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Journal Name

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.ora/

ARTICLE

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One Pot Green Synthesis of Polyaniline Coated Gold Nanorods and its Applications

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Morphology controlled high aspect ratio worm like polyaniline (PANI) layer coated Au-nanostructures (Au/PANI) have been successively synthesized by *in-situ* polymerisation techniques using aniline as a monomer with HAuCl₄ as an oxidising agent in absence and presence of citric acid (CA). Synthesized composites were characterized by HRTEM, FESEM, XRD, XPS, UV-Vis and FTIR study. Spherical morphologies are seen in absence of CA and Au-nanoparticles are coated by PANI thin layer with thickness ~30 nm. In presence of CA as well as depending upon CA to aniline molar ratio, morphology varies from irregular assemble to regular fiber to spherical like nanostructures. The nanostructures show fibrous morphology with an average diameter of ~100 nm and lengths of more than 5 µm when CA to aniline molar ratios are 1.0 and 0.2. When the ratios are 2.0 and 0.1, the nanostructure represents the granular like morphology. Nanofiber formation takes place by the assembly of the CA capped tiny Aunanorods in presence of aniline during the polymerisation and all Au-nanorods are finely coated by PANI thin layer of thickness ~5 nm. Importantly, fibrous Au/PANI nanostructures show superior catalytic activity than spherical/irregular Au/PANI nanostructures towards toxic aromatic nitro compounds reduction like 4-nitrophenol (4-NP), 4-nitroaniline (4-NA), 2,4-dinitrophenol (2,4-DNP) and 2,4,6trinitrophenol (2,4,6-TNP). It is because of the coating thickness of PANI over on Au-nanoparticles in fibrous Au/PANI nanostructures as well as enhanced surface area.

Introduction

In recent years fabrication of nanostructures with controlled morphology is challenging to scientists because dimensionality plays an important role for determining material properties. One-dimensional (1D) nanostructure including nanorods, fibers, wires and tubes have attracted more attention due to their unique optical, electronic properties resulting great attention in many potentials applications like field effective transistor,^{1,2} quantum wire laser,³ electronic memory devises,^{4,5} catalyst^{6,7} etc. Making of nanostructure material contain electrically conducting polymers and metal nanoparticles are attractive field of research nowadays due to their important physical properties and potential application in molecular memory device, batteries, display devices, bio-chemistry⁸, etc. Among all conductive polymer PANI is the most popular conductive polymeric materials^{9,10} due to its easy synthesis, good environmental stability,¹¹ low cost of the raw/starting materials, large range of conductivity, high thermal stability etc. Among the metal nanoparticles, Au-nanoparticles has been extensively studied in the scientific community due to its exclusive catalytic¹²⁻¹⁴ and unique optical properties.¹³ In-situ technique is one of the best techniques for synthesis because: a)

single step reaction, b) high percentage of yield and c) no need to step by step purification.¹⁵

Formation of Au/PANI nanostructures by soft template method¹⁷⁻¹⁹ is going through a series of step such as chemical reactions, nucleation and precipitation. Each and every step is influenced by many experimental parameter like external materials (additives/ dopant), concentration of starting and any externally applied materials, reaction temperature, reaction time etc. Actually nucleation step is a vital role for formation of nanosphere and nanofiber of PANI in solution state.²⁰⁻²¹ Homogeneous nucleation reveals the nanofiber morphology of PANI in bulk solutions while heterogeneous nucleation leads to irregular or/and nanosphere like morphology of PANI.²⁰ The aspect ratio of Au/PANI nanostructures also depend on the concentration of controlling agent, reaction temperature, pH and reaction time.^{10,16}

Here we report a simple solution mixing *in-situ* method for Au/PANI nanostructure synthesis at room temperature using HAuCl₄, CA and aniline. HAuCl₄ acts as an oxidising agent as well as proton donor to PANI and CA acts as a capping agent for Au-nanoparticles synthesis as well as secondary dopant for PANI (ES). The morphology of the nanostructure has tune by changes the molar ratio of CA to aniline. Nanostructures will be the regular nanofibers (worm) like morphology when CA to

aniline molar ratio 1.0 to 0.2 and irregular agglomerated morphology for 2.0 and 0.1. The mechanism of the nanostructure formation also established from HRTEM studies and result showed that CA play an important role for worm like nanostructure formation. Optimise the reaction condition for nanofibers formation by time dependent UV-Vis and HRTEM studies. The synthesized nanostructure showed good catalytic efficiency and recyclability to several nitro compounds reduction in aqueous medium. In addition the catalytic efficiency of worm like nanofibers is much more than that of the agglomerated structures under identical condition.

Experimental Details

Materials

Aniline was distilled under reduced pressure and store at 5 °C in dark place and Sodium borohydride (NaBH₄) purchased from Merck chemicals. Au(III) chloride trihydrate (HAuCl₄, 3H₂O, ACS reagent, \geq 49.0% Au basis) and citric acid (ACS reagent, \geq 99.5%) were purchased from Sigma-Aldrich, and used without further purification. The nitro aromatics compounds (4-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol and 4-nitroaniline) were purchased from Loba Chemicals, Mumbai. All solutions were prepared in deionised water (18 M Ω cm, Millipore Mili Q water).

Instruments

To observe the surface morphology of composites, little amount of prepared composites dispersed in Mili Q water then drop casted on a glass cover slip and dried, at room temperature. We used JEOL, JSM 6700F instrument, operating at 5 kV. To reduce the surface potential, samples were coated with platinum for 90 s due to accumulation of electrostatic charge.

The electron microscopy of Au/PANI nanostructure were carried out by using HRTEM (JEOL, 2010EX), image were taken using a CCD at an accelerating voltage of 200 kV. Samples were spreaded over on a 200 mesh Cu-grid coated with a holey carbon support film.

UV-Vis spectra of Au/PANI samples were recorded by using a Hewlett-Packard UV-Vis spectrophotometer (model 8453) in a 1.0 cm path length quartz cell.

XRD measurements were performed by using a Bruker AXS diffractometer (D8 advance) using CuK α radiation (λ =1.54 Å), a generator voltage of 40 kV and a current of 40 mA. The scanning rang of the samples 2 θ =15-85° the scan rate was 1s/step with a step width of 0.02.

The FTIR spectra were carried out in a FTIR-8400S instrument (Shimadzu) using KBr pellets of the samples.

XPS was performed using a focused monochromatized Mg- K_{α} X-ray source (1253.6 eV) in Omicron Nano-Technology 0571 XPS instrument.

Synthesis of Au/PANI@0.0 composite:

An aqueous solution of HAuCl₄ (1 mM, 10 mL) was taken in a culture tube then added 100 μ L of distilled aniline (to maintain HAuCl₄ to aniline molar ratio = 1:1) with constant stirring for 30 min then keep it in dark place without stirring for 12 hs to get spherical like composite called Au/PANI@_{0.0} composite.

Synthesis of CA stabilized Au seed solution

In the typical experiment 10 mL of 1 mM CA aqueous solution was mixed with 1 mM HAuCl₄ aqueous solution (v/v=1:1) in a culture tube equipped with a magnetic stirrer at room temperature (25 °C). After 1 h solution colour changed from greenish yellow to transparent pinkish violate, this solution (Au-60) actually considered as a active seed solution for Au/PANI formation.

Synthesis of Au/PANI@_{2.0}, Au/PANI@_{1.0}, Au/PANI@_{0.2} and Au/PANI@_{0.1} composite:

To making Au/PANI nanofiber, 20 mL Au-60 aqueous solution was taken in a culture tube then different amount (in μ L) of distilled aniline monomer was added (Table S1) to Au-60 aqueous solution with constant stirring until dissolving the aniline at room temperature (25 °C). After adding aniline, solution colour changed pinkish violate to deep blue to black immediately indicating Au/PANI composite started to form. The reaction mixture was kept in dark place without stirring for 12 hs. Finally products were collected by centrifugation at rpm 8000 and washed with water several times finally dry under vacuum at 60 °C temperature to obtain a dark powder of Au/PANI-composites.

Catalytic activity towards nitro compound reduction

For monitoring the reduction process, prepared yellow aqueous solution of aromatic nitro phenols compounds (4-nitrophenol, 4-nitroaniline, 2,4 di-nitrophenol, 2,4,6-tri-nitro phenols) of 1 mM and 3 mM concentration of ice cold NaBH₄ solution. Then in a quartz UV cell of 1 cm path length took 2 mL of water and added 100 μ L of aromatic nitrophenols compounds, water dispersed Au/PANI composites subsequently added Au/PANI (~0.3 wt %) as a catalyst then immediately added 100 μ L of 3 mM NaBH₄ solution. Now solution was quickly subjected to UV-Vis measurement for monitoring reduction processes.^{6-7,22}

Results and Discussion

Morphological Studies

Nanostructures of Au/PANI were prepared with different molar ratio of HAuCl₄ to aniline and were checked by FESEM observations (Fig.1). Spherical morphology of Au/PANI@_{0.0} (in absence of CA) was clearly seen in Fig.1a at equal molar ratio of HAuCl₄ to aniline. Whereas in presence of CA and at the equal molar ratio of HAuCl₄ to aniline, worm-like nanofiber morphology was observed. Important observation signified that there were tremendous effects of CA on the formation of Au/PANI nanostructures. It was also seen that morphology of Au/PANI depended on the molar ratio of CA to aniline. Fibrous

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network of Au/PANI were formed at the molar ratio of 1.0 and 0.20 (Fig.1c-d) and spherical aggregates with irregular aggregates were observed at the molar ratio of 2.0 and 0.10 (Fig.1b and Fig.1e). Without CA, aniline was directly added to HAuCl₄ aqueous solution at the identical reaction condition (Table S1) where Au³⁺ oxidised aniline to PANI and itself was reduced to Au¹⁺ ions that disproportionated to Au-nanoparticle and Au³⁺ ions (Scheme1).²³⁻²⁴ HAuCl₄ in presence of CA starts to form the CA capped Au-nanoparticle (Fig.S1). The surface of the Au-nano contains numerous –COOH groups which interact with aniline monomer to form anilinium ions which were polymerised in presence of Au³⁺ ions originated from the disproportion reaction. To minimise surface energy, PANI formed thus arranges one dimensionally to form worm-like nanofibers (Fig.1c and 2c).

Subsequent HRTEM images (Fig.2) unanimously support the earlier observations made by FESEM results. Au/PANI nanofibers with uniform diameter of 100–110 nm and lengths of more than 5 μ m were formed when the CA to aniline molar ratio was 1.0. The nanofibers were worm-like and growth of the fibers started from a spherical head (Fig.3a). The aspect ratio of the nanofibers decreased by the changing molar ratio 0.2 to 0.1 and finally small Au-nanoparticles covered with PANI layer were noticed. From the microscopic studies, we can optimize that 1:1 molar ratio of CA to aniline was required condition to prepare the high aspect ratio Au/PANI nanofiber. A typical high magnified image (Fig.3b and 3c) showed that tiny shaped Au-nanoparticals were assembled together to form a high and uniformly dispersed Au-nanofibers, which were coated by thin PANI layer. EDX studies from FESEM (Fig.1f) and from HRTEM (Fig.2f) indicated the presence of carbon, oxygen nitrogen and higher content of Au in the Au/PANI@1.00 nanofibers. By considering the contrast differences between Au-nanoparticle and coated PANI, thickness of PANI layer on Au was measured. It was found that in absence of CA the thickness of the PANI layer over on Au-nanoparticals was ~30 nm and in presence of CA it was ~5 nm. Dark field image (Fig.3e) and mapping image (Fig.3f) of the nanofibers cited the presence of dispersed Au-nanoparticles into Au/PANI nanostructures. Careful observation revealed that there tiny Au nanorods (Fig. S4c) are present instead of spherical shaped Aunanoparticles. FFT image produced lattice of distance 2.38Å that was exactly matched with (111)-plane of Au (Fig.5) and selected area electron diffraction (SAED) also confirmed the presence other plane of Au.



Fig.1 Influence of CA to aniline molar ratio on overall morphology in FESEM image of Au/PANI composites: (a) Au/PANI $@_{0.0}$; (b) Au/PANI $@_{2.0}$; (c) Au/PANI $@_{1.0}$ (d) Au/PANI $@_{0.2}$; (e) Au/PANI $@_{0.1}$; (f) EDX pattern, (where CA to HAuCl₄ molar ratio was 1:1, at room temperature (25 °C) for 12 h).

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Fig.2 Effect of CA to aniline molar ratio on TEM image of Au/PANI composites: (a) $Au/PANI@_{0.0}$; (b) $Au/PANI@_{1.0}$ (c) $Au/PANI@_{1.0}$ (d) $Au/PANI@_{0.2}$; (e) $Au/PANI@_{0.1}$; (f) EDX pattern, (where CA to HAuCl₄ molar ratio was 1:1, at room temperature (25 °C) for 12 h).



Fig.3 (a) High magnified head morphology of Au/PANI composite; (b) two fiber are connected by a thin PANI layer with clear contrast between Au-nanoparticals and PANI and polymer layer depth; (c) \sim 5 nm PANI film thickness on Au-nanoparticles; (d) layer pattern of Au-nanoparticles with SAED pattern; (e) dark field image of Au/PANI fiber; (f) corresponding mapping images shows presence of Au.



Scheme1 Chemical reaction of Au/PANI nanostructures synthesis.



Fig.4 UV-Vis spectra of different Au/PANI composites in water at room temperature (25 °C).

UV-Vis spectra of Au/PANI composites (Fig.4) have three absorptions peak centered at 284, 450, ~600 and a broad peak ~750 nm having extended tail in NIR region. Three peaks are assigned to π - π * transition of benzenoid ring, polaron- π * and π polaron transition of PANI, respectively.^{10,16} Surface plasmon resonance band of the Au nanoparticles is appeared at ~600 nm in the Au/PANI composites.^{25,26} Whereas, CA stabilized Au nanoparticles produces band at 545 nm with spherical particles size ~200 nm (Fig. S1). Red shift (~55 nm) of plasmon resonance band of Au in the Au/PANI composite primarily indicates the presence of tiny Au-nanorods (Fig.S4c) already supported by HRTEM observation (Fig.3d) ²⁵

XRD Study

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Au/PANI@	a (111) (2	00)	(22	0)	(311)	
Au/PANI@	, (111) ,			(22		(311)	(222)
Au/PANI@	• (111)			(220)		(311)	(222)
Au/PANI@2 PAN	111) 1			(0220)	Ì	(115)	(222)
Au/PANI@ ₀ PAN	° 1 (III)			(220)		(311)	(222)
20	30	40	50	60	70		0
darad VI		2	θ/ deg	ree	IQ	۸.	./D

Fig.5 Powdered XRD pattern of $Au/PANI@_{0.0}$, $Au/PANI@_{2.0}$, $Au/PANI@_{1.0}$: $Au/PAN@_{0.2}$ and $Au/PANI@_{0.1}$ composites.

In-situ synthesis of Au/PANI composites and presence of Au in PANI matrix are further characterized by X-ray



XPS Study

X-ray photoelectron spectroscopy (XPS) was used to study Au-NP formation (Fig. 6). The Au/PANI composite (Fig.6a) shows XPS signals at ~59, 85.6, 89.3, 110, 337.5, 355 and 547.5 eV respectively for Au (5p_{3/2}, 4f_{7/2}, 4f_{5/2}, 5s, 4d_{5/2}, 4d_{3/2} and 4p_{3/2}), carbon (at 287.5 eV, 1s), nitrogen (at 502.5 eV, 1s) and oxygen (at 535 eV, 1s).^{29,30} The binding energies for Au doublet are 85.6 eV (4f_{7/2}) and 89.3 eV (4f_{5/2}), peak to peak distance ~ 3.7 eV.³¹ The presence of Au 4f doublet (4f_{7/2} and 4f_{5/2}) has confirmed that Au-nanoparticles are formed and present in metallic (Au⁰) state. The absence of 2p_{3/2} electron signal at 197-200 eV indicate that Au is present in metallic state (Au⁰) and there is no possibility of the presence of AuCl₄⁻ (Au³⁺), AuCl₂⁻ (Au¹⁺) in the Au/PANI composite.³¹



Fig.6 (a) X-ray photoelectron spectra for $Au/PANI@_{1.0}$ composite synthesized by scheme1 and (b) represent Au^0 4f doublet (4f_{7/2} and 4f_{5/2}) of Au-nano produce in scheme1.

FTIR study

The Au/PANI composites was further characterized by FTIR spectroscopy Fig. 7. FTIR Spectra show characteristic bands of PANI at ~3435 cm⁻¹ is for N-H stretching, 1630 cm⁻¹ (consigned to the C=C stretching of the quinoid rings), 1480 cm⁻¹ (for C=C stretching of benzenoid rings), 1306 cm⁻¹ (C-N stretching mode), and 1143 cm⁻¹ (N=Q=N, Q representing the quinoid ring).^{10,16}



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Fig.8 Time dependent UV-Vis spectra of Au-nano and Au/PANI composite where aniline addition time is different: (a) 1h.; (b) 2h.; (c) 3h.; (d) 4h.; (e) 5h.;.(f) 12h.; All cases HAuCl₄ to aniline molar ratio is 1:1, and CA to HAuCl₄ molar ratio = 1:1, CA: aniline molar ratio is 1:1.

To further insight into the mechanism of formation of nanofiber, series of time dependent UV-Vis experiments were performed with seed solution (CA to HAuCl₄ molar ratio was 1.0). 1 mM aniline was added to the seed solution at different time interval (1 h, 2 h., 3 h., 4 h., 5 h. and 12 h.) and spectra were recorded. In absence of aniline (i.e. seed solution only), UV-Vis spectra (Fig.8) have two absorption bands at 220 nm for Au³⁺ species and 545 nm for surface plasmon resonance (SPR) peak of Au⁰. Subsequent HRTEM showed the presence of CA stabilised Au-nanoparticles (Fig.S1a). With time, the plasmon resonance peak is not shifted, but intensity enhances, indicating gradual increase of Au⁰ in the solution. The intensity of Au³⁺ peak (at 220 nm) decreases with time and after 4h the peak of Au³⁺ vanishes (Fig.S5) showing that formation of Aunano completes within 4h. In other words, it means that Au³⁺ ionwhich are essential for the oxidation of aniline to PANI, are available up to 4 h (Fig.8a-d). In presence of aniline and up to 4h, the formation of PANI is taking place as it is evidenced from the presence of π -polaron transition of PANI at ~750 nm as well as SPR peak of Au⁰ at 575nm. Significantly, it is shifted to higher wavelength with respect to 545 nm in seed solution. After 4h (Fig.8e-f), the peak of π -polaron transition of PANI is absent, After 4h, the π -polaron peak of PANI disappear, i.e., no polymerisation occurs after 4h due to the absence of Au³⁺ ions in solution (Fig.5e). To achieve a nanofibre of higher aspect ratio, seed solution (Au-60) was chosen. This is done to eradicate unwanted structures of Au (hexagonal, triangle, irregular Au-nano particle) (Fig.S2a and S3b).

Application of Au/PANI as hetero-catalysts for toxic aromatic nitro-compounds reduction

The catalytic reduction of toxic aromatic nitro-compounds to the corresponding amino-compounds derivative by $NaBH_4$ in the presence of heterogeneous Au/PANI catalyst, was selected as a model reaction to examine the catalytic activity as well as recyclability of Au/PANI composites.

UV-Vis spectra and change of concentration of 4nitrophenol compounds with time in presence of different Au/PANI nanostructures as a heterogeneous catalyst and NaBH₄ as a reducing agent illustrate in Fig.9. The absorption peak of 4-nitrophenol is centred at 317 nm, after addition of freshly prepared ice cold NaBH₄ solution; the absorption peak is shifted to 400 nm. It indicates the formation of 4nitrophenolate ions in the solution (Fig.S6). The peak centred at 400 nm for 4-nitrophenolate ion is gradually decreased as the reduction proceeds in the presence of catalyst (Au/PANI composites).^{6,22} With different Au/PANI nanostructures, the reaction rate depends upon thickness of PANI layer over on Au-nanoparticals (Fig.9f). In addition, the new absorption peak at 300 nm emerges and the intensity gradually increases owing to the formation of 4-aminophenol in the medium. Au/PANI@1.0 and Au/PANI@0.2 have excellent rate of the reduction compared to Au/PANI@0.0 nanostructures. It is possibly because of thinner layer of PANI (~5 nm) in Au/PANI@_{1.0} and Au/PANI@_{0.2} than that of Au/PANI@_{0.0} (~30 nm).

Thinner coating of PANI in Au/PANI@_{1.0} nanostructures facilitates the diffusion of nitrophenols that get easy contact to the Au-nano surface (Fig.10) to enhance the rate of reduction.



Fig.9 UV-Vis spectra of 4-NP reduction presence of NaBH₄ catalysed by (a) Au/PANI $@_{0.0}$ (b) Au/PANI $@_{1.0}$ (c) Au/PANI $@_{1.0}$ (d) Au/PANI $@_{0.2}$ (e) Au/PANI $@_{0.1}$ (f) rate of all reaction in water at room temperature (25 °C).

Au/PANI@_{1.0} has better catalytic activity compared to other composite towards 4-nitrophenol reduction. Reduction of other three aromatic nitro compound, 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrophenol (2,4,6-TNP)^{32,33} has been also achieved by Au/PANI@_{1.0} as a catalyst and NaBH₄ as a reducing agent (Fig.S7-S9).



Fig.10 Effect of PANI layer over on Au-nanoparticles on catalytic activity.

Conclusions

So we successfully synthesized PANI coated Au-nano with spherical and worm like morphology by changing CA to aniline molar ratio. Polymer (PANI) layer thickness over on Aunanoparticles also varies with the presence and absence of CA. Intense morphological observation indicates CA plays critical role in the formation of worm-like Au/PANI nanostructures. The length of nanofiber also depends on the CA to aniline ratio. Prepared composites act as a catalyst for reduction of different aromatic nitrophenols. Catalytic activity varies according to the thickness of PANI layer over on Au-nano. The rate of reaction changes from 0.00254 sec^{-1} to 0.00988 sec^{-1} when PANI thickness changes from ~30 nm to ~5 nm.

Acknowledgements

Dr. Malik acknowledges CSIR, INDIA (Project No.: 02(0161)/13/EMR-II) for the financial support. S.M. and U.R. are indebted to CSIR, New Delhi, India for their fellowship. The authors are thankful to the Unit of Nanoscience (DST, Govt. of India) at IACS for HRTEM and FESEM.

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[†]Electronic Supplementary Information (ESI) available: [Preparation of Au/PANI composite (Table-1), TEM image and UV-Vis spectra of synthesized Au-60 seed solutionand Au-240 seed solution, Synthesis of Au/PANI composite from different Au seed solution. Aspect ratio of a single Au-nano formation kinetics, UV-Vis spectra of 4-NP reduction by NaBH₄ without catalyst, UV-Vis spectra and rate calculation of 4-NA, 2,4-DNP and 2,4,6-TNP reduction.]. See DOI: 10.1039/b000000x/

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References

- 1 L. J. Lauhon, M. S. Gudiksen, D. Wang, and C. M. Lieber, *Nature*, 2002, **420**, 57.
- A. Babel, D. Li, Y. Xia, and S. A. Jenekhe, Macromolecules, 2005, 38, 4705.
- 3 (a) B. Hua, J. Motohisa, Y. Kobayashi, S. Hara, and T. Fukui, Nano Lett, 2009, 9, 112; (b) H. J. Choi, J. C. Johnson, R. He, S. K Lee, F. Kim, P. Pauzauskie, J. Goldberger, R. J. Saykally, and P. Yang, J. Phys. Chem. B, 2003, 107, 8721.
- 4 (a) C. O. Baker, B. Shedd, R. J. Tseng, A. A. Martinez-Morales, C. S. Ozkan, M. Ozkan, Y. Yang, and R. B. Kaner, *ACS Nano*, 2011, 5, 3469; (b) R. J. Tseng, J. Huang, J. Ouyang, R. B. Kaner and Y. Yang, *Nano Lett.*, 2005, 5, 1077.
- 5 (a) J. C. Scott, Science, 2004, 304, 62; (b) J. Ouyang, C.W. Chu, C. R. Szmanda, L. Mal, and Y. Yang, Nat. Mater., 2004, 3, 918.
- 6 (a) B. Baruah, G. J. Gabriel, M. J. Akbashev and M. E. Booher, Langmuir, 2013, 29, 4225; (b) X. Z. Li, K. L. Wu, Y. Yea, and X. W. Wei, Nanoscale, 2013, 5, 3648.
- 7 (a) F. Lin, and R. Doong, J. Phys. Chem. C, 2011, 115, 6591; (b) Q.
 An, M. Yu, Y. Zhang, W. Ma, J. Guo, and C. Wang, J. Phys. Chem. C, 2012, 116, 22432.
- 8 B. C. Sih, and M. O. Wolf, Chem. Commun., 2005, 3375.
- (a) H. S. Kolla, S. P. Surwade, X. Zhang, A. G. MacDiarmid, and S. K. Manohar, J. Am. Chem. Soc., 2005, 127, 16770; (b) D. Li, J. Huang, and R B. Kaner, Acc. Chem. Res., 2009, 42, 135; (c) E. Marie, R. Rothe, M. Antonietti, and K. Landfester, Macromolecules, 2003, 36, 3967.
- 10 (a) U. Rana, K. Chakrabarti, and S. Malik, J. Mater. Chem., 2012, 22, 15665; (b) U. Rana, and S. Malik, Chem. Commun., 2012, 48, 10862.
- (a) S. Virji, R. B. Kaner and B. H. Weiller, *Chem. Mater.*, 2005, 17, 1257; (b) S. Virji, J. Huang, R. B. Kaner, and B. H. Weiller, *Nano Letter*, 2004, 4, 491.
- (a) J. Chen, P. Xiao, J. Gu, D. Han, J. Zhang, A. Sun, W. Wang, and T. Chen, *Chem. Commun.*, 2014, **50**, 1212; (b) Y. S. Bao, M. Baiyin, B. Agula, M. Jia, and B. Zhaorigetu, *J. Org. Chem.*, 2014, **79**, 6715–6719.
- 13 M. C. Daniel, and D. Astruc, Chem. Rev., 2004, 104, 293.
- 14 (a) B. L. V. Prasad, S. I. Stoeva, C. M. Sorensen, V. Zaikovski, and K. J. Klabunde, J. Am. Chem. Soc., 2003, **125**, 10488; (b) Z. F. Zhang, H. Cui, C. Z. Lai, and L. J. Liu, Anal. Chem., 2005, 77, 3324.
- (a) H. Sun, Y. Luo, Y. Zhang, D. Li, Z. Yu, K. Li, and Q Meng, J. Phys. Chem. C, 2010, 114, 11673; (b) D. W. Wang, F. Li, J. Zhao, W. Ren, Z. G. Chen, J. Tan, Z. S. Wu, I. Gentle, G. Q. Lu, and H. M. Cheng, ACS Nano, 2009, 7, 1745.
- 16 (a) U. Rana, K. Chakrabarti, and S. Malik, J. Mater. Chem., 2011, 21, 11098; (b) U. Rana, S. Mondal, J. Sannigrahi, P. K. Sukul, M. A. Amin, S. Majumdar, and S. Malik, J. Mater. Chem. C, 2014, 2, 3382.
- (a) Z. Wei, Z. Zhang, and M. Wan, *Langmuir*, 2002, 18, 917; (b) Y.
 Yang, and M. Wan, *J. Mater. Chem.*, 2002, 12, 897; (c) J. Huang, S.
 Virji, B. H. Weiller, and R. B. Kaner, *J. Am. Chem. Soc.*, 2003, 125, 314.
- 18 (a) T. Xue, X. Wang, S. K. Kwak, and J. M. Lee, *Ind. Eng. Chem. Res.*, 2013, **52**, 5072; (b) Z. Peng, L. Guo, Z. Zhang, B. Tesche, T. Wilke, D. Ogermann, S. Hu, and K. Kleinermanns, *Langmuir*, 2006, **22**, 10915.

- 19 J. M. Liua, and S. C. Yang, Chem. Commun., 1991, 1529.
- 20 (a) D. Li, and R. B. Kaner, J. Mater. Chem., 2007, 17, 2279; (b) B.
 Zhao, S. Huang, R. Zhang, P. Xu and H. L. Wang, CrystEngCommum, 2012,14, 1542.
- 21 D. Li, and R. B. Kaner, J. Am. Chem. Soc., 2006, 128, 968.
- 22 S. Wunder, F. Polzer, Y. Lu, Y. Mei, and M. Ballauff, *J. Phys. Chem. C*, 2010, **114**, 8814.
- 23 S Kumar, K. S. Gandhi, and R. Kumar, Ind. Eng. Chem. Res., 2007, 46, 3128
- 24 C. H. Gammons, Y. Yu, and A. E. Williams-Jones, *Geochim. Cosmochim. Acta*, 1997, **61**, 1971.
- (a) S. E. Lohse, J. R. Eller, S. T. Sivapalan, M. R. Plews and C. J. Murphy, ACS Nano, 2013, 7, 4135; (b) A. F. Zedan, S. Moussa, J. Terner, G. Atkinson, and M. S. El-Shall, ACS Nano, 2013, 7, 627; (c) E. Hutter, S. Boridy, S. Labrecque, M. L. Hebert, J. Kriz, F. M. Winnik, and D. Maysinger, ACS Nano, 2010, 4, 2595; (d) T. K. Sau and C. J. Murphy, J. Am. Chem. Soc., 2004, 126, 8648; (e) N. R. Jana, L. Gearheart, and C. J. Murphy, J. Phys. Chem. B, 2001, 105, 4065.
- 26 (a) I. O. Jimenez, X. Lopez, J. Arbiol, and V. Puntes, ACS Nano, 2012, 6, 2253; (b) K. Huang, H. Ma, J. Liu, S. Huo, A. Kumar, T Wei, X. Zhang, S. Jin, Y. Gan, P. C. Wang, S. He, X. Zhang, and X. J. Liang, ACS Nano, 2012, 6, 4483; (c) C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorff, J. Gao, L. Gou, S. E. Hunyadi and T. Li, J. Phys. Chem. B, 2005, 109, 13857; (d) J. Gao, C. M. Bender, and C. J. Murphy, Langmuir, 2003, 19, 9065; (e) B. D. Busbee, S. O. Obare, and C. J. Murphy, Adv. Mater., 2003, 15, 414.
- 27 T. Zhang, W. Wang, D. Zhang, X. Zhang, Y. Ma, Y. Zhou, and L. Qi, *Adv. Funct. Mater.*, 2010, **20**, 1152.
- 28 K. Huang, Y. Zhang, Y. Long, J. Yuan, D. Han, Z. Wang, L. Niu, and Z. Chen, *Chem. Eur. J.*, 2006, **12**, 5314.
- 29 (a) A. Kumar, S. Mandal, P. R. Selvakannan, R. Pasricha, A. B. Mandale, and M. Sastry, *Langmuir*, 2003, **19**, 6277; (b) C. Jin, T. C. Nagaiah, W. Xia, B. Spliethoff, S. Wang, M. Bron, W. Schuhmann and M. Muhler, *Nanoscale*, 2010, **2**, 981.
- 30 (a) W. Luo, C. Zhu, S. Su, D. Li, Y. He, Q. Huang, and C. Fan, ACS Nano, 2010, 4, 7451; (b) X. R. Li, X. L. Li, M. C. Xu, J. J. Xu and H. Y. Chen, J. Mater. Chem. A, 2014, 2, 1697.
- 31 D. V. Leff, L. Brandt, and J. R. Heath, *Langmuir*, 1996, **12**, 4723.
- 32 B. Xu, X. Wu, H. Li, H. Tong, and L. Wang, *Macromolecules*, 2011, 44, 5089.
- 33 M. Megharaj, H. W. Pearson, and K. Venkateswarlu, Arch. Environ. Contam. Toxicol., 1991, 21, 578.