**Fig. S1.** FESEM image of the product by substituting sodium citrate (A) and L-tryptophan (B) for AA.
In our case, as shown in Scheme 3, it is Cu$^+$, not I$^-$ that is pivotal in electron transfer for the coupling reaction. For Marshite structured CuI, each ‘Cu’ is surrounded by a tetrahedron of ‘I’, and each ‘I’ has four ‘Cu’ neighbors as illustrated by its unit cell model (Scheme S1A). The Cu atoms on the different crystallographic planes of CuI are displayed (Scheme S1B to S1F). As mentioned above, the reflection peaks of [111], [220], [222], and [311] planes (especially [111] and [222] planes) are much stronger than the ones in JCPDS 06-0246, which possess active ‘Cu’ atoms, consequently inducing excellent catalytic properties.

**Scheme S1.** (A) The unit cell of the Marshite CuI, and (B–F) the atomic arrangement in (111), (200), (220), (222), and (331) planes of the CuI structure, respectively.