Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Hollow transition metal hydroxide octahedral microcages for single particle surface-enhanced Raman spectroscopy

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Supplementary Figures and Tables

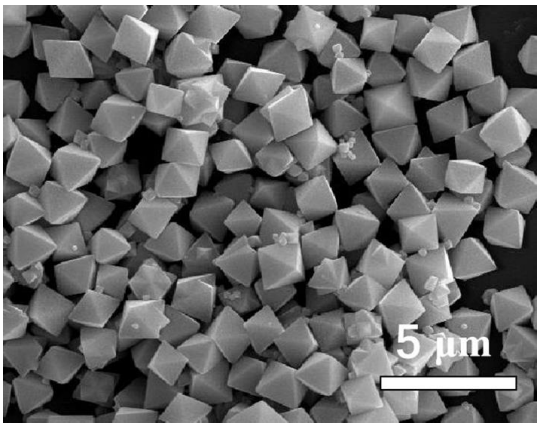

Fig. S1 SEM image of as-prepared precursor Cu_2O octahedron (1.5 μm).

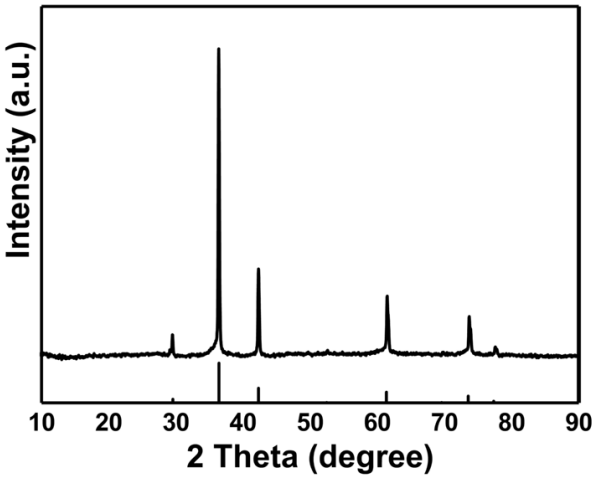

Fig. S2 XRD pattern of as-prepared precursor Cu_2O octahedron (1.5 μm).

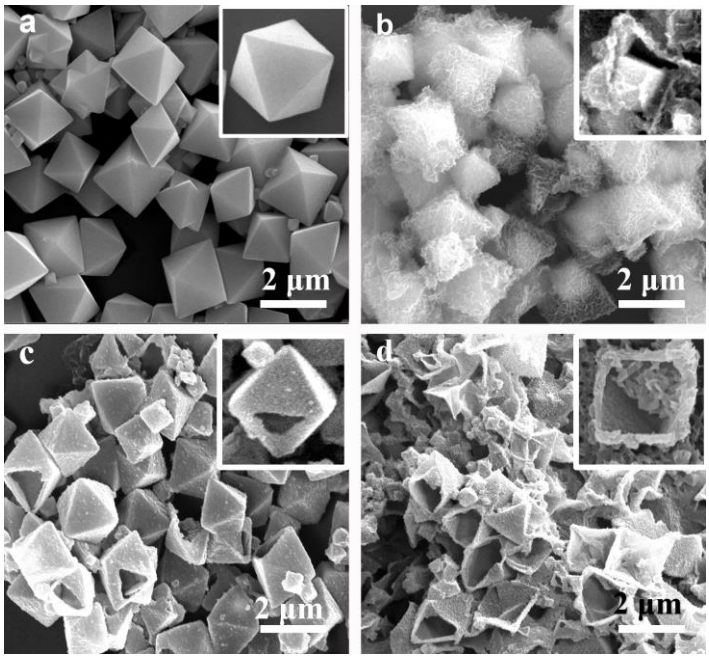

Fig. S3 SEM images collected at different reaction times: (a) 0 min, (b) 3 min, (c) 6 min, (d) 9 min. It can be clearly observed that the precipitation of transition metal hydroxide is synchronized with the dissolution of Cu_2O from a gappy particle (inset in b). As the reaction proceeds, Cu_2O core gradually disappears and the stacking of hydroxide nanosheets is gradually dense. The whole system is transformed from solid to hollow structure. When the reaction exceeds the optimal time of 9 min, the disappearance of template breaks the balance of the collaborative etching process, and the growth of hydroxides becomes scattered (inset in d).

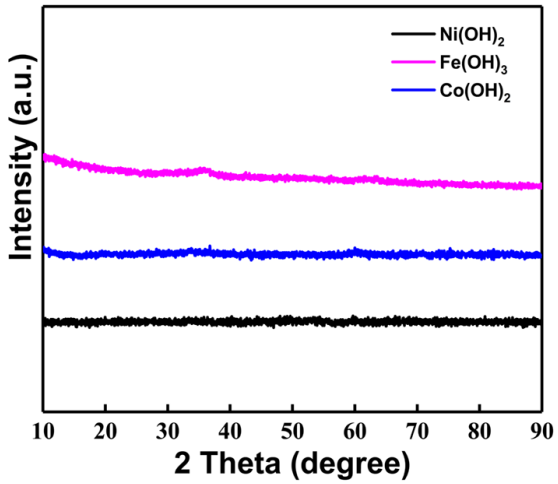

Fig. S4 XRD pattern of hollow $M(OH)_x$ (M=Fe, Co, Ni) octahedral microcages (1.5 μm) with Cu_2O as sacrificial templates.

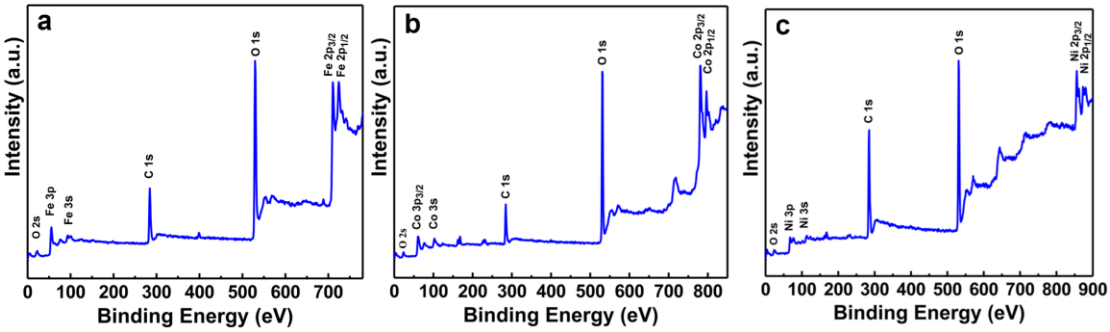

Fig. S5 Full range XPS spectra of the as-prepared (a) $Fe(OH)_3$, (b) $Co(OH)_2$, and (c) $Ni(OH)_2$.

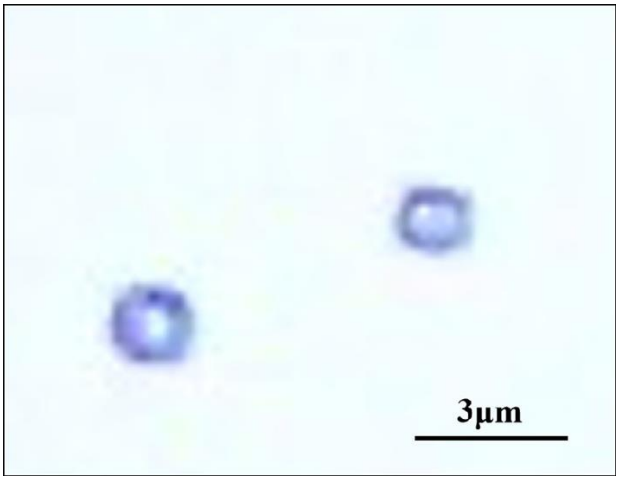

Fig. S6 Optical image of monodispersed $M(OH)_x$ micron-octahedron under Renishaw confocal Raman microscope.

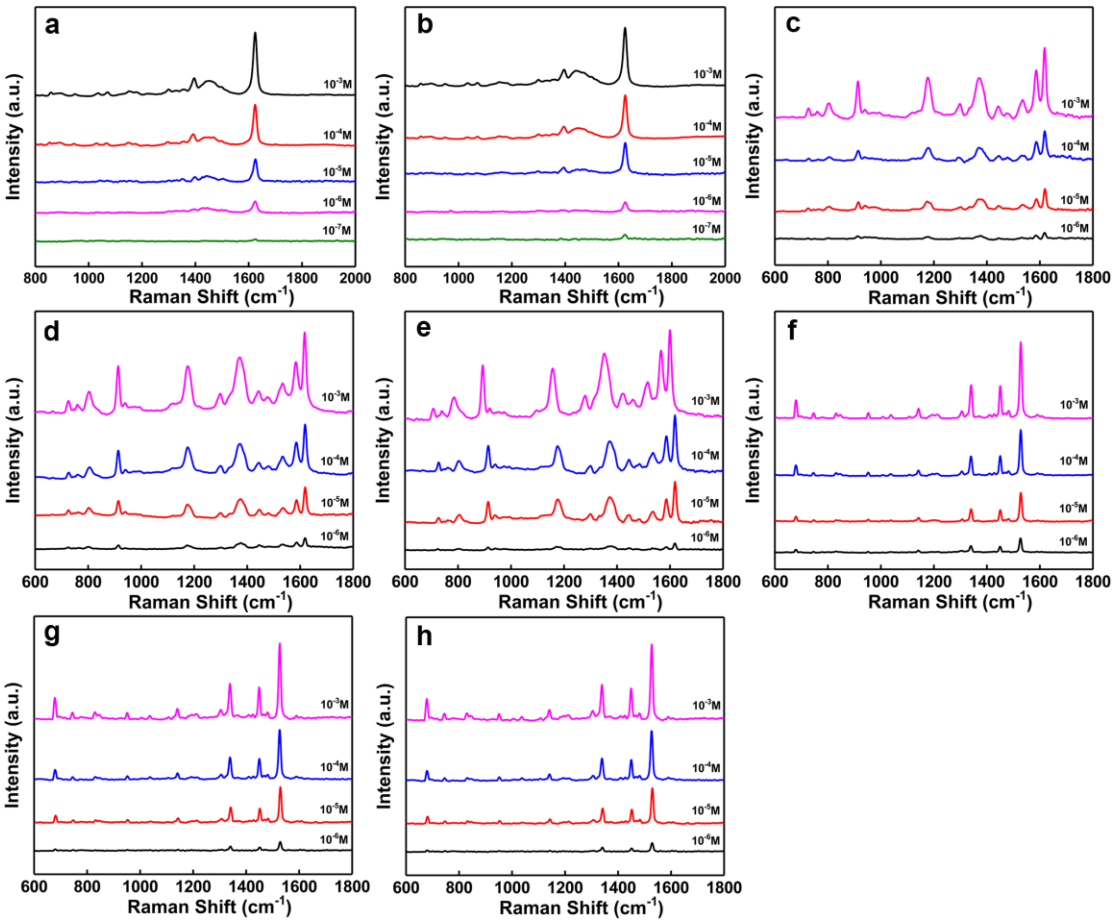

Fig. S7 Concentration-dependent SERS spectra of MB (b-c), CV (d-f) and CuPc (g-i) on $Fe(OH)_3$ (a, c and f), $Co(OH)_2$ (b, d and g), and $Ni(OH)_2$ (e and h) substrates under 532 nm laser excitation (148μw).

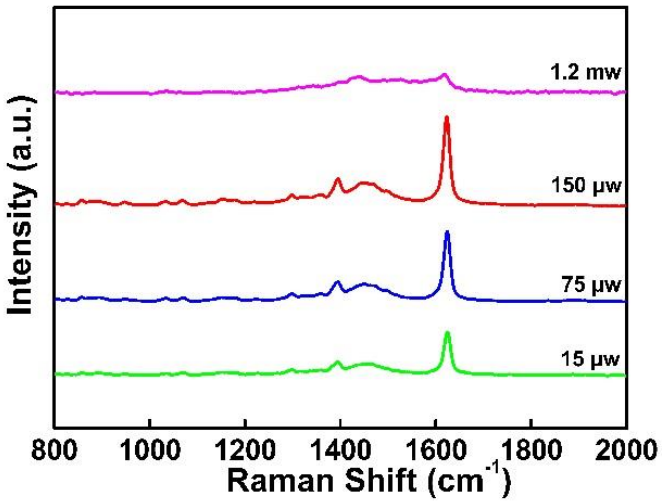

Fig. S8 Raman spectra of MB (10^{-5} M) molecules on $Ni(OH)_2$ substrates under different laser powers.

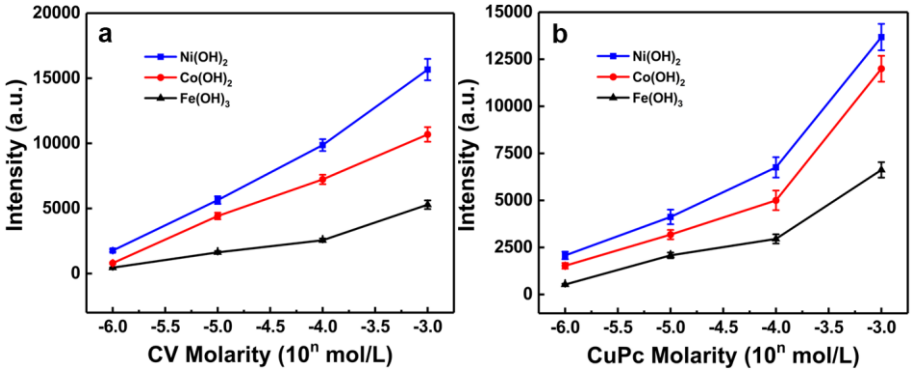

Fig. S9 (a) The Raman intensity of CV at 1618 cm^{-1} as a function of the molecular concentration on the $M(OH)_x$ substrate, (b) The Raman intensity of CuPc at 1528 cm^{-1} as a function of the molecular concentration on the $M(OH)_x$ substrate.

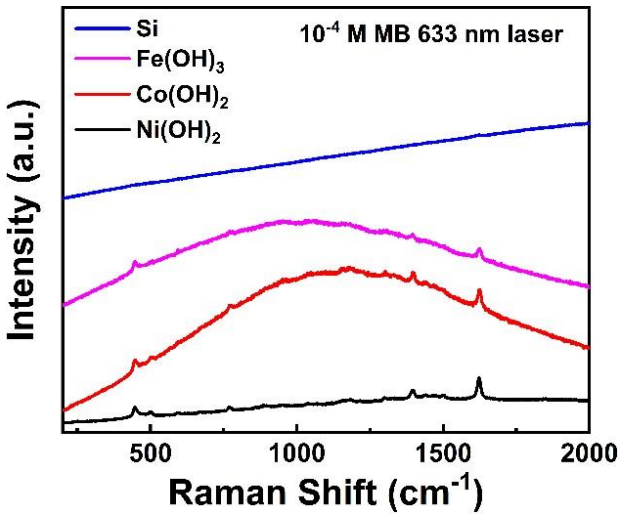

Fig. S10 Raman spectra of MB (10^{-4} M) molecules on three substrates collected with 633 nm laser.

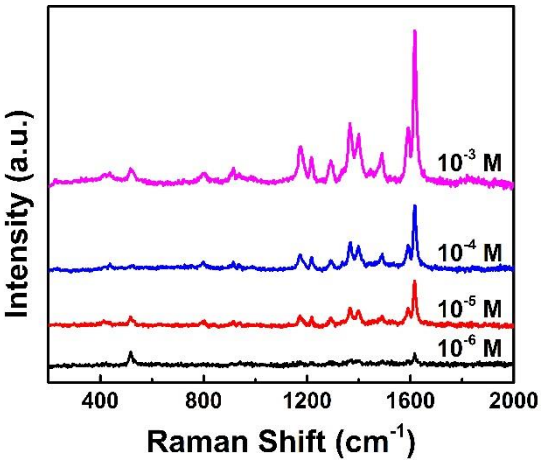

Fig. S11 Concentration-dependent SERS spectra of malachite green dye on the $Ni(OH)_2$ substrate collected with 532 nm laser.

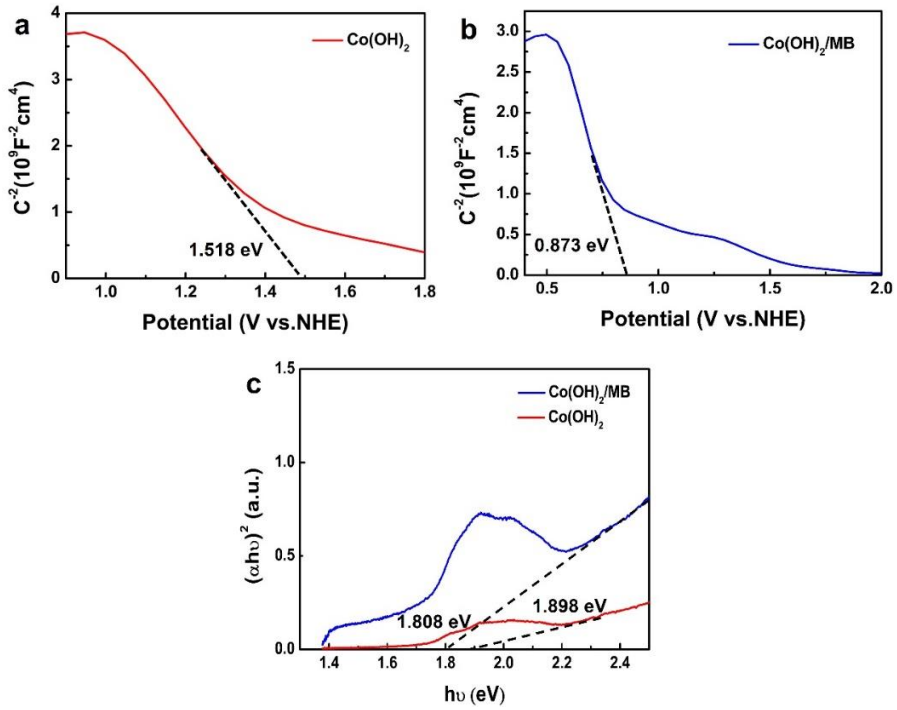

Fig. S12 Electrochemical Mott–Schottky (M–S) plots of $Co(OH)_2$ (a) and $Co(OH)_2$/MB (b). (c) Tauc plot of $Co(OH)_2$ before and after MB adsorption.

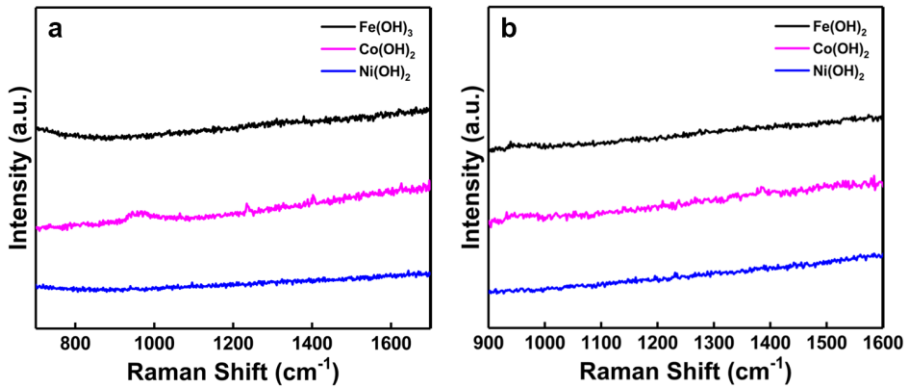

Fig. S13 SERS spectra of pyrene (a) and benzopyrene (b) on $M(OH)_x$ (M=Fe, Co, Ni) substrates at 532 nm laser excitation.

Table S1. Enhancement factor of some SERS-active metal hydroxides and metal oxides based on charge transfer mechanism.

Material(s)	Morphology	Probes	EF	Ref.
TiO_2	10 nm particle	4-MBA	10^3	1
ZnO	nanocage	4-MBA	10^5	2
Fe_2O_3	sphere	4-MBY	10^4	3
CuO	nanocrystals	4-MBY	10^2	4
$W_{18}O_{49}$	nanowire	R6G	10^5	5
$Co(OH)_2$	nanosheet	DTTCI	10^3	6
$Ni(OH)_2$	Hollow octahedra	MB	10^3	This work

Table S2. Deviation of binding energy after adsorption of MB molecule on different transition metal hydroxides substrate

Sample	N 1 s binding energy (eV)	
	Peak I	Peak II
$Fe(OH)_3$/MB	399.7	400.7
$Co(OH)_2$/MB	399.8	400.8
$Ni(OH)_2$/MB	399.7	401.9

Table S3. The Binding Energy of metal ions before and after adsorption of MB molecule

Metal ion	Fe^{3+}		Co^{2+}		Ni^{2+}	
Orbital split	$2P_{1/2}$	$2P_{3/2}$	$2P_{1/2}$	$2P_{3/2}$	$2P_{1/2}$	$2P_{3/2}$
Binding energy before absorbing MB (eV)	724.6 eV	711.0 eV	796.8 eV	781.0 eV	873.7 eV	855.7 eV
Binding energy after absorbing MB (eV)	725.2 eV	711.6 eV	797.4 eV	781.6 eV	874.2 eV	856.2 eV
The shift amount of binding energy Δ (eV)	0.6 eV		0.6 eV		0.5 eV	

Calculation of enhancement factor.

The enhancement factor was calculated according to the following equation (Angew. Chem. Int. Ed. 2017, 56, 9851 – 9855):

$EF = (I_{SERS} / N_{SERS}) / (I_{NR} / N_{NR})$

where I_{SERS} and I_{NR} are the Raman intensities of MB molecule on $M(OH)_x$ substrate and that without substrate (Si substrate in this study). N_{SERS} is the number of molecules absorbed on the $M(OH)_x$ substrate within the laser spot area, and N_{NR} stands for the number of molecules excited on the Si substrate. In order to obtain the value of N_{NR}, 100 μL of MB solution (1 mM) was dropped onto the Si wafer (0.5 × 0.5 cm^{-2}). N_{NR} can be estimated by the following equation：

$N_{NR} = c_{NR}V (A_{beam}/A) N_A$

where $A_{beam} = \pi(d/2)^2$ is the area of the focal spot of the laser, d is the diameter of the light spot estimated by $d = 1.22 \lambda/NA$, λ is the incident laser wavelength, i.e., 532 nm, and the numerical aperture (NA) of the objective lens NA = 0.75. Thereby, laser spot size is approximately 1.87 μm^2. A is the area of MB molecule layer which equal to the area of Si wafer (0.25 cm^2). N_A stands for Avogadro's constant. Therefore, N_{NR} equals to:

N_{NR} =40 μL × 0.001 mol / L × 0.59 μm^2 / 0.25 cm^2 × 6.02 × 10^{23} mol^{-1} =5.68× 10^8

Moreover, N_{SERS} is the number of absorbed molecules scattered in the area of laser beam, which can be estimated by the following equation:

$N_{SERS} = A_{beam}/\sigma$

where σ is the area occupied by a molecule of adsorbent at monolayer coverage, which is estimated to ~ 0.5 nm^2. It should be mentioned that the surface coverage must remain smaller than one monolayer when using this equation. The concentration of the MB solution was controlled lower than 1×10^{-4} M to prevent the supersaturation adsorption of probe molecule onto $M(OH)_x$ substrate. N_{SERS} is calculated to be 1.18×10^6. The intensity at 1626 cm^{-1} of MB molecule on Si and the intensity at 1624 cm^{-1} on $Ni(OH)_2$ substrate were used to calculate EF values. Here I_{SERS} =27000, and I_{NR} = 5530 (Fig. S14). By substituting these values into the equation, EF is calculated to be 2.35×10^3.

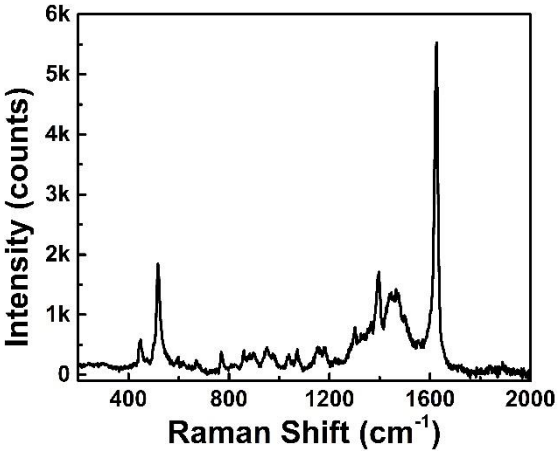

Fig. S14 The normal Raman spectrum of pure MB (1 mM) on Si substrate.

References:

1. L. B. Yang, X. Jiang, W. D. Ruan, B. Zhao, W. Q. Xu and J. R. Lombardi, J. Phys. Chem. C, 2008, 112, 20095–20098.
2. X. Wang, W. Shi, Z. Jin, W. Huang, J. Lin, G. Ma, S. Li and L. Guo, Angew. Chem., Int. Ed., 2017, 56, 9851-9855.
3. X. Q. Fu, F. L. Bei, X. Wang, X. J. Yang and L. D. Lu, J. Raman Spectrosc., 2009, 40, 1290–1295.
4. Y. Wang, H. Hu, S. Jing, Y. Wang, Z. Sun, B. Zhao, C. Zhao and J. R. Lombardi, Anal. Sci., 2007, 23, 787–791.
5. S. Cong, Y. Yuan, Z. Chen, J. Hou, M. Yang, Y. Su, Y. Zhang, L. Li, Q. Li, F. Geng and Z. Zhao, Nat. Commun., 2015, 6, 7800.
6. Q. Zhao, G. Liu, H. Zhang, Y. Li and W. Cai, Adv. Mater. Interfaces, 2018, 5,1700709.