SUPPORTING INFORMATION

Enhancing CO₂ photoreduction over ZIF-based reticular materials by morphology control of Au plasmonic nanoparticles

Jorge Becerra, Vishnu Nair Gopalakrishnan, Toan-Anh Quach and Trong-On Do*

Department of Chemical Engineering, Laval University, 1065 Avenue de la Médecine, Quebec, QC G1V 0A6, Canada

*Email: trong-on.do@gch.ulaval.ca

1. Experimental

1.1 Materials

All chemical reagents in the synthesis were used without further purification. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), 2-methylimidazole ($C_4H_6N_2$, 99%), chloroauric acid ($HAuCl_4 \cdot 3H_2O$), L-ascorbic acid ($C_6H_8O_6$, 99%), silver nitrate ($AgNO_3$, 99%), cetyl trimethyl ammonium bromide (CTAB, 99%), sodium iodide (NaI, 99%), sodium borohydride ($NaBH_4$, 98%), polyvinylpyrrolidone (PVP, molar mass 10000 g mol^{-1}) sodium bicarbonate ($NaHCO_3$), and triethanolamine (($HOCH_2CH_2)_3N$, 99%), were purchased from Sigma-Aldrich.

1.2 Synthesis of materials

1.2.1 Synthesis of gold nanotriangles (Au NTs)

Synthesis of Au NTs was done following the seed-mediated growth method previously reported [1–3]. In a typical procedure, the seed solution is prepared by adding 450 μl of freshly prepared 0.01 M $NaBH_4$ aqueous solution to an Au^{3+} solution consisting of 4.7 ml of 0.1 M CTAB and 25 μl of 0.05 M $HAuCl_4 \cdot 3H_2O$. After 2 h of stirring, the obtained seed solution was used for the subsequent synthesis of Au NTs (**Scheme S1**).

Then, two growth solutions were prepared for the synthesis of Au NTs: (a) 1.6 ml of a 0.1 M CTAB solution, 40 μl of a 0.05 M $HAuCl_4 \cdot 3H_2O$ aqueous solution, and 15 μl of a 0.01 M NaI solution were sequentially added to 8 ml of deionized water, followed by the addition of 40 μl of a 0.1 M L-ascorbic acid solution for Au^{3+} reduction; (b) 20 ml of 0.1 M CTAB, 500 μl of a 0.05 M $HAuCl_4 \cdot 3H_2O$ aqueous solution and 300 μl of a 0.01 M NaI solution were sequentially added to 20 mL of ion-exchanged water, followed by the addition of 400 μl of a 0.1 M L-ascorbic acid solution and 50 μl of a 0.5 M $AgNO_3$.
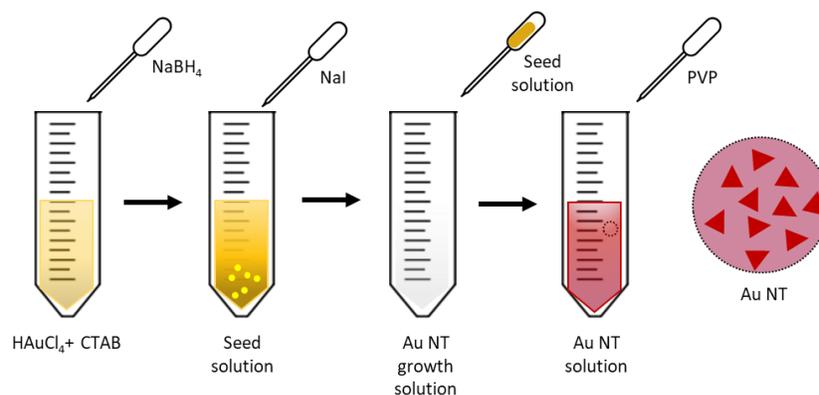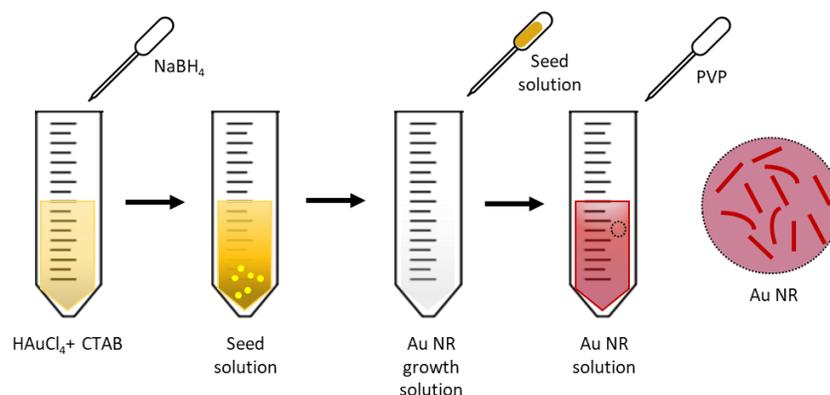
Scheme S1: Schematic **s**ynthesis of Au NTs.

A total of 100 µl of diluted seed solution, prepared by adding 100 µl of the synthesized seed solution to 0.9 ml of a 0.1 M CTAB solution, was added to solution a with manual stirring for 1 s. Then, 3.2 ml of this solution was immediately added to solution b. Afterward, PVP coating of Au NTs was done and the obtained Au NTs were centrifuged and washed several times with methanol to remove excess of CTAB and PVP.

1.2.2 Synthesis of gold nanorods (Au NRs)

Synthesis of Au NRs was done following the seed-mediated growth method previously reported [4,5]. Briefly, a 0.25 ml of $HAuCl_4:3H_2O$ aqueous solution (0.01M) was added to a 7.5 ml of CTAB solution (0.10 M) in a centrifuge tube and placed in a water bath kept at 25 °C for 2 h. Then, synthesis of Au NRs was done by a seed-mediated growth. In a typical procedure, 4.75 ml of CTAB (0.10 M), 0.20 mL of $HAuCl_4:3H_2O$ (0.01 M), and 0.030 ml of $AgNO_3$ solutions (0.01M) were added to a centrifuge tube one by one in order, and then gently mixed. Afterward, 0.032 ml of AA (0.10 M) was added. Finally, 0.010 ml of Au seed solution was added, and the mixture was gently mixed, and then left undisturbed for 4 h.

Scheme S2: Schematic synthesis of Au NRs.

The CTAB-capped Au NRs solution was centrifuged to get rid of the supernatants. Then 0.80 ml of PVP solution was added to 40 ml of the treated CTAB-capped Au NRs solution, and the mixture was stirred for 24 h at room temperature. CTAB on Au NRs was thus exchanged by PVP to form the PVP-capped Au NRs. Final Au NRs were centrifuged and washed with methanol several times to eliminate excess of PVP and CTAB.

1.3 Apparent quantum yield (AQY) measurement

Apparent quantum yield efficiency was calculated as the amount of generated product molecules divided by the amount of total incident photons. Mathematical approach is listed below. Light irradiated area was estimated as 8,83 cm^2, the total incident photon flux was $2,12 \times 10^{14}$ photons cm^{-2} s^{-1} at 420 nm.

$$AQY = \frac{Number\ of\ electrons\ x\ Number\ of\ molecules}{Number\ of\ incident\ photons} x100$$

$$Number\ of\ molecules = Number\ of\ moles\ x\ Avogadro's\ constant$$

$$Number\ of\ incident\ photons$$
$$= Total\ incident\ photon\ flux\ x\ Irradiated\ area\ (cm^2)\ x\ Irradiation\ time\ (s)$$
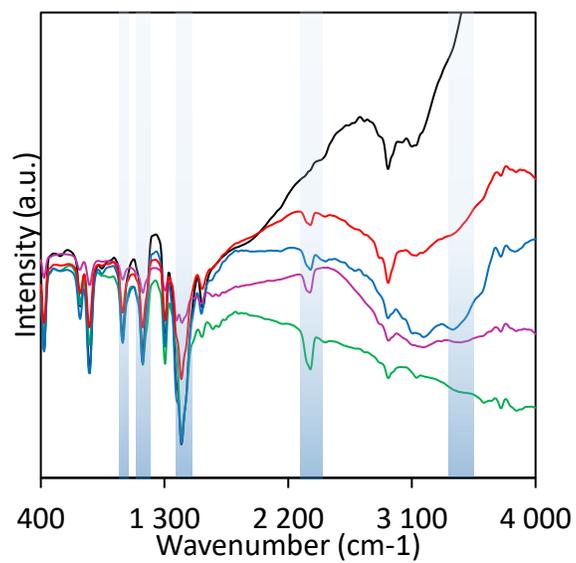
2. Results and discussion

2.1. UV-Vis
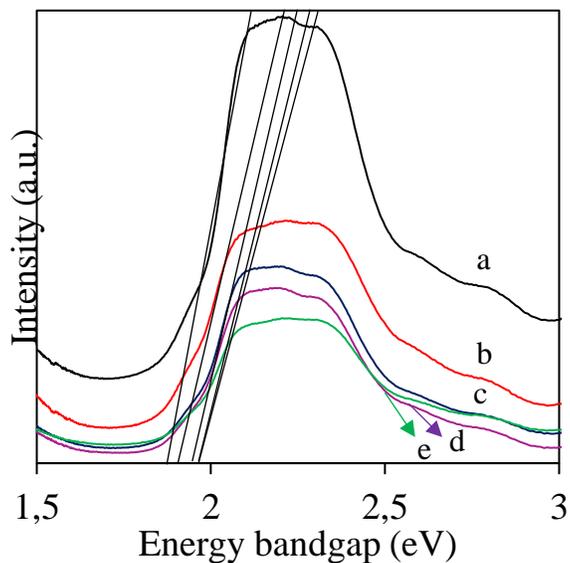
Figure S1. Bandgap energy calculation for different Au@ZIF-67 photocatalysts on a) ZIF-67, b) AuNR5 c) AuNT5, d) AuNT10 and e) AuNR10.

Table S1. Calculated bandgap energy for all nanocomposites by Tauc plot method.

| Sample	Calculated bandgap (eV)
ZIF-67	1,75
AuNT5	1,85
AuNT10	1,89
AuNR5	1,82
AuNR10	1,87

2.2. Fourier transformed infrared (FTIR)

Figure S2. FTIR spectra of a) bare ZIF-67, b) AuNR5, c) AuNT5, d) AuNT10 and e) AuNR10.

2.3. X-ray diffraction (XRD)

In order to calculate the size of the crystallite, Scherrer equation was implemented (Eq. S1), where λ is the X-ray wavelength, K is a dimensionless factor, β is the full width at half maximum (FWHM) of diffraction peak and θ diffraction angle in radians. For ZIF-67, FWHM is calculated based on the maximum peak, observed at 8°.

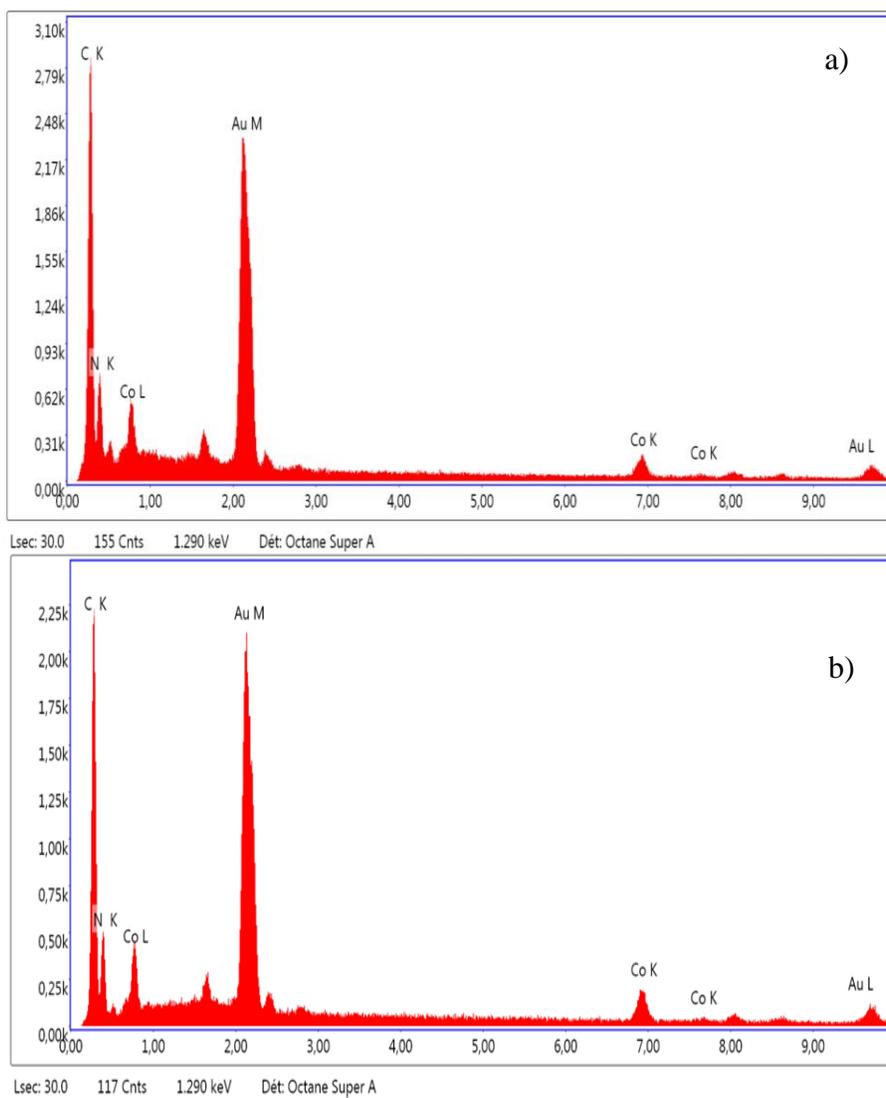$$\tau = \frac{K\,\lambda}{\beta\,\cos\theta} \qquad\qquad (Eq.\,S1)$$

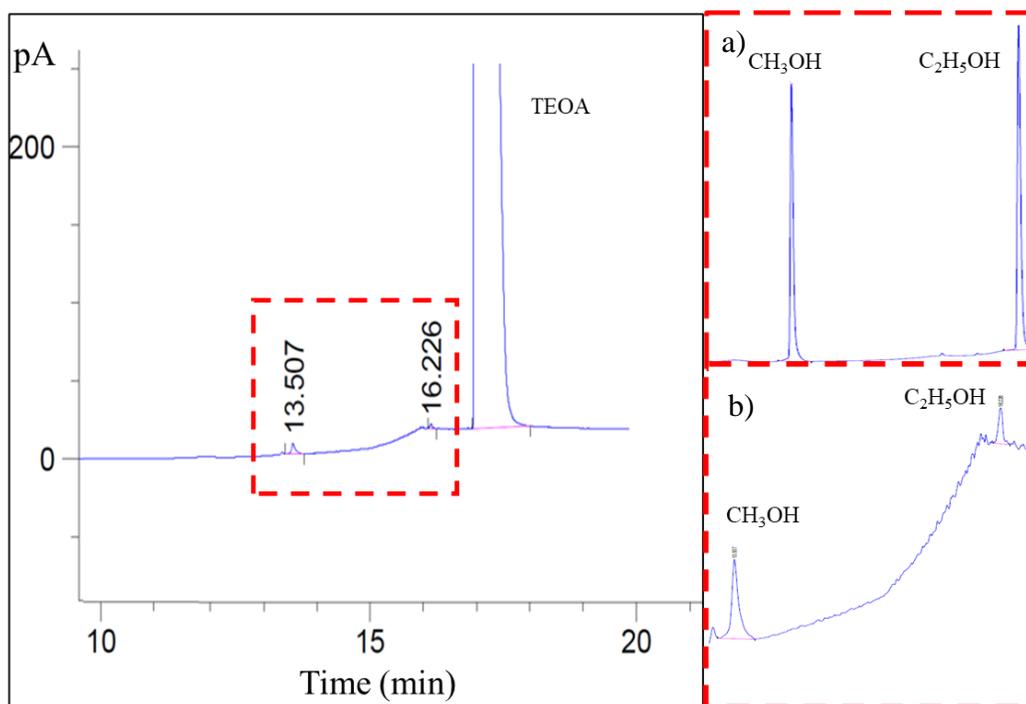## 2.4 Transmission electron microscopy (TEM)
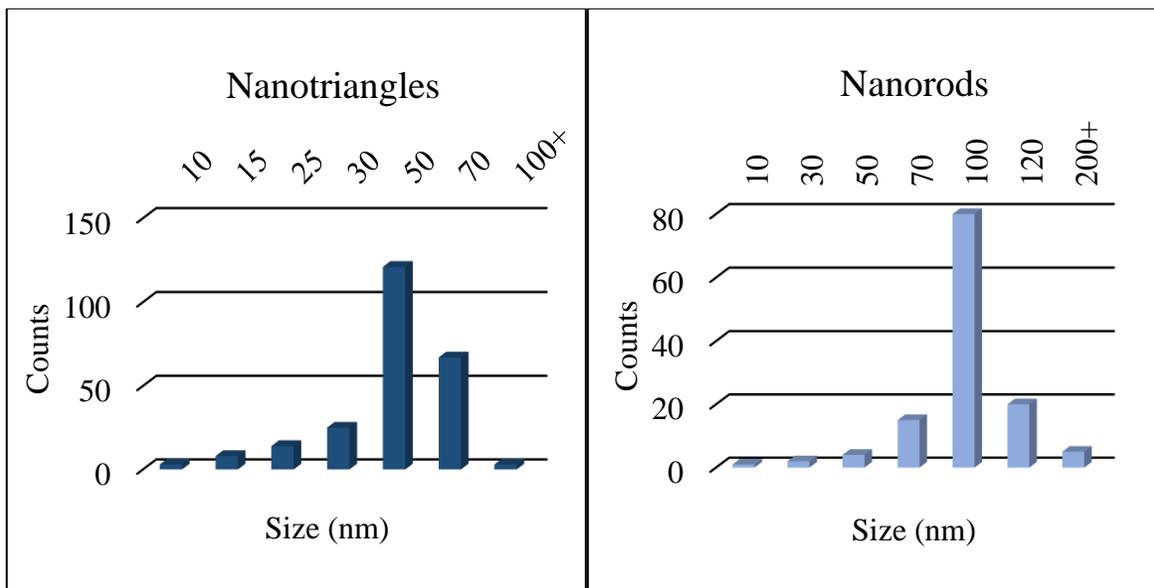
Figure S3. Particle size distribution for Au nanotriangles and nanorods.

2.5. Scanning electron microscopy (SEM)

Figure S4. Elemental analysis distribution spectra for a) AuNT10 and b) AuNR10.

2.6. Photocatalytic activity

Figure S5. Liquid phase chromatogram after a) CO_2 photoreduction and b) AQY reaction with AuNT10 at 420 nm.

2.7. Photoluminescence and lifetime

To determine the rate electron transfer, a decay mathematical approach was used, where τ represents the measured lifetime value, fit into a single exponential model using HORIBA scientific software.

$$K_{ET} = \frac{1}{\tau_{ZIF-67}} - \frac{1}{\tau_{Au@ZIF-67}} \quad (Eq. S2)$$

2.8. Photoelectrochemical characterization (PEC)
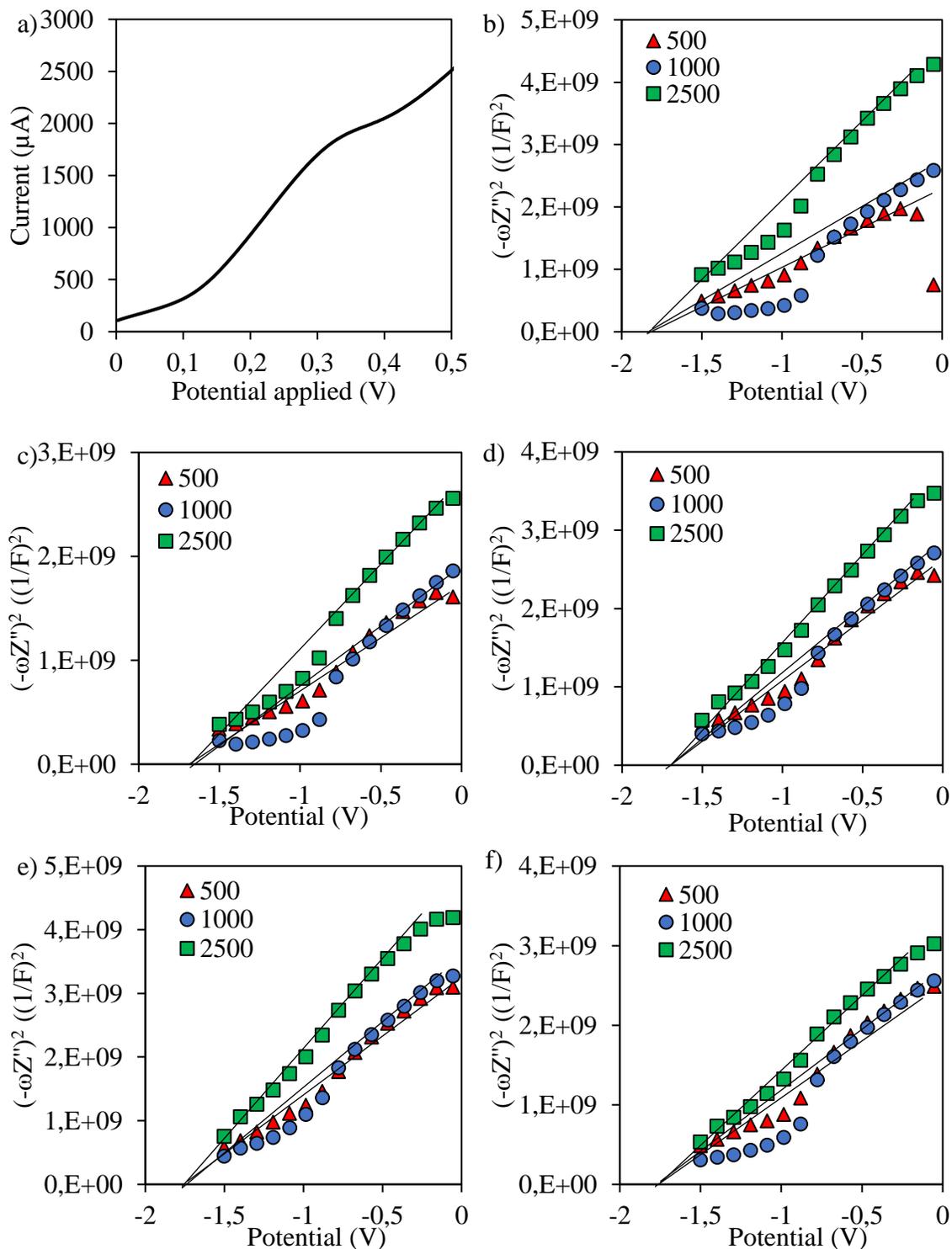
Figure S6. a) Linear sweep voltammetry for ZIF-67 and Mott Schottky spectrum for b) ZIF-67, c) AuNT5, d) AuNT10, e) AuNR5 and f) AuNR10. Used frequencies: 500, 1000 and 2500 Hz.

3. References

1   S. Kuwahara, Y. Narita, L. Mizuno, H. Kurotsu, H. Yoshino, M. Kuwahara and M. Kuwahara, *ACS Appl. Nano Mater.*, 2020, **3**, 5172–5177.

2   L. Ma, S. J. Ding and D. J. Yang, *Dalt. Trans.*, 2018, **47**, 16969–16976.

3   M. R. Langille, M. L. Personick, J. Zhang and C. A. Mirkin, *J. Am. Chem. Soc.*, 2012, **134**, 14542–14554.

4   W. Cai, J. Wang, H. Liu, W. Chen, J. Wang, L. Du, J. Hu and C. Wu, *J. Alloys Compd.*, 2018, **748**, 193–198.

5   S. Rodal-Cedeira, V. Montes-García, L. Polavarapu, D. M. Solís, H. Heidari, A. La Porta, M. Angiola, A. Martucci, J. M. Taboada, F. Obelleiro, S. Bals, J. Pérez-Juste and I. Pastoriza-Santos, *Chem. Mater.*, 2016, **28**, 9169–9180.