Supplementary Information of

A Mild Colloidal Strategy for Controlling the Morphology of Reduced Graphene Oxide–Ag Nanowire Hybrids

Alessio Massaro[a,§,§§], Rafique Ahmed Lakho[a,b], Adriana Grandolfo[a,c,d], Giuseppe Valerio Bianco[e], Elisabetta Fanizza[a,d,f], Marinella Striccoli[d,f], Roberto Comparelli[d,f], Maria Lucia Curri[a,d,f*], Chiara Ingrosso[d,f *]

[a]Department of Chemistry, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy

[b]Department of Aerospace Science and Engineering, Polytechnic of Bari, via Orabona 4, 70126 Bari, Italy

[c]Department of Electrical and Information Engineering, Polytechnic of Bari, via Orabona 4, 70126 Bari, Italy

[d]CNR-IPCF S.S. Bari, c/o Department of Chemistry, Università degli Studi di Bari, via Orabona 4, 70126 Bari, Italy

[e]CNR-NANOTEC Sez. Bari, c/o Department of Chemistry, Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy

[f]Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via G. Giusti, 9 50121 Firenze, Italy

§present address: Ghent University, Belgium

§§present address: Vlaamse Instelling voor Technologisch Onderzoek (VITO), Boeretang 200, 2400 Mol, Belgium

Email: c.ingrosso@ba.ipcf.cnr.it, marialucia.curri@uniba.it

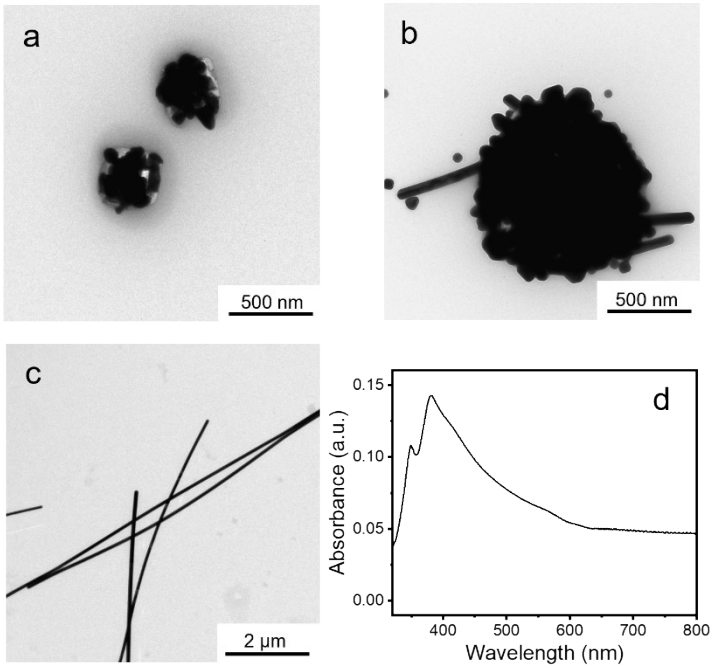

Figure S1. TEM images of nanostructures isolated by centrifugation from the synthesis solution of Ag NWs, after the (a) third and (b) seventh injection of $AgNO_3$. (c) TEM image and (d) UV-Vis absorption spectrum of Ag NWs synthesized with PVP (Mw = 360 kDa), 7.7:1 PVP:$AgNO_3$ molar ratio, 170°C, stirring rate of 600 rpm and reaction time of 2.5 h.

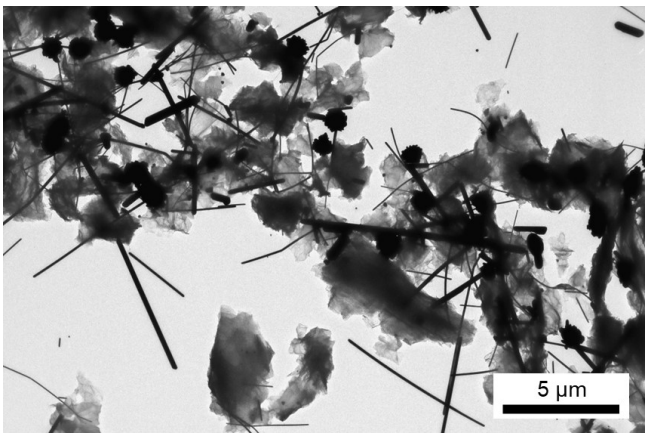

Figure S2. TEM images of hybrid nanostructures synthesized with the 10:1 $AgNO_3$:His-RGO w/w, 7.7:1 PVP:$AgNO_3$ molar ratio, at 170°C, reaction time of 2.5 h, PVP at Mw of 360 kDa, stirring rate of 600 rpm, by injecting His-RGO in the synthesis solution containing PVP and NaCl, between the seventh and eighth injection of $AgNO_3$.

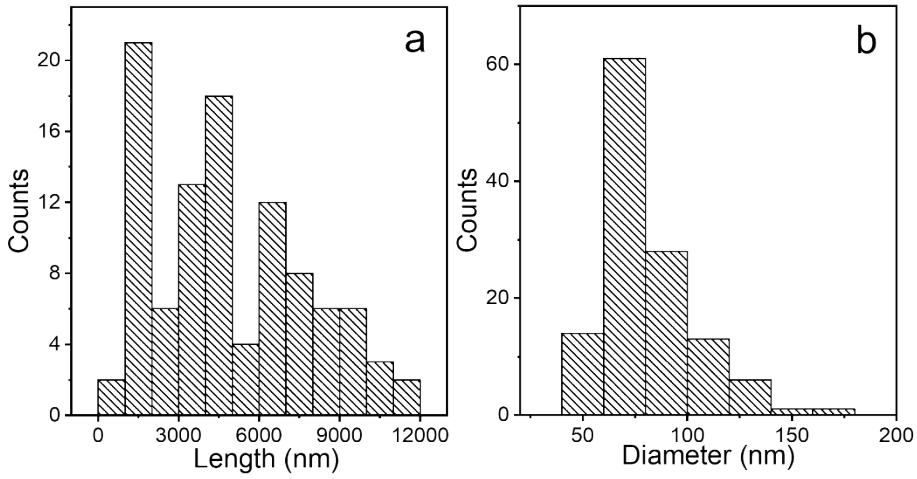

Figure S3. Histograms of (a) length and (b) diameter distribution of the Ag NWs in His-RGO/Ag NWs synthesized with the 10:1 $AgNO_3$:His-RGO w/w, 7.7:1 PVP:$AgNO_3$ molar ratio, PVP of 360 kDa, at 170°C and 600 rpm stirring rate, with His-RGO injected between the seventh and eighth $AgNO_3$ addition, at the reaction time of 5 h.

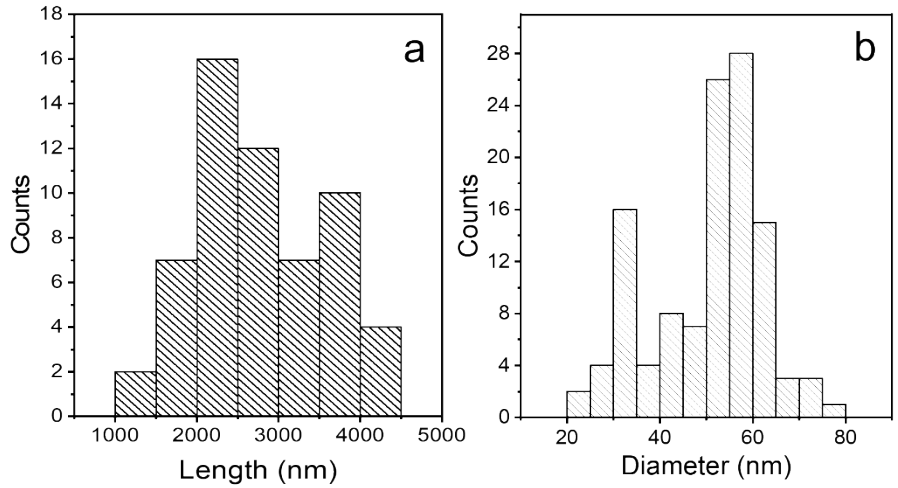

Figure S4. Histograms of (a) length and (b) diameter distribution of the Ag NWs in His-RGO/Ag NWs synthesized with the 10:1 $AgNO_3$:His-RGO w/w, 7.7:1 PVP:$AgNO_3$ molar ratio, PVP of 360 kDa, at 170°C and 600 rpm stirring rate, with His-RGO injected between the seventh and eighth $AgNO_3$ addition, at the reaction time of 6.5 h.

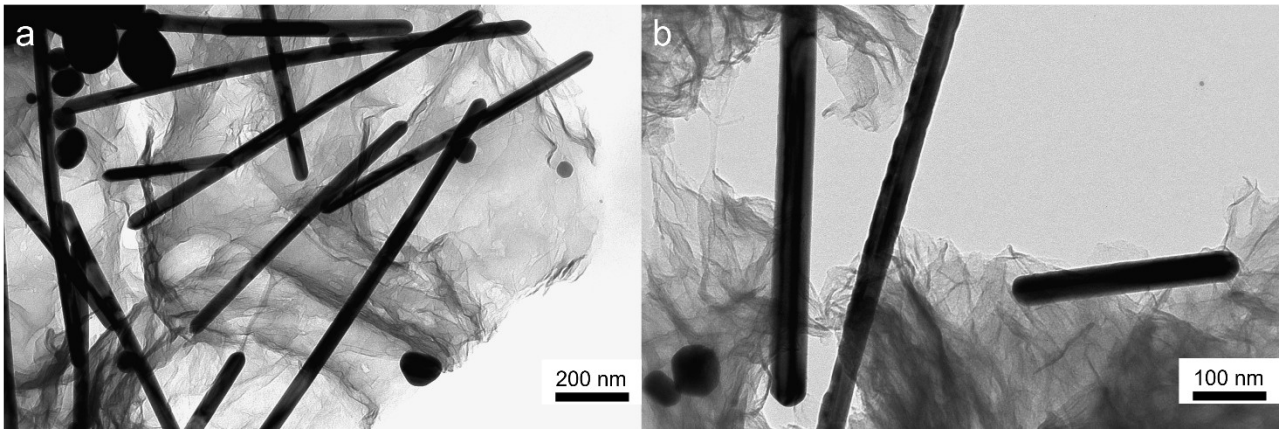

Figure S5. TEM images of His-RGO/Ag NWs synthesized with the 10:1 $AgNO_3$:His-RGO w/w, 7.7:1 PVP:$AgNO_3$ molar ratio, at 170°C, reaction time of 2.5 h, PVP at Mw of 360 kDa, stirring rate of 600 rpm, by injecting His-RGO in the synthesis solution, between the seventh and eighth injection of $AgNO_3$. In (a) the His-RGO/Ag NWs nanocomposite was purified six times with acetone and in (b) was treated with a concentrated ammonia/30% hydrogen peroxide solution (9:1 v/v).

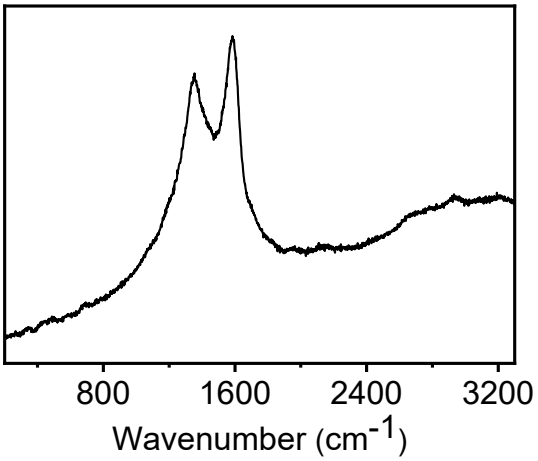

Figure S6. Raman spectrum of His-RGO/Ag NWs synthesized with the 10:1 $AgNO_3$:His-RGO w/w, 7.7:1 PVP:$AgNO_3$ molar ratio, at 170°C, reaction time of 6.5 h, PVP at Mw of 360 kDa, stirring rate of 600 rpm, by injecting His-RGO in the synthesis solution between the seventh and eighth injection of $AgNO_3$.

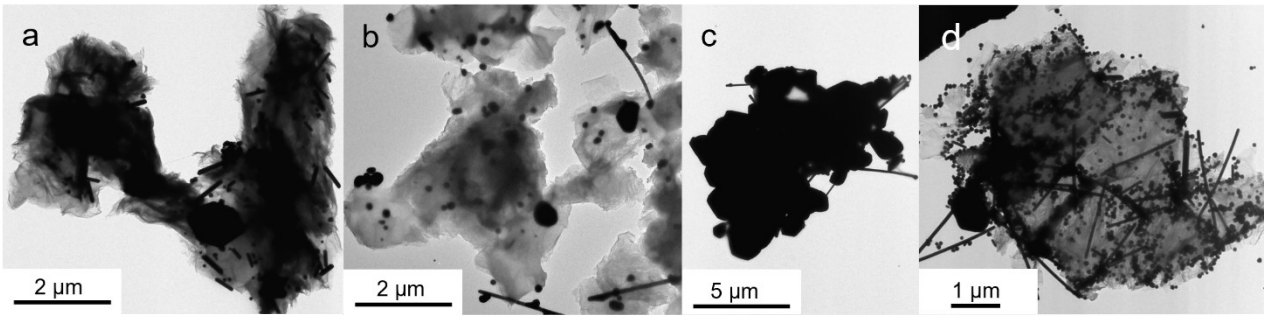

Figure S7. TEM images of His-RGO/Ag NWs synthesized with the 10:1 $AgNO_3$:His-RGO w/w, at 170°C, stirring rate of 600 rpm, time of reaction 6.5 h, injecting His-RGO between the seventh and the eighth injection of $AgNO_3$, by using (a) His-RGO isolated from a Milli-Q water solution at pH 11 and ζ-potential of –24.5±1.8 mV, with 7.7:1 PVP:$AgNO_3$ molar ratio and PVP 360 kDa, (b-d) His-RGO isolated from a Milli-Q water solution at pH 7 and ζ-potential of -20.1±1.5 mV, with (b-c) 7.7:1 PVP:$AgNO_3$ molar ratio and PVP 55 kDa and (d) 11.5:1 PVP:$AgNO_3$ molar ratio with PVP 360 kDa.

Figure S8 reports the UV-Vis absorption spectra and the TEM images of the His-RGO/Ag NWs hybrid nanocomposites synthesized by decreasing the $AgNO_3$:His-RGO w/w to 5:1 and stirring rate of the synthesis solution from 600 rpm to 200 rpm.

The hybrid nanocomposites achieved with the 5:1 $AgNO_3$:His-RGO w/w show the quadrupole resonance peak of the NWs at 355 nm, and the transversal plasmon peak not clearly detectable, because likely superimposed by the LSPR of spherical Ag NPs at 421 nm (Figure S8a). The TEM images show Ag NWs with mean length and diameter of 2.6 ± 0.9 µm and 40 ± 10 nm, respectively, and a high concentration of spherical Ag NPs (Figure S8b). Ag nodules are also observed (Figure S8b), and thus, to complete their conversion in NWs, the reaction time was increased to 7.5 h, and Ag NWs of 1.7 ± 0.9 µm and 60 ± 10 nm in mean length and diameter were observed (Figure S8c), with a quadrupole resonance peak at 355 nm (Figure S8a).

With the decrease in stirring rate of the reaction mixture from 600 rpm to 200 rpm, the hybrid nanocomposite shows the quadrupolar plasmon resonance and transversal plasmon peaks of Ag NWs at 355 nm and 383 nm, respectively, and a LSPR absorption peak of spherical Ag NPs at 417 nm (Figure S8d). The corresponding TEM images show NWs having mean length and diameter of 3.4 ± 0.9 µm and 60 ± 10 nm, respectively, in agreement with the shift of the transversal plasmon peak of the NWs towards higher wavelengths[1], spherical NPs, and nodules (Figure S8e). Increasing the reaction time to 7.5 h, the complete evolution of the nodules into NWs of mean length and diameter of 2.1 ± 0.5 µm and ca. 40 nm, respectively (FigureS8f) and quadrupolar plasmon resonance and transversal plasmon peaks at 353 nm and 386 nm, respectively were achieved (Figure S8d).

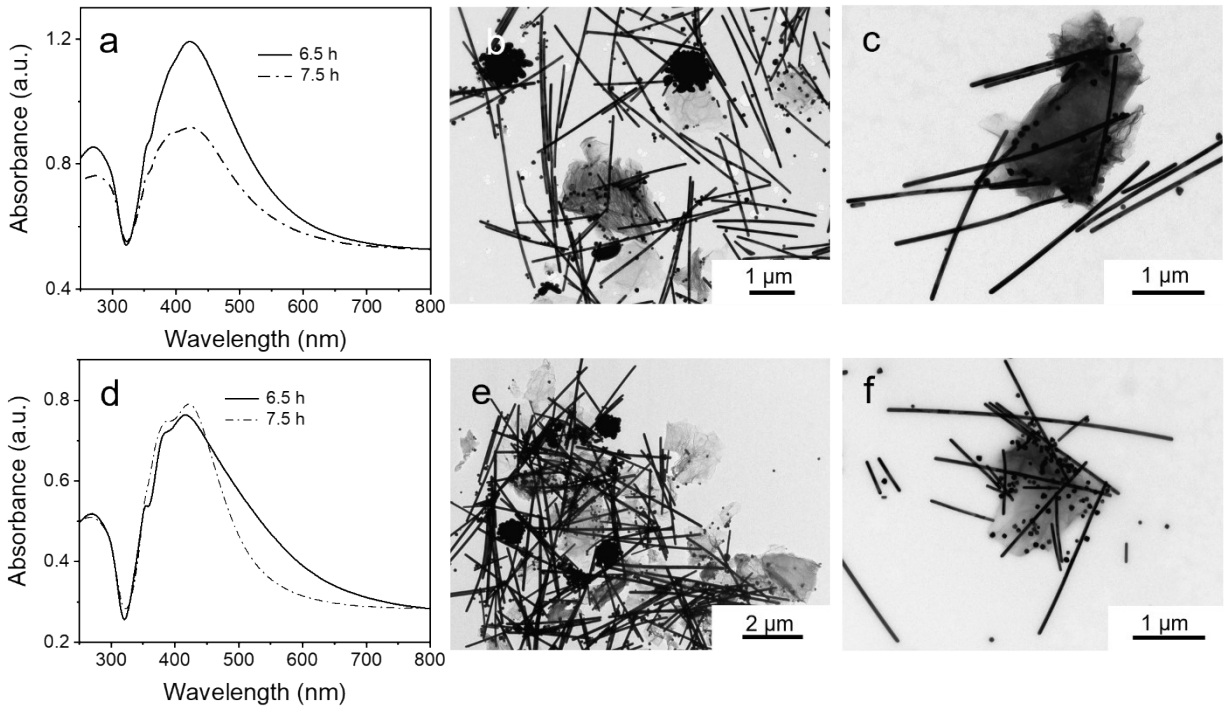

Figure S8. (a,d) UV-Vis absorption spectra and (b-c, e-f) TEM images of the hybrid nanocomposites synthesized with the (a-c) 5:1 $AgNO_3$:His-RGO w/w and stirring rate of 600 rpm and (d-f) 10:1 $AgNO_3$:His-RGO w/w and stirring rate of 200 rpm, at the 7.7:1 PVP:$AgNO_3$ molar ratio, 170°C, PVP of Mw of 360 kDa and at the reaction time of (a-b,d-e) 6.5 h (solid line) and (a,c,d,f) 7.5 h (dash-dot line), achieved injecting His-RGO between the seventh and eighth injection of $AgNO_3$. The absorption spectra of (a) and (b) were collected from ethanol dispersions 4 mg mL^{-1} in $AgNO_3$ and 2 mg mL^{-1} (a) and 1 mg mL^{-1} (b) in His-RGO.

The ATR-FTIR spectrum of the His-RGO/Ag NWs nanocomposite shows the stretching vibration of -OH (υ_{-OH}) moieties at 3322 cm^{-1}, which is also detectable in the spectrum of PVP at 3400 cm^{-1}, and that is ascribed to the cheto-enol equilibrium of C=O group in the pyrrolidine ring (Figure S9)[2]. In the spectrum of the hybrid nanocomposite are also detectable the symmetric and asymmetric stretching modes of -CH_2 ($\upsilon_{s,asCH2}$) at 2861 cm^{-1} and 2945 cm^{-1}, respectively that in the spectrum of PVP are located at 2882 cm^{-1} and 2969 cm^{-1}, and, in the spectrum of His-RGO, are instead at 2889 cm^{-1} and 2981 cm^{-1} (Figure S9). These results confirm the presence of PVP in the hybrid nanocomposite sample.

Going more into detail, the infrared spectrum of the nanocomposite shows a peak at ca. 1643 cm^{-1} accountable to the stretching of the C=O group ($\upsilon_{C=O}$) of PVP, the bending of CH groups (δ_{CH}) at 1367 cm^{-1} and the wagging C-N (υ_{C-N}) at 1280 cm^{-1}, that, in the spectrum of neat PVP, are at 1652 cm^{-1}, 1373 cm^{-1} and 1289 cm^{-1}, respectively (Fig. S9). In particular, the shift of the C=O group towards the lower wavenumbers provides evidence of the coordination of PVP at the (100) facets of the Ag NWs, and those of the stretching modes of -CH_2 ($\upsilon_{s,asCH2}$), bending of CH (δ_{CH}) and wagging of C-N (υ_{C-N}) towards lower wavenumbers demonstrate that these groups are closer to the Ag NWs surface[2].

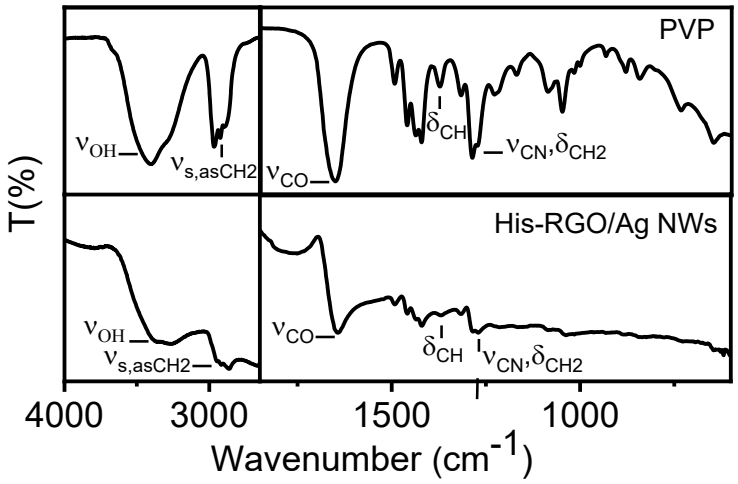

Figure S9. ATR-FTIR spectra of PVP (Mw= 360 KDa) and His-RGO/Ag NWs.

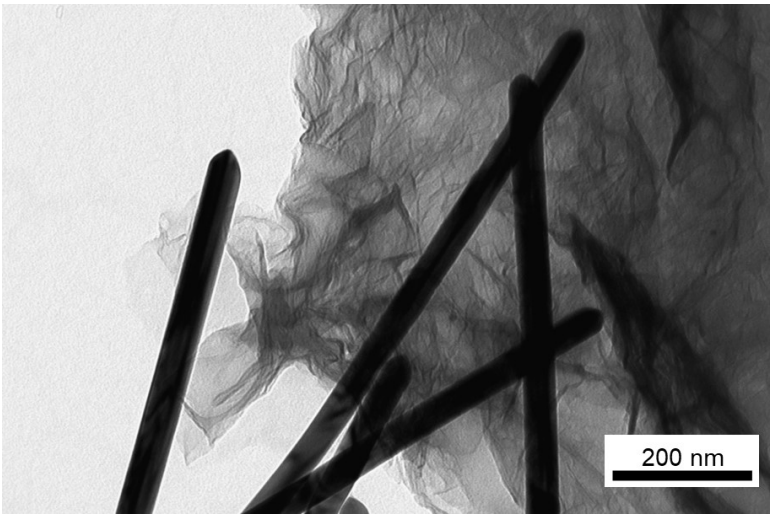

Figure S10. TEM images of His-RGO/Ag NWs synthesized with the 10:1 $AgNO_3$:His-RGO w/w, 7.7:1 PVP:$AgNO_3$ molar ratio, at 170°C, reaction time of 2.5 h, PVP at Mw of 360 kDa, stirring rate of 600 rpm, by injecting His-RGO in the synthesis solution between the seventh and eighth injection of $AgNO_3$.

References

1. E.-J. Lee, M.-H. Chang, Y.-S. Kim and J.-Y. Kim, *APL Materials*, 2013, **1**.
2. Y.-J. Song, M. Wang, X.-Y. Zhang, J.-Y. Wu and T. Zhang, *Nanoscale Research Letters*, 2014, **9**.