

GERMANY/HONG KONG JOINT RESEARCH SCHEME
THE PROJECT REPORT
(for Project Completion)

Project Number: G_HK005/12

Title

Effect of charge-transfer excitations on Surface Enhanced Raman Spectroscopy of an aromatic amine on Ag nanoparticles

Particulars

	Hong Kong team				German team	
Name of Project Co-ordinator (with title)	Rui-qin Zhang				Thomas Niehaus	
Name of Co-Investigator (if any)						
Institution or Institutional affiliation	<input checked="" type="checkbox"/>	CityU	<input type="checkbox"/>	HKU	<input checked="" type="checkbox"/>	University of <u>Regensburg</u>
	<input type="checkbox"/>	CUHK	<input type="checkbox"/>	HKUST	<input type="checkbox"/>	Others: _____
	<input type="checkbox"/>	HKBU	<input type="checkbox"/>	LU		
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Other project team members (if any)	Qi Wu				Vitalij Lutsker	

Funding Period

	1 st year	2 nd year (if applicable)
Start Date	01-Jan-2013	01-Jan-2014
Completion Date	31-Dec-2013	31-Dec-2014

Objective(s) as per original application

1. Method development to model the electronic excited states of large metal clusters bound to molecules. This involves the implementation of range-separated exchange-correlation functionals in the TD-DFTB framework.
2. Investigation of energetical and spatial localization of surface plasmons in isolated metal clusters
3. SERS impacting factors examination: To probe the dependence of SERS signals on shape, size and distribution of the Ag nanoparticles, as well as molecule-metal distance.

Details of Report [Please attach relevant document(s)]

i) Outline of proposed research and results obtained

Based on calculations using time-dependent density functional theory (TDDFT), we conducted detailed analyses of the surface-enhanced Raman scattering (SERS) of pyridine adsorbed on 13-atom icosahedral $M@Au_{12}$ and $M@Ag_{12}$ ($M = Mo, W$) clusters. Surprisingly, we find that, although the SERS enhancements for all complexes can reach the order of 10^4 , the signals of pyridine on $M@Ag_{12}$ at charge transfer (CT) transition excitations are twice as much as that of pyridine on $M@Au_{12}$, and the corresponding energies used for SERS excitations are significantly different in the range of 1.63-2.10 eV in the low-energy region. The interactive modulation between the core and shell can produce varying strong CT transitions from metal clusters to pyridine, which tune the SERS enhancements with altered optical properties. The complexes of pyridine on silver-caged clusters are more easily influenced by the tunability of the core than that of pyridine on gold-caged clusters.

ii) Significance of research results

Our analyses are expected to provide a theoretical basis for experimentally synthesizing multi-component SERS substrates and exploring the dependence of SERS enhancement on the synergies between the different components in core@shell binary metal clusters.

iii) Research output

1. Lei Chen, Yang Gao, Yingkun Cheng, Yanbin Su, Zhigang Wang, * Zhengqiang Li,* and Rui-Qin Zhang,* "Strong Core@shell Dependence in SERS of Pyridine on Stable 13-Atom Silver-Caged Bimetallic Clusters", **PCCP**, revised (2015) **119**, 17429-17437 (JUL 30 2015)
2. Yan Meng, Qi Wu, Lei Chen, Sonam Wangmo, Yang Gao, Zhigang Wang,* Rui-Qin Zhang,* Dajun Ding, Thomas Niehause and Thomas Frauenheim, "Signatures in vibrational and UV-visible absorption spectra for identifying cyclic hydrocarbons by graphene fragments", **Nanoscale** **5** (24), 12178-12184 (2013)
3. Yan Meng, Xing Dai, Minsi Xin, Chuanjin Tian, Hang Liu, Mingxing Jin, Zhigang Wang,* and Rui-Qin Zhang*, "Environmental confinement induced stability enhancement of chiral molecules", **Chemphyschem.** **15**(13):2672-5 (Sep 15, 2014)

iv) Potential for or impact on further research collaboration

In this project, we have conducted a detailed investigation of the computed absorption spectrum to answer the question in which energy range resonance enhancement due to charge-transfer is expected and to which extent. The collaboration will prompt us for further study on the nature of these excitations to reveal their strong dependences on the metal particle size, its shape, as well as the type of metal-molecule bonding.