

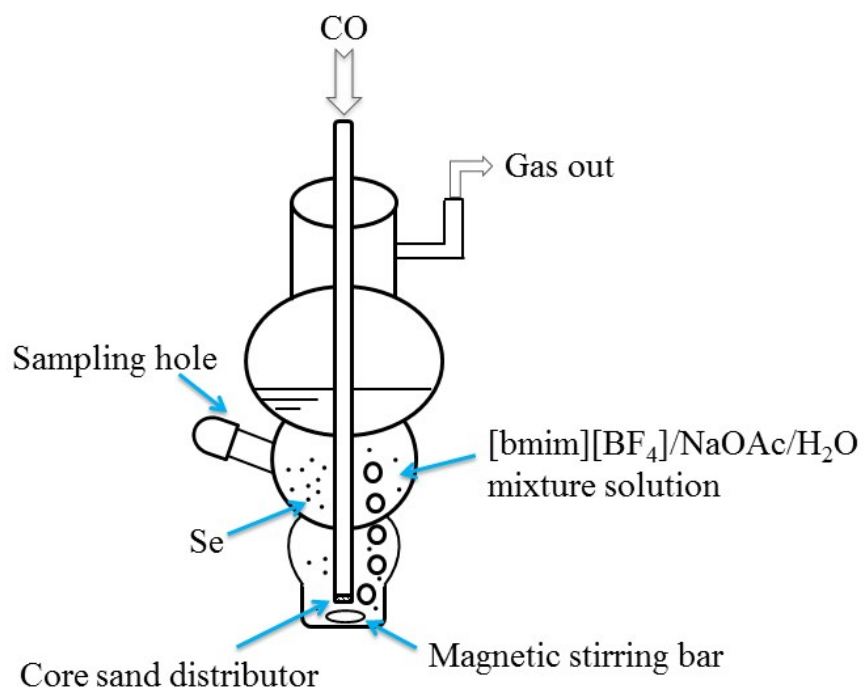
## Supporting information

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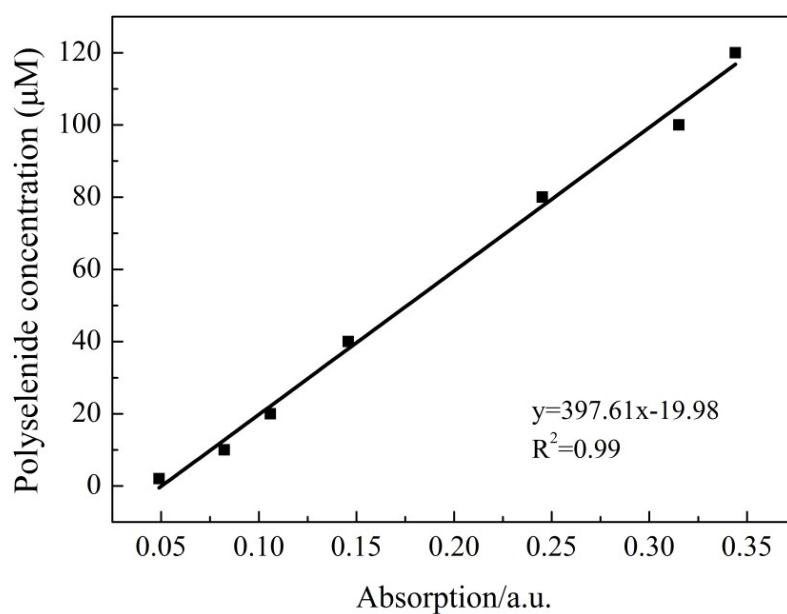
3 Figures.

1 Section.

**Figure S1.** The experimental apparatus for Se reduction by CO/H<sub>2</sub>O in the ILs



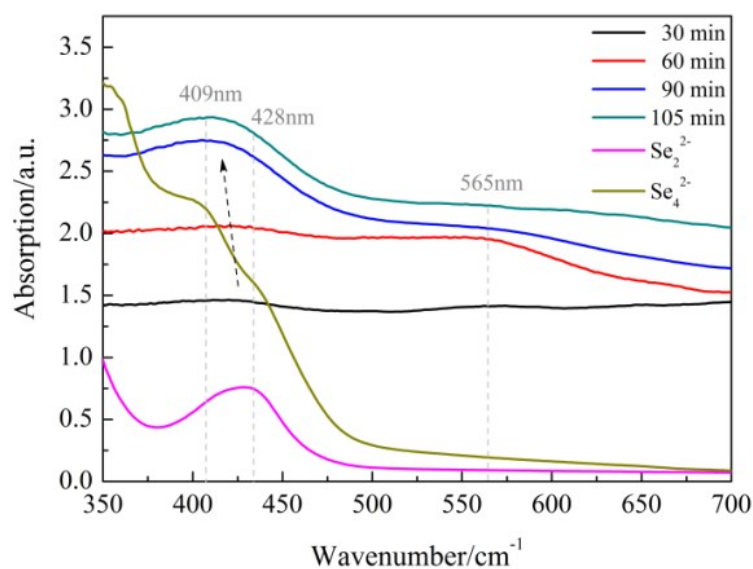
**Figure S2.** The standard curve of polyselenide concentration vs. absorption



### Section S1. The formation of $\text{Se}_2^{2-}$ and $\text{Se}_4^{2-}$

The UV–Vis transmittance spectroscopy was carried out during the 105 min of this reaction to verification the product of the solution (Figure.S3). All spectra in Fig.S3 were compared with those of standard substances ( $\text{Na}_2\text{Se}_2$  and  $\text{Na}_2\text{Se}_4$ ).

As shown in the graph, standard  $\text{Se}_2^{2-}$  had an obvious characteristic absorption peak at 428 nm and. As seen, within the 60 min, the absorbance at 428 generally increased, possibly attributed to the formation of some  $\text{Se}_2^{2-}$ . Meanwhile, a shoulder peak at 565 nm is observed with the reaction progressed (>60 min), indicating the formation of trace  $\text{Se}_4^{2-}$ . With further reaction, the absorbance at 428 nm was blue shift to 409 nm when reaction time was increased from 60 to 105min. The peak at 409 nm can be identified as the  $\text{Se}_4^{2-}$ . This phenomenon indicated that the formed  $\text{Se}_2^{2-}$  in this system seems unstable. Once  $\text{Se}_2^{2-}$  is formed, it will transform to  $\text{Se}_4^{2-}$  via disproportionation.



**Figure S3.** UV-vis spectra of reaction solution at different reacting times