XPS analysis

Experimental section

To obtain dried nanoparticle, 50 mL sol was diluted with ethanol (99.9%) at ratio (v) 1:1. The diluted sample was centrifuged at 10000 rpm for 30 min and the precipitated solid was collected and dried in vacuum dryer at 80 °C for 6 h. XPS data were acquired using a PerkinElmer PHI 5400 X-ray photoelectron spectrometer. This system was equipped with Mg X-ray source operated at 300 W (15 kV, 20 mA). The carbon (C 1s) line at 285.0 eV was used as the reference line.

Results and discussion section

A typical XPS spectrum of Copper nanoparticle was measured and the spectrum of Cu $2p_{3/2}$ is depicted in Fig. S1a. The Cu $2p_{3/2}$ spectrum shows that the Cu²⁺ peak lies at 932.98 eV¹, with two shake-up satellites at higher binding energy (BE 942.35 and 940.85 eV)^{2, 3}. The Cu¹⁺ peak was appeared at 931.55 eV which attributed to Cu₂O^{1, 4}. Apart from that, Fig. S1b shows O 1s core level spectrum is broad and fitted by 2 different peaks. The peak located at lower energy (BE 529.50 eV) is attributed to O²⁻ in CuO^{3, 5, 6} while the other peak at higher energy (BE 530.30 eV) is ascribed to O¹⁻ in Cu₂O^{5, 6}. The binding energy, FWHM and area of Cu $2p_{3/2}$ are summarized in Table S1. The XPS results indicate that the sample is composed of CuO and Cu₂O. The XPS result was not in agreement with XANES result, where 57.6% of CuO and 42.4% of Cu₂O was found in the solids separated from sol; while, 47% Cu⁰, 23% of CuO and 30% CuCl₂ was acquired in the sol via XANES fitting. The concentration of oxide species increased, it might be due to oxidation happened during the XPS sample preparation.

| Binding energy | Cu phase | FWHM | Area | Percentage (%) |
|----------------|-------------------|------|----------|----------------|
| (eV) | | | | |
| 931.55 | Cu ₂ O | 2.76 | 1852.811 | 42.43 |
| 932.98 | CuO | 3.39 | 860.6919 | 19.71 |
| 940.85 | CuO | 3.90 | 1074.291 | 24.60 |
| 942.35 | CuO | 2.36 | 579.304 | 13.26 |

Table S1 The results of deconvolution of XPS Cu $2p_{3/2}$ peaks





Fig. S1 Typical deconvolution of Cu $2p_{3/2}\left(a\right)$ and O 1s (b) main peak of 6 h sample.

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