 mA cm^{-2}) from the ionic liquid (a) [EMIM]TfO containing 50 mmol L^{-1}AgTfO onto GC substrate at 45 °C and (b) [$HMIM^{+}$][HSO_4^{-}] containing 50 mmol L^{-1}AgTfO onto GC substrate at 30 °C.

EDS spectrum in Fig. S1(a-b) shows distinct peaks from Ag and Au confirming that the chemical compositions of coatings are made of Ag. Since the presence of Au peaks is due to the thin thickness of coatings. In Fig. S1(a), a small peak of C can also be observed, it is due to some residual IL.

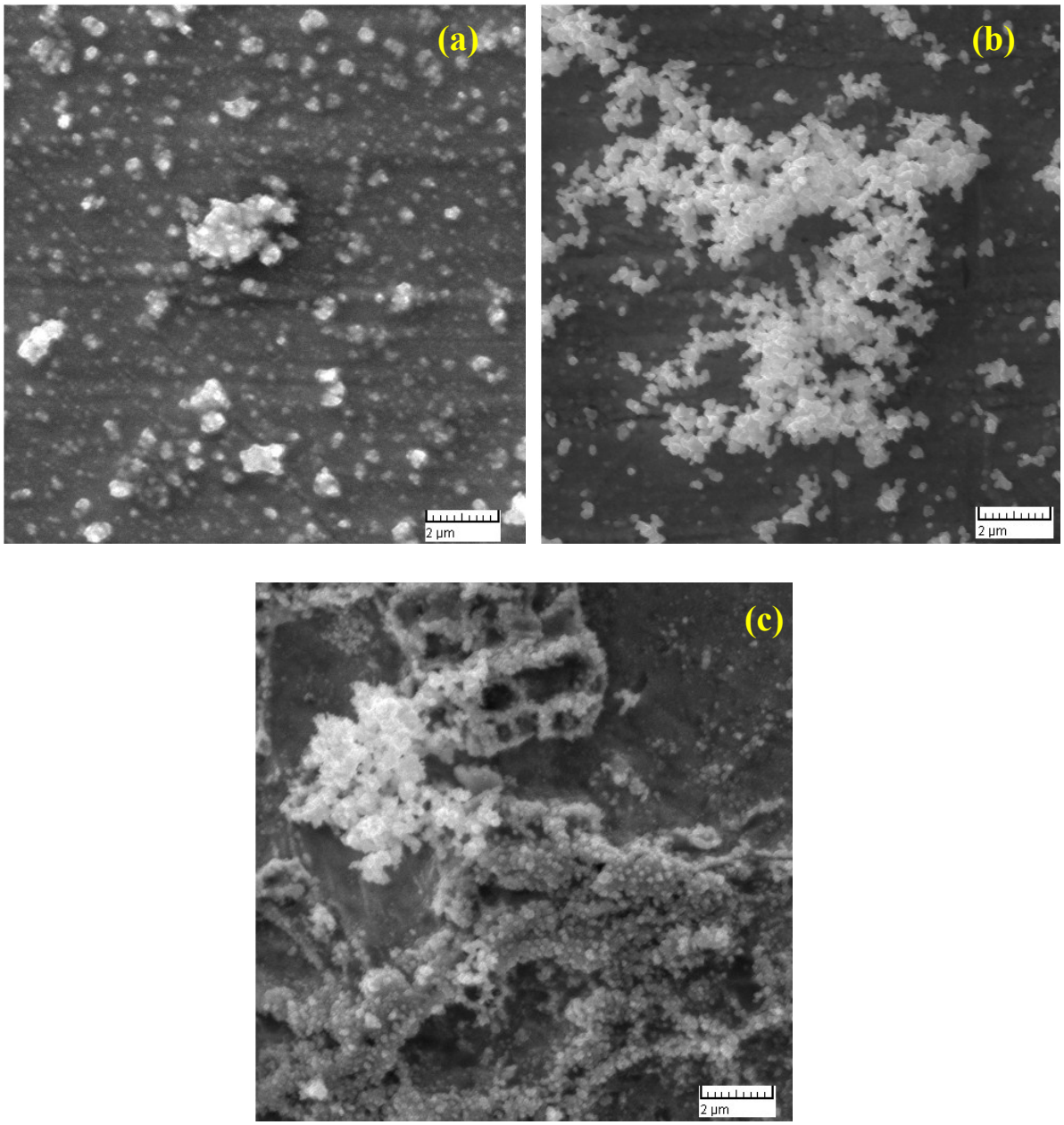

Fig. S2: SEM micrographs of Ag electrodeposits obtained by galvanostatic deposition (15 mA cm^{-2}) from the ionic liquid [EMIM]TfO containing 50 mmol L^{-1} AgTfO on gold substrate at (a) 30 and at (b) 45 °C, respectively, and (c) at 30 mA cm^{-2} at 30 °C.

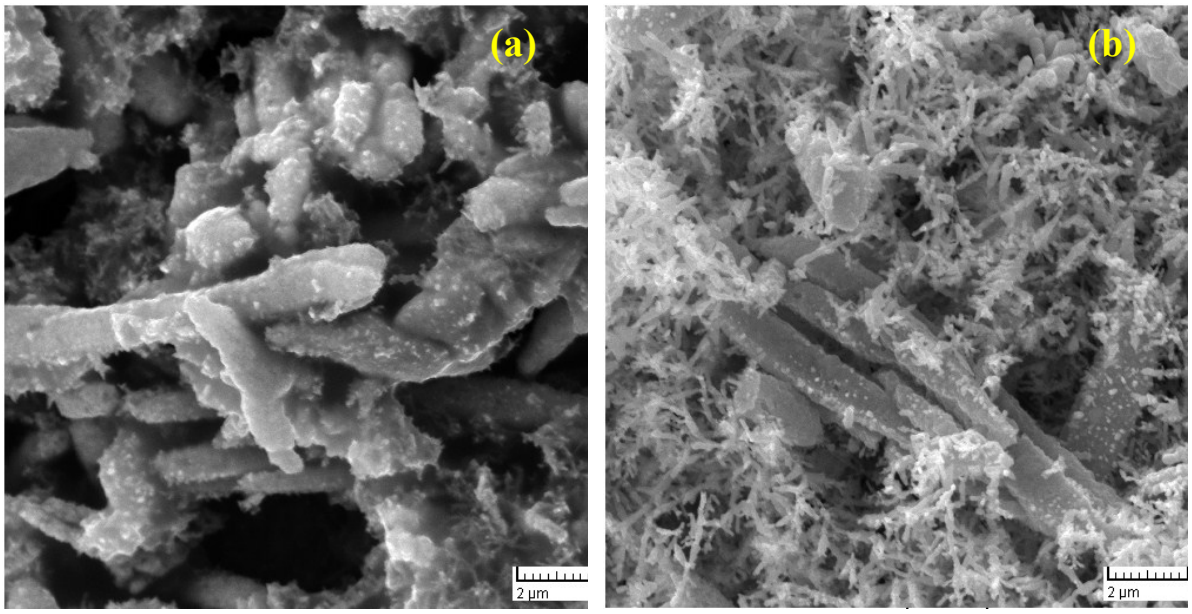

Fig. S3: SEM micrographs of Ag electrodeposits obtained by galvanostatic deposition from the ionic liquid [$HMIM^+$][HSO_4^-] containing 50 mmol L^{-1} AgTfO on gold substrate at 45 °C at (a) 15 mA cm^{-2} and at (b) 30 mA cm^{-2}.

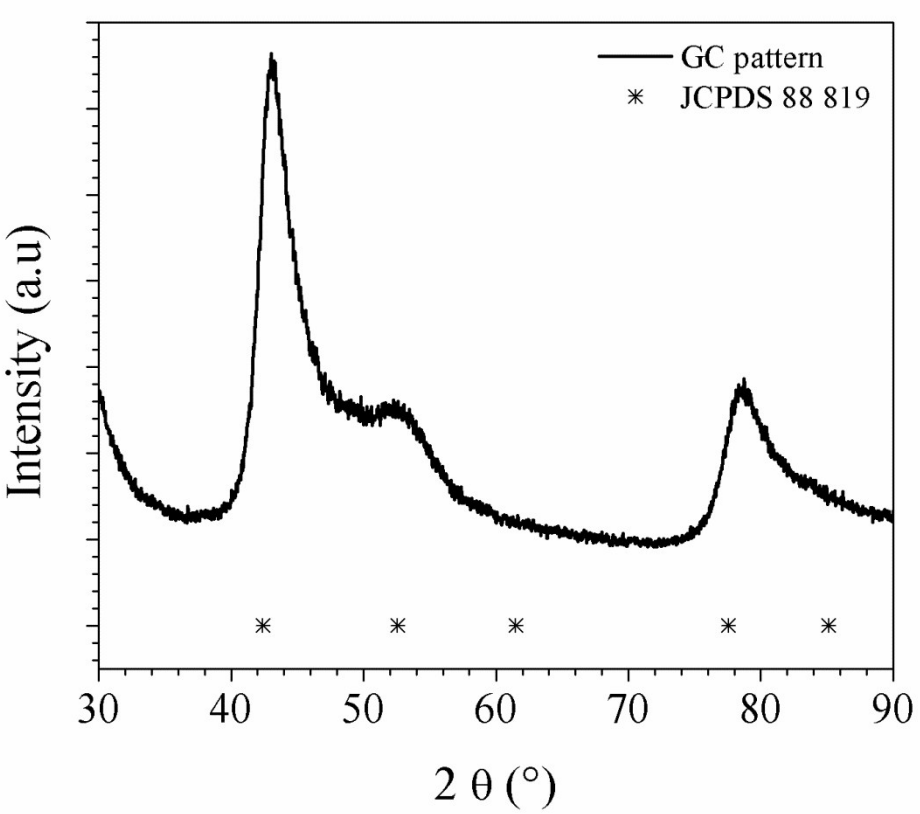

Fig. S4: XRD pattern taken for the GC substrate. Stars are related to the carbon peak positions.

Table S1. Coulomb (U_{Coul}) and van der Waals (U_{LJ}) components of the interaction energy between ionic liquid constituents. ΔU_{Coul} and ΔU_{LJ} terms correspond to energy differences between liquid with and without AgTfO ($\Delta U = \Delta U_{sol} - \Delta U_{pureliq}$). $\Delta U_{Tot} / n_{Ag+}$ corresponds to total energy differences ($\Delta U_{Coul} + \Delta U_{LJ}$) divided by the number of Ag^+ ions. All values are given in kJ mol^{-1}

	ΔU_{Coul}	ΔU_{LJ}	$\Delta U_{Tot} / n_{Ag+}$
$[EMIM]^+ - [EMIM]^+$	–1268.7	649.1	–12.4
$[EMIM]^+ - [TfO]^-$	–2942.0	–1096.3	–80.8
$[TfO]^- - [TfO]^-$	12111.5	–1515.6	211.9
$[EMIM]^+ - [Ag]^+$	4661.4	–176.8	89.7
$[TfO]^- - [Ag]^+$	–25395.0	1693.2	–474.0
$[Ag]^+ - [Ag]^+$	287.5	–0.9	5.7
$[HMIM]^+ - [HMIM]^+$	–1533.4	448.0	–36.2
$[HMIM]^+ - [HSO_4]^-$	6178.0	855.3	234.4
$[HSO_4]^- - [HSO_4]^-$	1919.6	–227.8	56.4
$[HMIM]^+ - [Ag]^+$	3947.1	–109.6	127.9
$[HSO_4]^- - [Ag]^+]$	–15490.9	1002.7	–482.9
$[HMIM]^+ - [TfO]^-$	–7721.3	–1439.8	–305.4
$[TfO]^- - [Ag]^+$	–619.8	34.5	–19.5
$[HSO_4]^- - [TfO]^-$	3090.2	–765.1	77.5
$[Ag]^+ - [Ag]^+$	75.6	–0.2	2.5

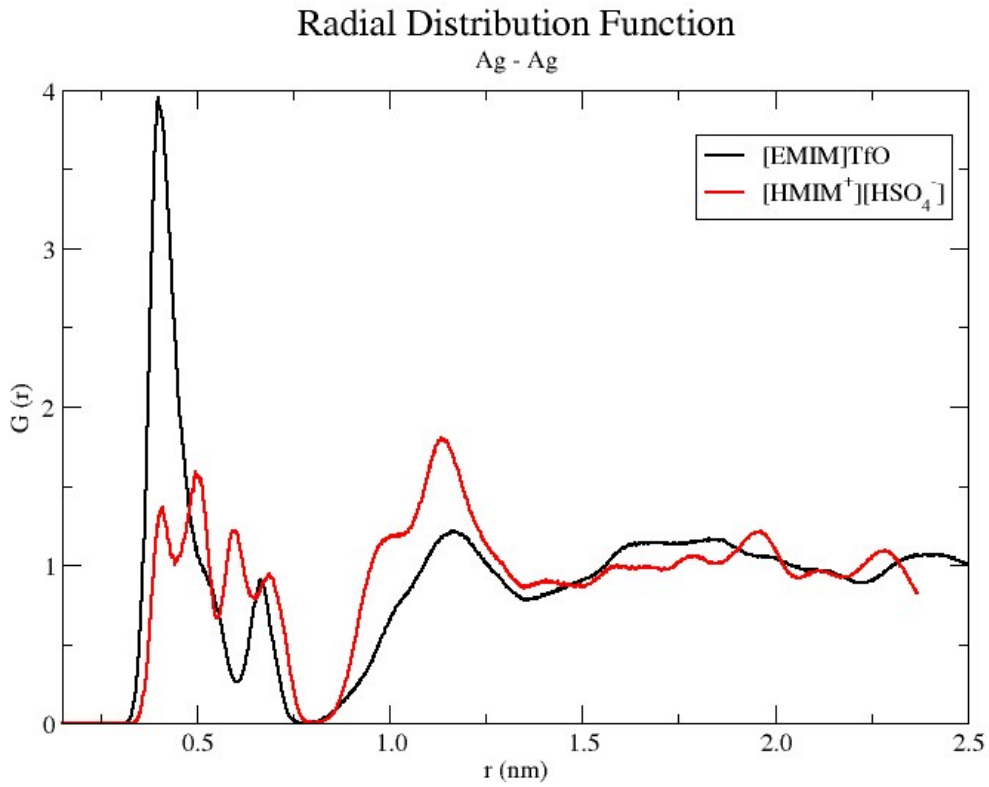

Fig. S5: Radial distribution function for Ag-Ag computed over 100 ns of simulation time. Red curve corresponds to Ag-[$HMIM^+$][HSO_4^-] and black curve corresponds to Ag-[$EMIM^+$]TfO solutions.