Table of Contents

Chapter 1 General Introduction 1

1.1 Natural Photosynthesis 3

1.2 Artificial Photocatalysis 4

1.2.1 Methods of solar energy conversion 4

1.2.2 Solar light capture and electron/hole pairs generation 5

1.2.2 Photocatalytic chemical reactions. 10

1.3 Photothermal Catalysis 13

1.3.1 Solar thermal heating 13

1.3.2 Local surface plasmonic resonance effects 14

1.4 The Development of Photocatalyst 15

1.4.1 Development of TiO_2 photocatalyst 15

1.4.2 Other metal oxide photocatalyst 19

1.4.3 ABO_3 type perovskites 20

1.4.4 Hybrid organic metal perovskite as photocatalyst. 22

1.5 N_2 Fixation. 31

1.6 Outline of the Experimental Chapters. 35

1.7 References 36

Chapter 2 Objectives 53

Chapter 3 Hybrid Benzidinium Lead Iodide Perovskite with 1D Structure as Photoinduced Electron Transfer Photocatalyst 59

3.1 Introduction 61

3.2 Results and Discussion 62

3.2.1 Material preparation and characterization 62

3.2.2. Photocatalytic activity 69

3.3 Conclusions 77

3.4 References 78

Chapter 4 Surface Silylation of Hybrid Benzidinium Lead Perovskite and Its Influence on the Photocatalytic Activity.....83

4.1 Introduction 85

4.2 Results and Discussion 87

4.2.1 Materials synthesis and characterization 87

4.2.2 Photocatalytic activity. 98

4.3 Conclusions 102

4.4 Reference 102

Chapter 5 Synthesis, Post-synthetic Modification and Stability of 2D Styrylammonium Lead Iodide Hybrid Material 107

5.1 Introduction 109

5.2 Results and Discussion 111

5.2.1 Perovskite synthesis..... 111

5.2.2 Material characterization 113

5.2.3 Post-synthetic modification 120

5.2.4 Photostability tests 125

5.3 Conclusions 128

References 129

Chapter 6 Photo-assisted N_2 Reduction by H_2 Using Cs-Promoted Ru/$SrTiO_3$ as Efficient Photocatalyst 137

6.1 Introduction 139

6.2 Results and Discussion 140

6.2.1 Ru(x)-STO preparation and characterization 140

6.2.2 Photo-assisted NH_3 production 143

6.2.3 Cs-promotion 144

6.2.4 Mechanism of the photo-assisted NH_3 production. 156

6.2.5 Stability. 166

6.3 Conclusions 167

6.4 References 168

Chapter 7 Nitrogen Reduction to Ammonia by Using Transition Metal Tris(3-tert-butyl-5-methyl-1pyrazolyl)borate Complex as the Catalyst 175

7.1 Introduction 177

7.2 Results and Discussion 180

7.2.1 Materials synthesis and characterization 180

7.2.2 Nitrogen reduction by conventional homogeneous catalysis 184

7.2.3 Nitrogen fixation by photocatalysis 185

7.2.4 Nitrogen reduction by electrocatalysis 187

7.3 Conclusions. 190

7.4 References 191

Chapter 8 Experimental Section 193

8.1 Material Synthesis.....195

8.1.1 Chemicals 195

8.1.1 Synthesis of BZ-3.1 195

8.1.2 Synthesis of BZI-3.1 196

8.1.3 Synthesis of BHP-3.1 196

8.1.4 Surface silylation of BHP-3.1 196

8.1.5 Synthesis of SA-5.1 197

8.1.6 Synthesis of HP-5.1 197

8.1.7 Synthesis of material PHP-5.1 from HP-5.1 197

8.1.8 Synthesis of Ru(x)-STO.....198

8.1.10 Synthesis of 3-methyl-5-tert-butyl-pyrazole.....198

8.1.11 Synthesis of potassium hydridotris(3-methyl-5-tert-butyl)pyrazolyl borate (Me^{t}Bu-tpzB).....198

8.1.12 Synthesis of Me^{t}Bu-tpzB transition metal complexes (Metal=Co, Fe, Cr and Ni) 199

8.1.13 Synthesis of vanadium Me^{t}Bu-tpzB complex 199

8.2 Reaction Procedure 199

8.2.1 Photoinduced cis-to-trans-isomerization of stilbene 199

8.2.2 Photocatalytic H_2 evolution for the stability test of material HP-5.1 and PHP-5.1 199

8.2.3 Photo-assisted nitrogen fixation with hydrogen for ammonia 200

8.2.4 ^{15}N isotopic experiments 201

8.2.5 Photocatalytic/conventional N_2 reduction by using metal Me^{t}Bu-tpzB as the catalyst 201

8.2.6 Electrochemical nitrogen reduction by using Me^{t}Bu-tpzB as electrocatalyst 202

8.3 Characterization Techniques 203

8.3.1 Transmission Electron Microscopy (TEM) 203

8.3.2 Scanning Electron Microscopy (SEM) 203

8.3.3 X-Ray Diffraction (XRD) 204

8.3.4 X-Ray Photoemission Spectroscopy (XPS) 204

8.3.5 UV-Vis Absorption Spectroscopy 204

8.3.6 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) 204

8.3.7 Diffuse Reflectance UV-Vis Spectroscopy (DRS) 204

8.3.8 Single Crystal X-Ray structure Analysis 205

8.3.9 Fourier Transformed Infrared Spectroscopy (FTIR) 209

8.3.10 Proton Nuclear Magnetic Resonance (^{1}H NMR) 209

8.3.11 X-Ray Fluorescence Spectroscopy (XRF) 209

8.3.12 Gas Chromatography (GC).....209

8.3.13 Optical Microscopy 209

8.3.14 Time-Resolved Fluorescence Spectroscopy.....209

8.3.15 In-situ IR Spectroscopy Measurements 210

8.3.16 CO Chemisorption 210

8.3.17 CO_2 Absorption..... 211

8.3.18 Ultra Performance Liquid Chromatography - Tandem Mass Spectrometer (UPLC-MS/MS) 211

8.4 Other Procedures.....212

8.4.1 Detailed calculation process for experimental formula of BHP-3.1 material.....212

8.4.2. Calculation of Valence Band edge of material HP-5.1....212

8.4.3 Quantification of Ammonia.....213

8.5 References 213

Chapter 9 Conclusions.....215

Abstract.....221

List of publications.....229